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Silica Production from Agricultural Waste: A Review

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ABSTRACT

Silica has occurred as a well-known material because of its high availability and has a wide range of applications in various technology like drug detection, water purification, and industrial application. It is extracted from agricultural waste by various methods like thermal treatment, acid leaching, alkali based, biologically, etc. Agricultural waste is a cheaper, safe, and environmentally friendly source for silica production. This review informed several sources of silica derived from agricultural waste, such as rice husk, rice straw, corn cobs, and bagasse. along with their characterization methods.

KEYWORDS

Agricultural wastes, Characterization, Drug, Environmentally friendly, Extracted.

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1. INTRODUCTION

Agro-based industries generate enormous amounts of waste in the form of sugarcane bagasse, corncob, rice husk, wheat straw, etc. Removal and disposal of such agrowastes by dumping and burning may cause environmental pollution. Removal of silica from these wastes can be used for the formation of useful materials which plays an important role in various fields [1]. Silica is an inorganic compound used in various applications and technology such as electronic components, drug delivery systems, catalysts, thermal insulators rubber, chromatography, and the ceramic industry [2]. In a current trend, silica has high demand and several applications extracted from the naturally occurring silica plants, including rice husk, rice straw, wheat straw, etc. [3]. In this review paper, we discussed various natural organic sources of silica and methods of extraction with currents trends. There are several methods used in the extraction of silica from agricultural waste: thermal treatments, hydrothermal treatments, biological treatments, and chemical treatments [4].

1.1. Chemical and Physical Properties of Silica

Silica minerals have many forms like quartz, tridymite, cristobalite, coesite, stishovite, lechatelierite, and chalcedony. Silica can be available in two forms: crystalline and amorphous. The crystallographic structures of silica minerals are in three dimensions system, each consisting of a silicon atom coordinated by four oxygen atoms. The pure

form of silica minerals is colorless and transparent with a luster. The minerals are nonconductors of electricity and are diamagnetic. The boiling point and melting points are 3265°C and 1410°C respectively [5].

1.2. Health Effects of Silica

The natural forms of silica like silica and silicate which are the most abundant in the earth's crust are non-toxic. But as silica is a very fine powder and amorphous, silica dust has few adverse effects on the lungs and the respiratory system. Silicon crystalline can irritate the skin and eyes. Lung cancer is caused by silica from quartz and cristobalite. Crystalline silica may harm the immune system, resulting in mycobacterial infections (tuberculous and nontuberculous) or fungi, particularly in workers with silicosis [6].

1.3. Natural Sources of Silica

1.3.1 Rice Husk

Rice husk is easily available in rice mills which is a by-product popularly used for livestock feed, fertilizer, and mushroom planting media on a household industrial scale. Many researchers found that rice husk is one of the rich sources of silica which contain about 95 to 98 % silica. Rice husk on burning produces rice husk ash (RHA) which is further used for the processing in the production of silica.

1.3.2 Rice Straw

Rice straw is an agricultural waste that can easily collect after harvesting the rice. The silica contains in the rice straw is relatively less than in the rice husk. There are so many components present in the rice straw-like cellulose, hemicellulose, lignin, and ash. The yield of ash may be depending on the type of rice, and the climatic, and geographical conditions where rice is grown [3].

1.3.3 Corn Cobs

Corn cobs are agricultural waste getting from the harvesting of corn. Corn cobs contain 70 to 85 % silica. The ash of corn cobs is very fine so there is no need of grinding again. Silica production from the corn cobs is economically friendly [7].

1.3.4 Wheat

waste and mainly used for energy production in the industry. Wheat husk ash contains nearly 90 to 92 % silica in an amorphous form. On the burning of wheat husk at 500° C, wheat husk ash is obtained which is further used for processing [4, 8].

1.3.5 Bagasse

Bagasse is an industrial waste obtained after processing sugarcane in the industry. Bagasse is a rich source of silica which contain about 95 to 98 % silica in it. Bagasse

is a cellulose fiber remaining after the separation of sugar-bearing juice from sugarcane [9].

1.3.6 Coconut Husk

Coconut husk ash is employed as a raw material to produce silica. Coconut consists of 33-35% of husk and coconut husk is a mesocarp of coconut. Nowadays coconut shells and husk are used as fuel on a household scale as well as raw materials for ropes and mats [6].

2. EXPERIMENTAL METHODS

There are several methods used for extraction of the silica from agricultural waste.

- 2.1 Thermal treatment
- 2.2 Acid Leaching
- 2.3 Alkali-based treatment
- 2.4 Biotransformation process
- 2.4 Heteropoly blue process

2.1. Thermal Treatment

Rice husk, Rice straw, Wheat straw, Bagasse, and Coconut husk, all these agricultural wastes are dried and can burn in a furnace at a high temperature. First, collect the agricultural waste from the source of waste and then process it. Agricultural waste first undergoes some pre-treatment to remove the impurities. Rice husk, Rice straw, Wheat straw, Bagasse, and Coconut husk this waste were washed with water four to five times to remove dirt. Then washed with 30% HCl to remove the metallic impurities. The washed agricultural waste is dry in a hot air oven at 300°C for 3hr. This dry agricultural waste is burned in the muffle furnace for the formation of ash. This process is carried out at 600°C for 3hr. [10].

Usman et al. extracted the silica content in the bagasse using thermal treatment with a temperature variation at a temperature of 500, 600, and 700° C, which ash obtained of 12.65, 10.89, and 9.95% respectively.

Usman et al., 2014) XRF analysis results indicated that the levels of silica in the ash of the bagasse in a row according to the experimental temperature are 76.168, 76.292, and 77.286%.

2.2. Acid Leaching

After washing the agricultural waste with distilled water, it is washed with 30% HCl is the most efficient. Acid leaching of 50g of agricultural waste sample with 30% HCl at 100°C for 2hr, to remove the metallic impurities from agricultural waste. The acid leaching agricultural waste sample is dried at 100°C for 3hr in a hot air oven [5]. **Table-1** shows the yield of silica at a different pyrolyzing temperature.

Acid Leaching	, ,	Yield at temperature	a different	pyrolyzing
Type of Acid	Acid concentration	700 ⁰ C	750 ⁰ C	800 ⁰ C
HCL	10%	52.18	62.27	49.21
	30%	87.02	91.82	87.94
H_2SO_4	10%	42.38	36.51	19.63
	30%	23.51	14.18	8.78

Table-1. Yield of silica at a different pyrolyzing temperature.

2.3. Alkali-based Treatment

Agricultural waste ash is extracted with sodium hydroxide solution. Hence 4gm of ash prepared is boiled with 100ml of 1N NaOH for 2hr, so that silica in agricultural waste ash is converted into sodium silicate (Na_2SiO_3). The filter sodium silicate solution treated with 1N HCl to convert the sodium silicate solution is added drop by drop tilled the pH solution touched 6 [11].

Yuvakkumar et al. carried out the extraction of silica from rice husk using a chemical treatment with alkaline and acid precipitation. they studied the initial treatment and the effect of the concentration of sodium hydroxide (NaOH) on the powder purity nano-silica. The optimum concentration of 2.5 N NaOH with nano silica resulting powder having a purity of 99.90%, an average particle size of 25 nm, and a surface area of 274 m² g⁻¹.

Velmurugan et al. Used corn cobs for extraction of silica sol-gel method and alkali-base treatment. (Velmurugan et al., 2015) From the research, amorphous silica with an average size of 50 nm can be obtained. FTIR spectra show the broad band at 3528-3596 cm⁻¹.

2.4. Biotransformation Process

The sample of agricultural waste like corncobs husk is dissolved in 100ml of distilled water and after sterilization in an autoclave or without sterilization, the biocatalyst (10gm of wet fungal biomass) was added. Biotransformation flasks were incubated on a rotary shaker for 16 days. The sample for further analysis was collected daily and placed in the freezer (-18°C). Silica concentration in the sample was determined by the heteropoly blue method to define the most effective day biotransformation [12]. Silica reacts with ammonium molybdate under the acidic condition to produce yellow molybdosilicic acid which is reduced by

aminonaphtholsulfonic acid to form heteropoly blue. The resulting blue color is directly proportional to the silica concentration of the sample. The result is expressed as ppm (mg/l) SiO_2 [1, 12].

3. CHARACTERIZATION TECHNIQUES

3.1. X-ray diffraction (XRD)

X-ray diffraction is a popular analytical technique, which has been used for the analysis of both molecular and crystal structure, qualitative identification of various compounds, quality resolution of chemical species, measuring the degree of crystallinity, isomorphous substitution, stacking faults, polymorphisms, phase transition, particle size, etc.

3.2. Energy Dispersive X-ray Spectroscopy (EDX)

EDAX is a leading provider of innovative material characterization systems encompassing energy dispersive spectroscopy (EDS), electron backscatter diffraction (EBSD), wavelength dispersive spectrometry (WDS), and Micro X-ray fluorescence (Micro-XRF), and X-ray metrology.

EDAX develops the best solution for micro and nano-characterization where elemental and structural information is required, making analysis easier and more accurate.

EDAX designs produce, allocate, and service product for a wide range of industry, technical institution, and research organizations.

3.3 Fourier Transmission Infrared Spectroscopy (FTIR)

FTIR spectra reveal the composition of solids, liquids, and gases. The most common use is in the identification of unknown material and confirmation of production materials (incoming or outgoing). The information content is very specific in most cases, permitting fine discrimination between likes and material. The speed of FTIR analysis makes it particularly useful in screening applications while the sensitivity empowers may advance research applications.

3.4 Scanning Electron Microscope (SEM)

A scanning electron microscope (SEM) is a type of electron microscope that images a sample by scanning the surface with a focused beam of electrons. It is used to determine the particle length, form, and texture of silica. In SEM a high-quality beam of electrons scans across the prepared pattern in a series of parallel tracks. The electrons interact with the sample and convey several distinctive indicators which may be detected and displayed on the screen of a cathode ray tube. The electron beam is scanned in a raster scan pattern, and the position of the beam is combined with the intensity of the signal to produce an image.

4. APPLICATIONS OF SILICA

Silica is usually obtained in amorphous form and has a variety of applications. It is used as an absorbent, catalyst, refining agent, and so forth. Due to its glass-like appearance is used in glass wires and optical element production. It is also used in silicate base materials like silicon carbide, soluble silicates, zeolite, silicon alloy, and so on.

It is likewise utilized in ceramic, glass, rubber, and refractory industries. It can also be used as an inexperienced corrosion inhibitor to prevent metal corrosion. Its use may be in beauty products as, a thickening agent and an absorbent. In the production of inks, silica is used as a matting and thickening agent. Silica nanoparticles have also been used for DNA detection, separation, and purification [12, 13, 14]. Silica nanoparticle is widely used in drug delivery system. A targeted drug delivery system is mainly used in cancer treatment.

5. REVIEWS ON SILICA REMOVAL

Many scientists and researchers did many works on the removal of silica. A brief view of the work done by the different researchers is presented here. All researcher's study was based on the use of treatment method for the extraction of silica

Aleksandra et al [2020]: FTIR checks the existence of siloxane bonds and O-Si-O bonds in the post-biotransformation fluid. Heteropoly Blue Method was used, to check the highest concentration of silica during the period of 16-days, and biotransformation reductions on the 7th day of the process. Substrate sterilization and the process of biocatalyst starvation both were very important. Using the STEM and EDX analysis, it was verified that get nanoparticles are the shape of a sphere form and their dimensions are ~40 and ~70 nm. ICP-OES verified that the overall process productivity was 47%. Such nanoparticles can be effectively used in the medical industry

Alexya et al [2018]: Carried out the extraction of silica from Rice husk ash. Characterization of silica nanoparticles was done using UV-Vis Spectroscopy, X-Ray Diffraction (XRD), and Scanning Electron Microscopy (SEM). UV-Vis Spectroscopy and XRD analysis show that the SiNPs extracted from RHA at 750°C exhibited the highest peak at 260 nm and $2\theta=26^{\circ}$ respectively and XRD and SEM analysis expression that crystallite and particle size were in close agreement with each other. At a temperature of 750°C, silica gel which was prepared at pH 6 is more stable, transparent, and thicker than silica gel formed at different pH. Also, the sodium silicate sample shows a bright green fluorescence and the intensity of fluorescence was higher for the sodium silicate ready at the 750°C range than at any other temperature.

Noorul et al [2021]: In this study, silica was extracted from sugarcane bagasse, for the first time, more than 70% of the silica from the bottom ash could be extracted for the synthesis of mesoporous silica using a low-temperature alkaline dissolution method instead of the customary elevated-temperature process. The sequential extractions with optimized con- ditions of 100°C for 72h were employed to attain maximum silica extraction efficiency.

Anusara et al [2018]: coconut husk was burned in the electrical furnace at 500, 600, and 700 °C. These ashes were reacted by using two different chemical treatments to recover the maximum yield of silica. XRF check-up of coconut husk ash (CHA) exposed that the content of SiO_2 diverges between 8 and 11% and increased up to 90% after chemical treatment. Based on the XRD spectrum, the silica is found in crystalline form after acid treatment, but after the alkali treatment it gets an amorphous form.

Javed et al [2015]: the wheat husk ash was reacted with sodium hydroxide at different molar ratios and reaction times to get sodium metal silicate. Every time sodium meta silicate was reacted with 0.1 N HCl to get silica in precipitated form. XRD and FTIR results check the amorphous nature of precipitated silica. It was experimental that one hour of boiling with a molar ratio of Na/Si =2 is enough for optimum conversion into sodium metal silicate.

6. CONCLUSION

This review paper shows that agrowastes can be successfully used as a raw material for the extraction of silica. This work would provide agricultural wastes as a low-cost raw material for the extraction of silica and helps to minimize environmental pollution to some extent.

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Adsorption of Heavy Metal Ions from Water Using Iron Oxide Nanoadsorbents: A Review of the Recent Literature

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ABSTRACT

The presence of heavy metal ions in drinkable water is a major global challenge for mankind. Employing nanomaterials in this scenario proves to be an effective way to solve this problem due to the inimitable properties that they possess. Iron Oxide nanoparticle-based water filtration systems are the way of the future due to their ease of separation and low-cost production procedures. In this review, we will focus on how heavy metals with negative environmental consequences may be removed using an adsorption approach that involves iron oxide nanoparticles, which has been shown to be effective in this field. We discuss current advancements in Iron Oxide nanoparticles for heavy metal ion adsorption from water. The discussion covers candidate synthesis of Iron Oxide nanoparticles, mechanisms that enable the applications, advantages, and limitations as compared to existing processes and their adsorption mechanism.

KEYWORDS

Iron oxide nanomaterials, Heavy metal, Magnetic nanoadsorbents.

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1. INTRODUCTION

Water is one of the most vital natural resources available on the planet which satisfies various needs of humans including its survival [1] and is one of the most copious resources on earth. Though about 70% part of the earth is covered with water, a maximum of it is present in the ocean and seas. But less than 1% of fresh water is available for human consumption. However, water pollution is increasing at an unprecedented rate due to various factors including but not limited to an increase in human population, prolonged droughts, dumping an assortment of sewage and solid waste, discharging toxic industrial effluents, harmful chemicals, nuclear waste, residues from pharmaceutical plants, etc. [2–5]. Amongst these factors water polluted by heavy metals such as Cd, Cr, Hg, and Pb is becoming a serious problem for mankind. Any metallic element with a relatively high density that is toxic and

non-biodegradable even at low concentrations is referred to as a "heavy metal." This is due to the fact that many metals are non-biodegradable and may cause cancer even in low quantities. Heavy metal ions including Cr(VI), Pb(II), and Cd(II), which are widely found in mining and battery effluents, have been classified by the United States Environmental Protection Agency (USEPA) as a priority and harmful pollutants that must be cleaned before being discharged into the discharge of sewage. Heavy metals are significant environmental pollutants, and their toxicity is a problem of increasing significance for ecological, evolutionary, nutritional, and environmental reasons. These toxic metal ions are liberated into the natural environment as a result of numerous human activities [6,7].

Living organisms need these elements in minute quantities but their high concentrations prove to be fatal. Another concern is that most of the heavy metals are carcinogenic and mutagenic [8,9]. In an attempt to solve this problem various methods (Fig. 1) like adsorption [10,11], photocatalytic oxidation [12,13], flocculation [14,15], electrochemical [16,17], bioremediation [18–22], ion exchange [23,24], membrane filtration [25,26], reverse osmosis [27,28], etc. are employed.

Amongst these methods adsorption proves to be the most promising technology because of various factors such as less complicated nature, ease of operation, low running cost, high retention potential, and regeneration efficiency [29–33]. Adsorption is a surface phenomenon in which a species gets accumulated onto the surface of another phase by physical and/or chemical interactions which are usually solid or liquid. These materials on which the adsorption process takes place are known as adsorbents. The properties of these adsorbents vary significantly as a function of its surface area, size of particles, number of active surface sites, low rate of intraparticle diffusion, and high adsorption capacities [34].

One drawback of this method is that the adsorbent to be used should have a smaller size since smaller size adsorbents have a high surface area which results in high adsorption capacity. However, employing smaller adsorbents creates another problem that is the smaller absorbents are difficult to recover after they have reached their saturation adsorption capacity [35]. To overcome this problem nanomaterials are being studied exhaustively around the globe for their application in environmental remediation [36,37].

Among these nanomaterials magnetic ones are particularly looked upon due to their superior characteristics such as large surface area, small size, and interesting magnetic properties [38] which can be employed as nanoadsorbents to remove a number of pollutants from water including heavy metals [39] along with easy separation of the metal ion from the solution merely using an external magnetic field [40].

2. SYNTHESIS OF IRON OXIDE NANOPARTICLES

Figure-1 shows the various processes employed to treat polluted water. Thereafter, iron oxide nanoparticles can be synthesized by a number of different methods which are shown in (**Figure-2**) [41–44]. Aggregation and interference from other chemicals, on the other hand, may prevent the metals from adsorbing. Surface modification of NPs, which can be achieved by attaching inorganic shells and/or organic compounds to them, not only stabilizes them and eventually prevents oxidation but also provides specific functionalities that can be selected for ion uptake and thus improve heavy metal uptake capacity in water treatment procedures [35]. Particle size control and particle size distribution, crystal structure, shape control, pH, and alignment are the key issues in synthesizing iron oxide nanoparticles [45].



Figure-1. Schematic representation of various processes employed to treat polluted water.





Figure-2. Different methods employed for the synthesis of nanoparticles.

3. ADSORPTION

Adsorption is defined as the accumulation of one substance on the surface of another substance as a non-selective process which is exploited as an advantage for utilizing this technique for non-selective process in water treatment. In fact, adsorption in a molecular context is a process that results from the attractive interactions between the molecules of the adsorbate and the molecules of the adsorbent surface. It is a safe and green technique that eliminates the production of any harmful waste by-products.

3.1. Study of Adsorption Isotherms

In the adsorption, compound concentration (mg/L) and the compound concentration remained on solid particles q (mg/g) can be investigated The equation q = f(C) gives rise to the sorption isotherm. Due to the uniqueness of this correlation, several requirements must be met: (I) all adsorption/desorption equilibria must be accomplished, and (II) All other physical and chemical parameters must remain unchanged. Because temperature is so important in sorption processes, the term "isotherm" was particularly adopted (temperature must be constant and specified) [46]. Sorption isotherms were classified by Giles et al. [47] Based on their initial slopes and curvatures. They classified constant partition (C), Langmuir (L), high affinity (H), and sigmoidal-shaped (S) isotherm classes [48].

3.1.1. Langmuir Adsorption Isotherms

The Langmuir isotherm models were chosen based on the premise that the adsorption sites on the catalyst's surface are monolayer, homogeneous, and finite, and that molecules adsorbed on nearby sites do not interact. There can be no further sorption at a surface site after it has been filled. As a result, the surface will ultimately approach a saturation point, at which point its maximum adsorption will be accomplished [49]. The Langmuir isotherm model equation's linear form is as follows:

Where, 'q_e' is the amount of adsorbate adsorbed (mg g^{-1}), 'C_e' is the adsorbate equilibrium concentration (mg/dm³), 'a' is the monolayer coverage adsorption capacity (mg g^{-1}), 'b' is the Langmuir constant (dm³ mg⁻¹).

3.1.2. Freundlich Adsorption Isotherms

The Freundlich adsorption isotherm is based on the assumption of non-linear, multilayer heterogeneous adsorption and exponentially distributed active sites. The Freundlich isotherm is based on the idea that in both monolayer (chemisorption) and multilayer (physisorption) adsorption, the adsorbate adsorbs onto the heterogeneous surface of an adsorbent. Freundlich's equation is written as follows in the linear form:

 $\log q_e = \log K_F + 1/n \log C_e \qquad \dots \dots (2)$

The Freundlich constants ' K_F ' and 'n' represent the adsorption capacity and intensity, respectively. ' q_e ' is the amount of adsorbate adsorbed (mg g⁻¹), ' C_e ' is the adsorbate equilibrium concentration (mg/dm³) [50,51].

3.1.3. Temkin Adsorption Isotherms

The Temkin-isotherm was an early model used to analyze hydrogen adsorption on platinum electrodes under acidic environments. The isotherm contains a component that explicitly considers interactions between adsorbent and adsorbate. Because it ignores extremely low and high concentrations, the model assumes that the heat of adsorption (a function of temp.) of all molecules in the layer declines linearly rather than logarithmically with coverage. As anticipated by the equation, the derivation is characterized by a uniform distribution of binding energies (up to maximum binding energy)[52].

Temkin's equation is often unsuitable for modeling complex adsorption systems, including liquid-phase adsorption isotherms (where the organization in a densely packed structure with a similar orientation is not required). The constants were found by graphing the amount of sorbed q_e versus lnCe and determining the intercept and slope from the slope and intercept, as specified in the equation. The equation that describes the model is as follows:

The Temkin-isotherm Constant is related to the heat of sorption 'B' (RT/b_T) (J/mol), R is the universal gas constant (8.314 J/mol/K), T is the Temperature at 298K, A_T and b_T represent the Temkin isotherm equilibrium binding constant (L/g) and constant, 'q_e' is the amount of adsorbate adsorbed (mg g⁻¹), 'C_e' adsorbate equilibrium concentration (mg/dm³).

3.1.4. Kinetic Models

The concentration of the adsorbate adsorbed in the solution as a function of time was studied in an adsorption kinetic study using the Lagergren pseudo-first-order model [53] (Eq. 4) and Ho's pseudo-second-order model [54,55] (Eq. 5).

$$q = q_e (1 - e^{-k_1 t})$$
(4)
 $q = q_e k_2 t / 1 + q_e k_2 t$ (5)

 q_e denotes the equilibrium adsorption capacity (mg/g), q the quantity of adsorbate adsorbed (mg/g) at time t, k_1 the pseudo-first-order sorption rate constant (1/min), and k_2 the pseudo-second-order sorption rate constant (g/mg min).

4. ADSORPTION OF HEAVY METALS BY IRON OXIDE NANOPARTICLES

4.1. Cadmium

Cadmium ion is one of the most toxic heavy metal ions found in industrial wastewater along with arsenic and lead. They may enter through food, water, and air into the human body and even a tiny concentration of these elements can cause damage to internal organs [56] and are a recognized nephrotoxic agent [57]. It is a metal of more toxicology concern due to its property of bioaccumulation and non-biodegradability even at minute concentration levels. The United States Environment Protection Agency classified cadmium as a group B1 carcinogen and is also responsible for the itai-itai disease [58]. It also readily accumulated in the living organism causing multiple serious damage of tissues [59] and its short-term exposure can lead to vomiting, nausea, impaired senses, and liver damage. It is difficult to separate cadmium from water hence it is necessary to develop a method that is both economical and effective in removing cadmium from water.

Ghasemi et al. [60] studied the adsorption properties of superparamagnetic EDTA functionalized Fe₃O₄ on various metals including Cd(II). In order to have a high removal efficiency, the effects of different parameters having an influence on the adsorption were optimized using the box-Behnken design (BBD) which showed that the optimum pH for removal of Cd ions was at a pH of 7.9. As the pH was lower a decrease was seen in the removal efficiency which could be due to the competition between excessive H^+ ions and the metal ions for the same active sites of Fe₃O₄@EDTA nanoparticles. The optimum time for the reaction was 17 min and the average particle size obtained was 35 nm. The maximum removal efficiency of 99% was obtained.

In a recent study carried out by a group of researchers, Fe_3O_4 sulfonated magnetic nanoparticle (Fe_3O_4 -SO₃H) was developed for the removal of cadmium along with lead [61]. The characterization was carried out using SEM, TEM, FT-IR, and BET. The adsorption capacities of Fe_3O_4 -SO₃H magnetic nanoparticles increased as the ions concentration increased until it reached its maximum adsorption capacity which was 99%. The magnetic property was measured by a superconducting quantum interference device (SQUID) at 300 K which displayed the saturation magnetization values of 80.3 and 69.0 emu g⁻¹ for Fe_3O_4 and Fe_3O_4 -SO₃H indicating that these nanoparticles could be easily separated from the solution after treatment due to their superparamagnetic property. The regeneration of the adsorbents was carried out using a 1% HCl solution and the Fe_3O_4 -SO₃H nanoparticles showed high

removal efficiency even after 10 cycles indicating their potential for further application.

 α -Fe₂O₃ coated volcanic rock was synthesized and studied by Zhu et al. [62]. Batch experiments conducted showed the highest cadmium adsorption value occurred at a pH of 6. Temperature variation played an important role in the adsorption capacity. The maximum adsorption capacity of the Cd(II) ions increased steadily from 127.23 mg g⁻¹ to 146.41 mg g⁻¹ to 158.48 mg g⁻¹ as the temperature was increased from 293K to 303K and 313K. The adsorption kinetics was of the pseudo-second-order model. More than 98% of the dissolved Cd(II) was removed within 240 min and the state of equilibrium was attained within 720 min. The Cd(II) ion adsorption onto the α -Fe₂O₃ coated volcanic rock involved both film and intraparticle diffusion. The BET surface area was determined to be 1.8701 m² g⁻¹ and the pore volume of the α -Fe₂O₃ nanoparticles coated volcanic rock was 0.005627 cm³ gm⁻¹.

Another innovative study carried out in Spain displayed how magnetic coreshell Ce-Ti@Fe₃O₄ nanoparticles could be a boon for treating contaminated water [63]. This nanocomposite combined distinctive properties of magnetism, crystallinity, stability, and massive adsorption capacity altogether. The as-prepared nanoparticles had a potential effect for the removal of anionic contaminants while that of cationic contaminant cadmium was low which was about 45.28% for an initial concentration of Cd^{2+} as 10 mg L⁻¹ with the initial dose Ce-Ti@Fe₃O₄as 1.0 g L⁻¹.

4.2. Chromium

Chromium can exist in different oxidation states such as metallic Chromium [Cr(0)], Chromos [Cr(II)], Chromic [Cr(III)] and Chromates [Cr(IV)]. Cr(IV)compounds are about 500 times more hazardous than Cr(III)compounds especially for living organisms[64,65]. Chromium is considered to be mutagenic, teratogenic, and carcinogenic[66,67]. The international agency for research on cancer (IARC) identified Cr(IV) to be a class 1 human carcinogen. It has adverse effects on the human body such as skin ulcers, ulceration of the nasal mucosa along with perforation of the nasal septum [68].

Lei and his co-workers[69]were able to effectively synthesize graphene oxide foam-Fe₃O₄ nanocomposites and employed them for chromium removal. These composites were porous and they were 3D interconnected. The synthesis method included a combination of coprecipitation and microwave plasma chemical vapor deposition techniques. The adsorption mechanism of GO-Fe₃O₄ for chromium played a vital role in the reduction of Cr(IV) to Cr(III). As the nanocomposites were porous, they exhibited a large specific surface area of 574.2 m² g⁻¹. Hence, they showcased an amazing adsorption performance for the removal of Cr(IV) ions with a maximum adsorption capacity of about 258.6 mg g⁻¹ at a pH of 2 using the Freundlich isotherm model.

Lingamdinne et al.[70] used a biogenic reduction method for the preparation of iron oxide nanoparticles having an inverse spinel structure for the adsorption of Cr(III) and Pb (II). The AFM imaging gave a result of 49.45 nm as the average particle size which was close to the size predicted by PXRD analysis as 45.4 nm. The authors conducted a BET analysis of the nanoparticles and found the surface area to be 122.54 m² g⁻¹. The degree of magnetic saturation was 54.60 emu g⁻¹. The maximum sorption capacity of the nanoparticles continued for up to four cycles without the loss of stability. The desorption capacity of the magnetic nanoparticles also extended for up to five cycles at more than 95% without loss of stability. Subsequently, after five cycles it dropped to less than 80% for Pb(II) and Cr(III). The batch experiments were carried out with the variation in the initial metal concentration of 10.0 and 25.0 mg L⁻¹ and the nanoparticle dosage was 0.2 and 0.5 g L⁻¹. For Cr(III) for 10.0 mg L⁻¹ the adsorption capacity was 55.94 ± 0.34 and 22.64 ± 0.17 for 0.2 and 0.5 g L⁻¹ and 82.53 ± 0.28 and 32.24 ± 0.25 mg g⁻¹ for 0.2 and 0.5 g L⁻¹ for 25.0 mg L⁻¹ of Cr(III).

Recently Xiao et al.[71] demonstrated an efficient chromium removal using iron-based nanoparticles synthesized using a biogenic route. Spherical nanoparticles with an average particle size of 13.7 ± 5.0 nm were obtained and the Cr(IV) removal efficiency was nearly 70% within the first min and as high as 90% in a 90 min run. The authors also studied the dosing effects of Fe nanoparticles on the removal efficiency and found out that the efficiency increased tremendously from 26.13% to 99.45% as the Fe dosage increased from 0.1 to 0.6 ml with constant Cr(IV)concentration with an enormous removal capacity of 983.2 mg g⁻¹.

Highly active Fe/Ni bimetallic nanocomposites were synthesized employing the liquid-phase reduction method and the removal of Cr(IV)was done using an ultrasound-assisted arrangement by Zhou et al. [72]. The morphological characterization of the nanocomposites showed that the newly prepared immaculate Fe/Ni nanocomposites are quasi-spherical and have a diameter ranging between 30-50 nm while the same nanocomposite when characterized after the Cr(IV) reduction showed slight rough surface morphology which the authors predicted could be due to the corrosion of the Fe⁰ and that most of the surface of the particles was covered with flocculent clusters after the treatment of Cr(IV). The removal of Cr(IV) in an aqueous solution was investigated at 303K and showed the removal efficiency of 66.0% for the initial dosage of Fe⁰ of 0.1 g L⁻¹ and 96.1% when the concentration of Fe⁰ increased to 0.15 g L⁻¹along with the increase in dosage of Ni⁰ from 0 weight % to 5.0 weight%. Moreover, the removal efficiency of Cr(IV) at 20 mg L⁻¹was almost 100% which dropped to 76.7% and 61.0% as the concentration was increased to 30 and 40 mg L⁻¹. To comment on the equilibrium condition, it was attained within 10 min with the use of ultrasonic radiation which was much quicker than that shaking which took 60 min to reach the equilibrium state.

Another experiment employed electrospinning along with the hydrothermal method to fabricate $PA6@Fe_xO_y$ nanofibrous membranes to study chromium removal which showed excellent performance for chromium removal from a solution of K₂Cr₂O₇[73].

4.3. Mercury

Chronic mercury exposure could harm the brain, heart, kidney, lungs, and even immune system of the human [74]. Moreover, when an unborn baby is exposed to mercury in the womb and infants it may damage their nervous system and reduce their IQs [75].Hg(II) is an inorganic form of mercury that via biological methylation can be converted into an organic form which is even more toxic[76]. It is classified as a toxic pollutant by the Clean Water Act (CWA) under section 307 (a) and has the potential to bio accumulate owing to very low regulatory concentrations[77].

Liu et al. [78] used ethylene diamine functionalized magnetite/graphene oxide nanocomposite as an adsorbent for Hg(II) in an aqueous solution. These nanocomposites exhibited a tremendous adsorption capacity which was around 127.23 mg g⁻¹at an equilibrium concentration of 92.68 mg L⁻¹and were separated rapidly from the solution with the help of an external magnetic field. They carried out an identical experiment with Fe₃O₄-NH₂ and graphene oxide which exhibited reduced sorption capacities at 65.319 mg g⁻¹ and 40.275 mg g⁻¹. Thermodynamic properties were 27.045 kJ mol⁻¹ for enthalpy ΔH^0 and 100.182 J mol⁻¹ K⁻¹ for entropy ΔS^0 in the range of 298-313K along with the change in Gibbs free energy ΔG^0 as -2.857kJ mol⁻¹. This negative value of ΔG^0 confirmed that the adsorption process was spontaneous. Langmuir isotherm model and pseudo-second-order kinetics were used as the adsorption and kinetic model for the experiment.

Diagboya et al. [79] studied the adsorption of mercury Hg^{+2} ions with Iron oxide nanoparticles functionalized with graphene oxide by reaction with APTES. They also studied the adsorption with pristine GO sheets and concluded that the nanocomposite adsorption is 5 times more than that of the pristine GO sheets. The authors also concluded that higher temperatures had an adverse effect on the adsorption of mercury by carrying out the reactions at 20^oC 30^oC and 40^oC.

Azari et al. reported magnetic adsorption of mercury using magnetic chitosan modified with glutaraldehyde (MCS-GA) [80]. The experiments yielded optimum results of 96 mg g⁻¹ adsorption capacity at a pH of 5.0 and temperature of 298K respectively. The magnetic chitosan had a spherical shape when characterized but as it was modified with glutaraldehyde the shape became irregular and the particles became aggregated which could be due to the grafting reaction of magnetic chitosan with glutaraldehyde. Varying the pH influenced the adsorption capacity greatly. At a

pH of 2.0, the adsorption was as low as 36% while it improved to 34% and 41% at pH 3.0 and 4.0 respectively. Finally, at a pH of 5.0, the Hg(II) adsorption increased tremendously to 97.3% [80]. This could be because of the interactions between Hg(II) ions and H⁺ protons since amino groups of chitosan are protonated at pH less than 5.0 and would induce electrostatic repulsion between Hg(II) and H⁺.

Thiol-modified $Fe_3O_4@SiO_2$ showed the maximum adsorption capacity of 148.8 mg g⁻¹ for mercury Zhang et al.[81]. The nanomaterials were 10 nm in diameter as shown by TEM characterization. HCl solution of 6 mol L⁻¹was used for desorption of the adsorbed mercury and showed over 98% desorption.

Mercury removal from aqueous solution using Thiol-functionalised magnetic nanoparticles (TF-MNPs) was also reported by [82]. The TF-MNPs had sizes in the range of 15-30 nm which was revealed by the XRD and FESEM analysis. The excellent adsorption capacity of TF-MNP was reported which stood out to be 344.82 mg g⁻¹ calculated from Langmuir isotherm. A batch adsorption procedure was carried out for the Hg(II) removal. This was executed by adding 0.07g of TF-MNPs to a 50 ml solution containing 300mg L⁻¹ of Hg(II) ions. The pH was adjusted to 6.0 and the time for mixing was set as 90 min. The atomic absorption technique was employed to determine the amount of the remaining Hg(II) in the solution.

4.4. Lead

The presence of lead in the environment can be ascribed to the release of leadcontaining wastewater primarily from battery manufacturing, mining, and metallurgical industries. Its presence only in a minute quantity is also a matter of important concern[83]. Lead accumulation in the body can cause neurological, cardiovascular, and renal problems along with nausea, cancer, and convulsions to name a few[84]. Due to its high toxicity, the USEPA has set the maximum contaminant level for lead in drinking water as 15 μ g L⁻¹[85].

Lingamdinne et al. [70]also performed the same test runs for the adsorption of lead from water with all the parameters identified as that of chromium and the results they got showed that the adsorption capacity was 33.28 ± 0.26 and $6.540 \pm 0.35 \text{ mg g}^{-1}$ for 0.2 and 0.5 g L⁻¹ nanoparticle dosage for 10.0 mg L⁻¹ of Pb(II)concentration and 88.92 ± 0.29 and 35.06 ± 0.32 for 0.2 and 0.5 g L⁻¹ for 25.0 mg L⁻¹ of Pb(II) concentration. They also revealed the thermodynamic parameters for the adsorption of Pb(II) on the prepared magnetic inverse spinel structure nanoparticles. For a dosage of 0.2 g L⁻¹ at 298 \pm 2.0 K ΔG^0 was -5.61 \pm 0.11 kJ mol⁻¹ and ΔH^0 as 2.141 \pm 0.11 kJ mol⁻¹ and ΔS^0 as 0.026 \pm 0.02 kJ mol⁻¹ K⁻¹ respectively.

Recently Xiang et al. [86] prepared a 3D hierarchical flower-like nickel Ferrite/Manganese dioxide nanocomposite for lead removal from an aqueous solution. SEM images of NiFe₂O₄ and NiFe₂O₄/MnO₂. These nanocomposites exhibited fast lead adsorption with 85.78 mg g⁻¹ as the maximum adsorption capacity

using the Langmuir model and saturation magnetization of the nanocomposite was calculated to be 15.7 emu g⁻¹. The authors showcased that 100% removal efficiency was obtained for initial Pb(II)concentration of less than 15.0 mg L⁻¹ and 92.2% for 20.0 mg L⁻¹initialconcentration which was further reduced to 74.9% and 42.5% for 25.0 and 50.0 mg L⁻¹ respectively. Hence it was concluded that the removal capacity depends on the initial concentration of Pb(II).

Shipley et al.[87] synthesized Fe₃O₄ magnetite nanoparticles having a size of 37.0 nm. These Fe₂O₃nanoparticles were used for the adsorption of Pb(II) along with Cd(II)Zn(II) and Cu(II). The study showed that it was able to attain a 100% lead removal from the solution at a pH of 8 and a contact time of 120 min. The initial loading of lead ion was 500 μ g L⁻¹ and the adsorbent loading varied from 0.05 to 0.5 g L⁻¹. It was also observed that as the adsorbent loading increased the adsorption rate also increased which is due to the increase in available sites of the adsorbent for the metal ion.

5. LIMITATIONS

Employing these magnetic metal nanoparticles as adsorbents for heavy metal removal has certain drawbacks which also need to be considered. One such factor is when there is a transition from bulk to nanoscale the nanoparticles in spite of offering high surface area also causes instability [88]. This instability ultimately leads to the agglomeration of the nanoparticles mainly caused by the interactions due to van der Waals forces. This agglomeration results in the nanoparticles losing their desired capacity and selectivity. Therefore, to avoid this phenomenon, nanoparticles are usually incorporated into other bulk adsorbents or porous supports [88]. The advantages of these magnetic nanoparticles are counteracted by their ability to enter into organisms during ingestion or inhalation as reported by Holsapple et al. [89] and have the potential to translocate within various organs and tissues in the body [90] where they can cause toxicological effects.

6. CONCLUSION

This short survey gives a limelight on the fact that a lot of work is being carried out around the globe for heavy metal removal from water using nano adsorbents, particularly magnetic ones. It is due to the distinctive properties that they exhibit at the nanoscale that a lot of work is underway to further explore its uses in environmental remediation along with other fields. Additionally, nanomaterials can also be functionalized with a number of different chemical compounds increasing their selectivity for toxic metals and other compounds. This review showcased an overview of the application of magnetic nanoadsorbents for the removal of various heavy metal ions such as Cd(II), Cr(III), Cr(IV), Hg(II), and Pb(II). On a laboratory scale, these nanomaterials showed promising results but their application in a fullscale plant is obstructed by certain hurdles such as its cost-effectiveness, scale-up potential, safety, and reliability of the large-scale particle production processes. Little is known about its toxicological effects on human health and the environment. Research is being carried out to determine its effects on the ecosystem and to find methods to reduce it.

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Biodiesel From Algae: A Review

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ABSTRACT

An initiative has been taken to develop alternative source of fuels as fossil fuel feedstock will run out in near future. The Current technological developments focus on third generation biofuels from microalgae rather than first- or second-generation biofuels from animal fat, corn etc. so, algal biomass can be processed to biodiesel, bioethanol and other valuable co- products. This review concentrates on microalgal properties of haematococcus pluvialis, harvesting and its biodiesel preparation by using various methods and processes. Different methods are discussed such as mechanical, solvent, ultrasonication for the oil(lipid) extraction from algal biomass. Further, lipids i.e., triglycerides are converted to FAME (Fatty Acid Methyl Esters) by transesterification process that is nothing but Biodiesel which is a promising source of biofuel.

KEYWORDS

Haematococcus pluvialis, Microalgal Biodiesel, Solvent extraction, Ultrasonic extraction, Transesterification.

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1. INTRODUCTION

Since, the non-renewable resources like coal, natural gas, oil are getting depleted over past few decades, and the need for energy is growing continuously and will grow further. Hence, for all this an alternative source of energy is needed which should also be renewable. Also, pollution is caused by burning of fossil fuels. Hence, alternative source for energy generation is being developed using newly emerging technologies [1]. But, as per estimated records, about 85% of energy comes from fossil fuels and remaining by renewable sources. In recent years, researchers are mainly inclined towards using biomasses of which 1st, 2nd and 3rd generations using different types of biomasses are already done. Now, main focus is on microorganisms-based biomass. So, in this generation, microalgae came in picture as it is seen that it contains a high-lipid content. It grows with a fast rate, and can grow in natural environment as well as man-made ponds. After comparing algal biomass to

others, it was seen that it has capacity to produce oil 10 times more per acre than other biofuel crops used before. But yet, it is not suitable for commercial production due to production cost. Hence, still many new techniques are being studied. Initially, biofuel extraction was carried out with oil press, but now many new techniques like ultra-sonication, using various solvents, supercritical conversion methods are being studied [2]. As for now, the largest producer of biodiesel is Brazil, estimated to have produced 35 billion liters. Now, another reason that other crops from previous generations are replaced by microalgae is that the other crops are primitively used as food crops. Now, as huge amount of total produced crop was used as raw material for biodiesel production, it falls short to supply the agricultural needs. But on the other side, algae are considered as a biological waste, causing various serious issues that are extremely hazardous to environment, like eutrophication. Hence, if algae are used as raw material. Therefore, in this paper we mainly focus on biodiesel obtained from microalgae [3].

1.1. Microalgae

Microalgae are infinitesimal organisms found in marine, brackish and freshwater. They contribute in CO_2 fixation and reduction from atmosphere [4]. Estimated that red algae have many species approx. 6,500-10,000. About 3% of red algae are seawater specific [3]. Their cultivation may be carried out in open/closed ponds as well as in bioreactors, as they require only carbon dioxide and a simple inorganic nitrogen compound for metabolic synthesis of organic molecules [3].

The most common methods to harvest algal biomass from the culture medium are: - Microfiltration and recirculation, Divergent centrifugation, Coagulation or agglomeration, Floatation [5]. Generally, microalgal growth and overall process is done by following steps: Firstly Source i.e., algal biomass growth initiation and its embellishment then development of that particular genus (species) and resource rectification [6].

Some of the advantages are huge amount of biomass can be obtained as its growth is rapid, also their cells contain lipid contents, also some species have a typical pigment which is used for other commercial products like cosmetics, food, etc. As microalgae have lipids, they are now being cultivated to produce fuel [4]. As regarded to have high lipid content mark ably content estimates about 20-70% of dry biomass weight [6]. These lipids are fatty acids, hence, on application of any method of extraction we get crude bio-oil, which is further processed and converted to biodiesel by applying various methods. Apart from oil various valuable components like vitamins, minerals, etc. are present and nevertheless, the waste algal ash can be used as a bio-fertilizer [7].

The microalgae that have been mass cultured for biodiesel production or other biotechnological applications are Arthospira, Chlorella, Dunaliella, haematococcus...etc. as it has lipid content [8]. Haematococcus pluvialis is a great source of astaxanthin. Haematococcus is the general term used for carotenoids [6]. At first, H. pluvialis is seen as free-swimming, green biflagellate microalga. H. pluvialis when exposed to various stress conditions it influences the cell's structural changes throughout their life cycle like pH and temperature. The cell is typically spherical to an ovoid shape having a diameter of $\approx 30 \,\mu m$ [9]. H. pluvialis must be grown in 2 stages: - firstly, culture is grown in closed photobioreactor in nutrient rich media. Then culture is grown in large quantities in open pond raceway system. The other properties of haematococcus include, H. pluvialis has many stages, red color resting stage followed by green colored swimming stage and then again red resting stage. Therefore, the algae are harvested after the reddening cycle. Astaxanthin, the red pigment in the algae is collected for the following use- Enhancing eye health, increasing muscle strength, skin protection from premature ageing, UVA damage and inflammation, immunity, etc. [10,11].

Properties of haematococcus that make it a potential resource for oil feedstock for biodiesel production as It has capacity to accumulate lipids in response to high light intensity or nitrogen deprivation, for trans-esterification, neutral lipids are the main part i.e., substrate preferred for biodiesel production. hydrocarbon chain length shorter than C18, With the production of biofuel, we also get astaxanthin which a valuable co-product. Independence of cultivating algae in photobioreactors and at large scale in open ponds. Haematococcus p. has bigger cell size which makes it easier in harvesting and economic at the same time. The only drawback of this species is, it needs freshwater conditions [4]. Procedure for harvesting culture include Algal cultures were obtained by means of serial dilutions. The cells were cultured in Bold's Basal Medium (BBM), containing 3.4 mM of sodium nitrate [4]. For media preparation the culture medium was modified BG11. The H. Pluvialis cultivation was suspended in 0.5 and 2 L Erlenmeyer flasks (culture time was about 10 and 14 days, respectively) at 21–25°C temperature. The green algae were illuminated by FLs at 40 μ mol photons m⁻²/s, using a 14/10 h light/dark cycle [12]. The cells were kept at 24°C with continuous air supply at (500–700 cm³/min). The pH was adjusted to 7.0 with NaOH before autoclaving. An inoculum of 45×10^3 of cells colony/ml was resuspended for a two-week period in one litre of full medium, under the same conditions as those indicated above (control). The first cysts appeared after four days. Other three replicates of the cultures were done [4]. Sterilization of culture is very essential as the algal culture of haematococcus or any is easily exposed to pathogens, bacteria, fungi, virus, protozoa, etc. so to avoid this condition sterilization is very important. The contamination by other microorganisms can cause changes in the cell structure and reduce the concentration and microalgal yield in very short period of time. To avoid contamination these parameters should be thoroughly maintained: pH (9.0 to 11.0), using high concentrations of nutrients or salinity, and using antibiotics and fungicide [3].

1.2. Biodiesel

Due to increase in demand of fossil fuel, world need to find alternative source which can be generated from renewable sources like animal fat, plant oil etc. This promising solution can create economic development as well as huge impact on environment. Biodiesel is one of alternative source of fuel which is non-toxic, biodegradable and reliable [13].

Benefits of biodiesel include; Biodiesel is energy efficient fuel and byproducts of biodiesel in auto engines are CO₂ and water only. Sources of biodiesel like algae will absorb CO_2 and release oxygen [13]. Other than that, mostly ethanol must be mixed with regular gasoline in order to work in gasoline engines whereas, biodiesel can be used directly in diesel engines. Compared to Petro diesel, biodiesel takes less energy. For certain pollutants like SO_X, CO and particulate matter biodiesel has lower emission rates. Tailpipe emissions of SO_X completely eliminated by biodiesel. Due to environmental regulations Petro diesel require less sulfur content, but sulfur was needed to increase the lubrication. In case of biodiesel, it does not require sulfur for lubrication which is better for environment prospective. We can use biodiesel in diesel engine without any conversions or alterations. This goes for all blends like B2(2% biodiesel, 98% conventional diesel) to B100(100% biodiesel). The only concern is that in cold weather i.e., below 30°F biodiesel's viscosity increases, blocking fuel lines. This issue can be solved by simply adding additives such as high percentage of Petro diesel or by just installing heated fuel lines. Another benefit of biodiesel in terms of average density and heating values as shown in Table-1.

Fuel	Density[gm/cm ³]	Heating value avg, [BTU/gallon]	%Difference vs no. 2 diesel avg.	Ref.
Biodiesel(B100)	0.880	118290	8.60%	[14]
B20 blend	0.847	127250	-1.73%	[15]
B2 blend	0.843	129271	0.19%	[13]

Table-1. Average density	and heating values	of biodiesel and	diesel fuels.
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Biodiesel from algae have high content of fatty acid and has potential benefit over other sources of crops [5]. Algae can be easily grown and does not require any additional fertilizers or pesticides. It requires CO_2 and sunlight to grow. It can also be grown in waste water and nitrogen rich ponds. Algae biodiesel is carbon neutral i.e., CO_2 released through biodiesel combustion is equal to CO_2 consumed by the algae for photosynthesis. The leftover biomass after the extraction can be used for many purposes like animal feed, generation of electricity etc. [14].



Figure-1. Oil yields of feedstocks for biofuel [14, 16, 17].

From **Figure-1**, we can say that biodiesel from Microalgae has higher yield in terms of oil. In case of palm oil and soyabean it needs to be maintained and irrigated which uses lot of valuable resources and leads to problems like soil erosion, greenhouse emission [14].

Factors affecting on biodiesel quality most important criterion is to match appropriate standard biodiesel fuel for example in US the standard is ASTM D 6751-02 "Standard Specification for Biodiesel Fuel (B100) Blend Stock for Distillate Fuels" and for European union EN14214. Quality of feedstock, fatty acid content of parent source, manufacturing process and additional materials used in the process and post- production parameters [13].

1.3. Cavitation

Cavitation can be defined as the phenomena of the formation, growth and subsequent collapse of microbubbles or cavities occurring in extremely small intervals of time(millisecond) releasing large magnitudes of energy over a small location [9]. Cavitation is nothing but disfigurement (spoilation) of molecules of composite hydrocarbons, etc. The effects are amazing as it occurs overall in reactor at single time. Temperature and pressure gradients are essential. Due to vibrations, the voids within molecules go through intense breakdown and OH° radicals' form [9]. Cavitation is divided into main 2 types which are found efficient for trading engrossment because of its simplicity of performance, based on manner of production:

In acoustic cavitation Sound waves of frequency about 16 kHz - 100 MHz are used to produce pressure resonance effect in a liquid medium. This process of cavitation caused by sound waves which results in a chemical change is known as "sonochemistry". In hydrodynamic cavitation the system is tended to erect velocity alteration which gives rise to pressure variances [9].

2. MATERIAL AND METHODS

Haematococcus pluvialis is tested to have 26.02 lipid content of mg/g of dry weight according to [16]. Direct extraction of lipids from H. pluvialis of moisture-rich microalgae was successfully achieved, in a lipid extraction yield of 30.0% of the dry weight of the microalgae as mentioned in [2]. Generally Green algae Haematococcus pluvialis is an interesting strain for lipid extraction since it has been reported to contain about 17-46% of lipids (dry weight). Moreover, with the lipids it is evident that we also get the co-production of valuable products such as astaxanthin is necessary for economic bio fuel processes. So, the lipids or oils from the algae h. pluvialis can be extracted from the following process mentioned below:

2.1. Mechanical Extraction

Techniques used for mechanical extraction are: mechanical pressing, bead milling or bead beating and homogenization. These are the widely and large scale used methods for disruption of algal cell.

2.1.1. Mechanical Pressing

In this method, due to high mechanical pressure on cell wall lipids can be extracted and collected [18].

2.1.2. Bead Milling or Bead Beating

Bead mills are designed to grind or disperse particles down to the micro and nano scales due to collision and shear force of the beads. It is very useful method to release intracellular products by supplying low energy inputs and mild conditions. Factors affecting ball mill efficiency are agitator geometry, biomass concentration, bead filling ratio, bead type and bead diameter [7]. It is found that optimal high bead ratio is (>55% v/v) for disruption. Also, Zirconium oxide beads are found to be more efficient as compared to glass bead due to their higher specific density [7].
2.1.3. Homogenization

Generally, this method is used for emulsifying liquids or non-soluble liquid one another. In these method, three different pressures- 10000,20000,30000 psi was applied to disrupt H. pluvialis cyst [19].

2.2. Solvent Extraction

The basic principles applied for this process is microalgal lipids are anchored on the basic chemistry concept of 'like dissolving like' [20].

Mechanism for solvent extraction: - When a microalgal cell of any species is exposed to a non-polar organic solvent, such as hexane and methanol, etc., the organic solvents like hexane and methanol penetrates the cytoplasm through the cell membrane and by van der Waals force they react with the neutral lipids present in the algae and form an organic solvent-lipids complex. This organic solvent–lipids complex is then determined by a concentration gradient, which helps it to diffuse the cell membrane. Subsequently, the neutral lipids are extracted out of the cells which is nothing but oil [20]. Presence of water causes difficulty, forming a barrier to solvent penetration so the yield will be better if the cell walls are ruptured prior to solvent contact to improve lipid yield. They can be ruptured by mechanical methods of bead beating, ultrasonication, or using heat or pressure, to achieve better lipid recovery, shorten process time, and recover solvent for re-use etc. [2,13].

Chloroform/methanol or ethanol (1:2 v/v) is the most frequently used organic solvent mixture for lipid extraction from any living tissue as its yields are also high and it does not require the complete drying of microalgal biomass. [20,19,6].

2.3. Ultrasonic (Acoustic Cavitation) based Extraction

Acoustic Cavitation: In this, ultrasound waves with oscillation range of 16 kHz-100 MHz are used. The reason to apply such high frequency is to generate gaps between liquid molecules by reducing the intermolecular space. Due to these large bubbles generate which enlarge as a result of continuous and rigorous contraction and diffraction pattern, on which huge proportion of energy releases. Intensity can be calculated by [9]:

Intensity of ultrasonic equipment = Power input of system / Transmitting area of US transducer

2.3.1. Algal Cell Disruption using Acoustic Ultrasonicator

A specimen of certain alga is taken and put in sonicator apparatus and process was started. Time required for process to complete efficiently is different for different species due to different thickness of cell wall of each alga. Hence, until all cells get disrupted and release oil, along with other components like pigments and nutrients (proteins, vitamins, etc.) the process continues [10]. After the oil is extracted from the above methods, we study the fatty acid (lipid) composition and lipid content. The fatty acid profile in H. pluvialis was palmitic, estearic, oleic, linoleic, linolenic and linolelaidic acids were the major components under control and stress conditions. The lipid content was high under a) stress conditions tested (34.85% weight of dry biomass), but not high enough to meet the requirements for commercial biodiesel production. Therefore, it will be necessary to further optimize culture conditions for this organism so that it becomes a viable source of biofuel [4]. Calculation of lipid content is calculated by following equation [5]

Oil yield of 100 Microalgae biomass = Mass of extracted oil/mass of dried algae

3. TRANSESTERIFICATION PROCESS

In the process of transesterification, the fatty acid containing lipid fractions are reacted with alcohol (methanol, ethanol, isopropanol, butanol) and converted to fatty acid alkyl esters. When methanol is used in the process of transesterification it produces fatty acid methyl ester (FAME) i.e., biodiesel [20]. Catalyst like (H₂SO₄) or an alkali such as (NaOH or KOH) can be used for transesterification. Alkali Catalysts are preferred as they are non-flammable and have comparatively few safety risks, they have low solubility in methanol and have faster reaction rates (estimated at 4000× faster) and contain higher conversions than acid catalysts for the transesterification of acylglycerols [20,21]. To ensure quantitative transesterification in a lab scale experiments, where just very small quantity of microalgal oil is produced like in few grams just add large amount of methanol to it, this is done for the same [20]. Once transesterification is completed, the product containing biodiesel, glycerol, reformed alkali catalyst, excess methanol, and un-transesterified lipids, are then passed through post transesterification purification to remove by-product contaminants like glycerol, alkali catalyst, and excess methanol. A laboratoryscale post-transesterification purification method basically include these 2 steps. The reaction mixture is left to settle under gravity which to induce partitioning (top biodiesel/un-transesterified lipids phase and bottom glycerol phase). Once the biodiesel/un-transesterified lipids phase are separated, it is washed repeatedly and thoroughly with water to eliminate any alkali catalyst and excess methanol [20].

4. COMPARISON

4.1 Extraction Methods

The comparison of different extraction methods explained in **Table-2**.

Method of Extraction	efficiency rating	lipid extracted %	Biodiesel yield	Ref.
Ultrasonication	High	18	60%	[22],[15],[23], [11]
Bead beating	Moderate	16	-	[22], [23]
Microwaves	High	10-12	-	[22], [23]
Solvent: 1:2 (v/v) chloroform: ethanol/ Methanol, Hexane	Moderate- High	8	4.1- 6.5%	[22], [23], [24]

Table-2. Extraction methods

From the above **Table-2**, it is cleared that sonication and solvent extraction have higher efficiency and lipids extracted are in considerable quantity. So, by combining the two methods i.e., Solvent extraction followed by ultrasonication we get maximum results

4.2. Use of Different Solvents

The percentage oil extraction yield using different solvents is explained in Figure-2.





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5. CONCLUSION

Here in this paper, we have discussed about the conversion of algae to biodiesel, which can be achieved by the methods discussed above. Including the study of algal species haematococcus pluvialis and its properties, why it is fit for biodiesel production as it has 34.58% of lipids per dry weight, harvesting the species and sterilization. These lipids can be extracted by the methods of Sonication (Acoustic cavitation), Solvent Extraction, and Mechanical methods with the comparison between these extraction methods and also comparison between solvents that can be used for the same purpose. Ultrasonication followed by solvent extraction of lipids give impressive results. The most convenient process applied for the conversion of lipids/ microalgal oils to biodiesel (FAME) is transesterification. That is nothing but the conversion of lipids to fatty acid methyl esters (FAME). After the biodiesel is obtained it is refined. Biodiesel obtained from the transesterification process is less viscous and that's why it is easy to replace petroleum diesel. This report focuses on lab scale production and hence it requires a lot of effort to achieve a commercial scale production of green and cost-effective algal biodiesel.

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Impact of Re-establishment of Central Administrative Building on Vijaynagar Area, Sangli during Period of 2014 to 2021

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ABSTRACT

The scope of project work is limited to study of impacts of reestablishment of central administrative building on surrounding properties in the study area. Vijayanagar is the central area connecting Sangli and Miraj city in the eastern part of SMKC and is selected for the study considering the increasing residential and commercial development in the said area after Re-establishment of Central Administrative Building in this area. Vijayanagar is rapidly developing residential and commercial area having flats, bungalows, shops, godowns, theatres, various colonies, apartments etc. The study Period considered for this project is from 2014 to 2021. Information and data of sale instances and Rental instances has been collected personally from the study area and sub registrar office, also from web site of IGR. After the commencement of construction of the Central Administrative Building, gradual changes in the area started occurring. This place started attracting many private investors. They started investing in surrounding properties. This report involves methodological study and analysis of various data collected like sales and rental instances from a residential locality Vijayanagar Sangli City. An Honest approach has been adopted to investigate Sale instances and rental instances transactional effect in the residential market from a period of 2014-21. Also, Parallel study also has been enlightened comparing pricing effect in Share market, gold investment with respect to residential market within this period.

KEYWORDS

Realestate, Realestate sector, Re-establishment, Rate of interest.

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1. INTRODUCTION

Before the year 2014, Vijaynagar Area was the most underdeveloped area in Sangli City. There were fewer commercial activities and fewer property transactions. Economic and Social growth was mediocre. Lesser employment opportunities were available and therefore the lifestyle of native people was not so good. After the commencement of construction of the Central Administrative Building, gradual

changes in the area started occurring. This place started attracting many private investors.

They started investing in surrounding properties. As a result, slight rise in property rates were observed during this period. Also, the surrounding area started to develop with the progress of construction of the Central Administrative Building. After the completion of construction of the structure, large amount of development in that area is observed and there is still scope for future developments as many new projects are getting introduced in that area. Also, it has become one of the value adding factors in the development of the Sangli City.

Hence, construction of one value adding structure in City can boost the economic, social and real estate sector prospective of the entire city and helps in enhancing the lifestyle of the community as well as give fame to the city and boost its moral.

1.1. Literature Review

This study has reviewed the concept of valuation for the building and the specific nature and challenges for valuer, engineer and surveyor to calculate the market value of the building [1]. Based on comprehensive research in the field of valuation, Parmar et al. Pune is a metro city and 9th most popular city in India. The focus of this paper is to study the current rate variation for commercial properties in different areas of the Pune city, India and also to find out the factors affecting the commercial property valuation. Commercial property is referred to as property used for revenue generation [2]. Many studies have seen analysis of commercial property valuation parameters that affect their value [3]. presented the general field practise of real estate property value. The methodology in this study has been confirmed by a government-approved valuer and a concerned field specialist. Valuation is the technique of estimating or determining the fair price or value of a property such as a building, a factory, other engineering structures of various types, land etc. The present value of a property is determined by valuation. The present value of the property may be decided by its selling price, or income or rent it may fetch. The value of property depends on its structure, life maintenance, location, bank interest, legal control, etc. [4]. There is a strong correlation between urbanization and economic development, where cities presently contribute approximately 60% to the GDP and which is expected to increase to 75% by 2030, also affect on the development of Real Estate market. The Guwahati city is rightly termed as the engines of economic growth and innovation. This pace and scale of urbanization is unprecedented for India [5]. Valuation is the analytical process of determining the currents worth of an asset such as residential, commercial, industrial, agricultural land. Value is determined on basis of its selling price and rent or income it can fetch. The purpose of this study is to introduce people with general field practice of valuation of real estate property. The objective of this study is to identify the market value of properties for bank finance purpose which is situated in urban, semi urban and rural area of Dhule (Maharashtra), India. This study is carried out under the guidance of government approved valuer [6].

1.2. Need of the Study

To boost development and economy government decided to shift the Central Administrative Building of Sangli District in Vijaynagar Area which have created drastic impact on almost all sectors including real estate. The said reform increases a sense of hope and confidence in the prospective buyers. As a Civil Engineer and Student of Valuation, it is required to study how exactly re-establishment of main administrative building of a district affects value, growth, transparency and increase in transactions over a period of time and to draw out some conclusions/findings which would be helpful for future.

1.3. Aim and Objectives

To showcase the effects of Re-establishment of the Central Administrative Building on Vijaynagar Area of Sangli, before and after its construction from the year 2014 to 2021

- To study the effects of construction of the Central Administrative Building on the development of surrounding areas
- To study its contribution on the development of Sangli City
- To study its effect on the community/society residing in that area
- To analyse the growth in Real Estate Valuation of surrounding properties
- To study the overall growth in terms of Employment, Entertainment, Social life, Amenities etc.

1.4. Scope

The scope of project work is limited to study of impacts of reestablishment of central administrative building on surrounding properties in the study area.

1.5. Methodology

The study Period considered for this project is from 2014 to 2021. Information and Data of sale instances and Rental instances has been collected personally from the study area and sub registrar office, also from web site of IGR. Oral Information of sale is noted down on note book, similarly, detailed collected data of Rentals are noted down on note book. Detail information of the Flats, Shops, Open Land is gathered. Also information gathered from various Estate dealers and Builders and Developers. During site visits, all 43 points which are given in the weightage criteria table for Residential properties (Annexure - 3) for both sale instances and Rental instances have also been considered. Levels from level number 5 to 1 have been

considered for all the 43 points given in the weightage criteria table. Considering levels and weightage for each point and making calculation of total weightage scores, levels and weightage for each point have been considered and calculated for residential properties. Site inspection is a very important criterion, and has been used for collecting information of all data that is for genuine sale transaction and genuine rental transaction. **Figure-1** shows the location of Vijayanagar area.



Figure-1. Location of Vijayanagar Area

Various important points such as Plot area, Shape of plot, Access of property, Orientation, Access on roads, various facilities, Specification, Workmanship, Type of structures, Age and future life, maintenance, Title of property, Ownership and other points are noted and have been considered while inspecting the sites. For Property analysing, instances of sale price, paid consideration including unaccounted or black money paid has been considered. Additional information of Index II in Registrar office is considered for price paid consideration during the period from 2014 to 2021 For analysis of fair market rent 1 sale instances has been compared with 2 Rentals instances and fair market rent for each sale has been calculated accordingly. Rates of interest have been calculated for each sale considering the date of Transaction, Price Paid consideration, built up area, Weightage score, estimated fair rate of rent, Annual rent, Outgoings per year, estimated. future life and Years Purchase. As properties under consideration have estimated future life more than 60 years, Years purchase is calculated on Single Rate basis. Various Economic indices are compared with rates of interest. Graphs are prepared showing rates of interest yielded by the properties sold and various economic indices (along vertical or Y axis) against the dates of transaction of sale (along horizontal X axis) which made comparison easy. Indices like BSE sensex, NSE, Gold rate, Dollar exchange rate, WPI index and Government bonds are compared with Rates of interest.

2. STUDY AREA

Vijaynagar is the central area connecting Sangli and Miraj city in the eastern part of SMKC and is selected for the study considering the increasing residential and commercial development in the said area after Re-establishment of Central Administrative Building in this area. Vijaynagar is rapidly developing residential and commercial area having flats, bunglows, shops, godowns, theatres, various colonies, apartments etc. The road transport facility is dominant as it has access through Sangli Miraj Highway State Road. Before construction of CAB, this area was less prominent, developed but after construction and inauguration of CAB development boosted rapidly. Construction of CAB was commenced in 2015 and it was inaugurated in 2017.

Actual operations and official work of CAB started in early 2018. Hence, the period of 2014 to 2021 is considered for study. Also, it is surrounded by churches, temples, parks, hospitals etc. Considering facilities, infrastructure and increasing population residential and commercial structures in Vijaynagar have come up largely in the current decade.

3. DATA COLLECTION AND ANALYSIS

3.1. Rate of Interest of Properties under Study

The rate of interest for properties involved in sale instances is calculated asRate of Interest = $100 \div \text{Y.P.}$ The rate of interest varies indicating that market values were more or less steady. Also, it is observed that as built up area decreases, rate of interest increases and vice versa. MASTER OF COMMERCE (VALUATION OF REAL ESTATE) Page 50 During and after year 2017, it indicates increasing rate of interest resulting in decrease in the market values of residential properties due to central administrative building re-establishment. Details are given in Annexure 7. The rate of interest varies in the range of 2.33% to 4.63% during the period of study as shown in graph below.

3.2. Rate of Interest and Economic Indices

Investment in the real estate cannot be considered in isolation. It needs to be considered as one of the alternative forms of investment. The rates of interest yielded by investment in real properties and in other forms of investment are affected by overall national and international economic conditions. The rate of interest yielded by real estate thus needs to be compared with the returns from other alternative forms of investment.

This can be done by comparing rate of interest yielded with various economic indices like B.S.E and N.S.E index, Dollar exchange rate, Gold rate etc. Thus, this comparison is shown further graphically in Annexure 8. The dates of transactions are taken along X-axis, Rate of interest along one side of Y-axis and Economic indices along other side of Y-axis.

3.3. Comparison of Rate of Interest and B.S.E Index

During the study period in stock market, the B.S.E index has increased from 25,329 to 56,124 with growth rate of 14-18%. The ROI is slightly fluctuating and increasing after Jan 2017 (after re-establishment of CAB). In comparison with B.S.E, ROI drops down while B.S.E shoots up in the year 2019. **Figure-2** shows the comparison of Rate of interest and B.S.E index.



Figure-2. Comparison of Rate of interest and B.S.E index.

3.4. Comparison of Rate of interest and N.S.E Nifty

During the study period in stock market, the N.S.E nifty has increased from 7,568 to 16,705 with growth rate of 14-18%. The ROI is slightly fluctuating and increasing after Jan 2017 (after re-establishment of CAB). In comparison with N.S.E, ROI drops down while N.S.E shoots up in the year 2019. **Figure-3** shows the comparison of rate of interest and N.S.E Nifty.



Figure-3. Comparison of Rate of interest and N.S.E Nifty.

3.5. Comparison of Rate of Interest and Dollar Exchange Rate

During study period dollar exchange rate has increased from Rs. 61.145 to Rs. 73.466 with growth of 40% to 50%. The dollar exchange rate is gradually increasing however ROI slightly fluctuating.



Figure-4. Comparison of Rate of interest and Dollar Exchange Rate. Figure-4 shows the rate of interest and dollar exchange rate.

3.6. Comparison of Rate of interest and Gold Rate:

Gold Rate recorded big growth of 72% between the year 2020-21. Then a small growth of 5% is observed in the year 2021 and thereafter it starts declining by a small rate of 11% to 7% per year. ROI and gold rate both are slightly fluctuating as shown in the graph. **Figure-5** shows the rate of interest and gold rate.



Figure-5. Comparison of Rate of interest and Gold Rate.

3.7. Comparison of Rate of interest and Government Bonds

The yield on Government bond drop is about 3% to 4.5% is observed. It is 8% in 2014 and decrease by 7% upto year 2015. Then it decreases to 6% in early 2016 and rises to 7% at the end of 2016. In 2017, it drops to 6% and it keeps fluctuating at 5-6% from 2017 to 2021. ROI is less as compared to Government bonds rate. **Figure-6** shows the comparison of Rate of interest and Government Bonds.



Figure-6. Comparison of Rate of interest and Government Bonds.

4. **RESULTS**

To analyse the effect of re-establishment of CAB on surrounding real estate properties registered sale instances of residential and commercial units for period 2014-2021 is considered which are listed in Annexure 9

Total 181 sale instances are analysed from Vijaynagar area to study the effect earlier and after construction of Central Administrative Building. Details are shown in Annexure 9.

Total 66 sale instances of open land are considered for study of effect of reestablishment of CAB on land rate. Details are shown in Annexure 10

Total 83 sale instances of commercial units are considered for study of effect of re-establishment of CAB on shop units rate. Details are shown in Annexure 11

Total 32 sale instances of residential flat units are considered for study of effect of re-establishment of CAB on flat rate. Details are shown in Annexure 12

Highest, Lowest and Average built-up area rate per sq.mt. are recorded to get clear picture of residential and commercial real estate market.

Year	ar Number of Sale	Year Number Highest of Sale		sq.mt	ate per	e per Lowest built up rate pe sq.mt		ate per	Average built up area rate per sq.mt.		a rate per
	Instances	Land	Shop	Flat	Land	Shop	Flat	Land	Shop	Flat	
2014	25	5,091	77,288	31,210	1,242	13,826	27,202	5,712	84,201	44,811	
2015	47	27,454	80,317	29,270	621	27,210	19,565	27,764	93,922	39,052	
2016	24	15,953	63,540	32,218	1,561	30,869	26,585	16,733	78,974	45,510	
2017	20	15,317	53,893	52,356	1,740	32,244	28,096	16,187	70,015	66,404	
2018	24	15,351	61,020	42,341	53	30,820	29,910	15,377	76,430	57,296	
2019	15	34,050	51,706	48,704	8,306	26,202	30,773	38,203	64,807	64,090	
2020	16	24,642	56,426	54,883	6,058	35,245	29,919	27,671	74,048	69,842	
2021	10	20,049	62,913	43,140	18,223	25,839	29,860	29,160	75,832	58,070	

Table No. 1 - Number of Sale Instances and Rate per sqmt. (2014-2021)

 From registration department, on state level, total number of transactions and their values are collected which is useful to study the effect on the frequency of transaction. Table No. 2 - Number of Transactions and Total collection in Maharashtra

(2014-2021)

Year	Number of Transactions	Total collection (Rs.)
2014-2015	22,97,929.00	19,959.09
2015-2016	23,08,809.00	21,767.01
2016-2017	21,22,591.00	21,052.13
2017-2018	21,93,149.00	26,470.80
2018-2019	22,91,922.00	28,579.59
2020-2021	16,38,936.00	21,012.00

Table-1 and **Table-2** show the number of sale instances and rate per sqmt (2014-21) and number of total transactions and total collection in Maharashtra (2014-21).

4.1. Analysis of Number of Sale Instances

Total 181 sale instances are analysed from Vijaynagar area as shown in graph below. The number of sale instances are 25 in 2014 have increased to 47 in 2015 which suddenly drops to 24 in 2016 and 20 in 2017 which again rises to 24 in 2018 which further drops to 15 in 2019 till 2021. The rise of sales in 2015 indicates the effect of CAB in surrounding area as the construction of CAB was commenced which starts vanishing in 2018 onwards. In the concerned area, numbers of sale transactions increase in 2018 are also due to new projects are ready for sale.

The growth rate of number of transactions from 2014 to 2015 is about 100% which suddenly drops by 50% in 2017.

From 2019 onwards it indicates that the numbers of transactions are attaining the previous situation.

The effect of re-establishment of CAB can be clearly seen in increase of number of sales immediately after commencement of construction of CAB in the study area. **Figure-7** shows the frequency of sale instances.



Figure-7. Frequency of sale instances.

On state level, the same situation is observed in terms of number of transactions i.e., indicates increase in number of transactions immediately after reestablishment of CAB. This effect remains continued for a year and then onwards it regaining its past position. It also increases the revenue of State Government. **Figure-8** shows the frequency of sale instances in Maharashtra.



Figure-8. Frequency of sale instances in Maharashtra.

5. CONCLUSIONS

Rate of interest yielded by residential real estate properties in my study area is between the ranges of 2.33 to 4.63 during the period 2014 to 2021. After graphical representation of ROI, in comparison with various indices there is no well-defined relation between ROI and various indices.

Data from IGR website indicates that the Sale transactions are less before reestablishment of CAB i.e., before 2014, for next one year they are increasing and after January 2016, it started growing gradually. And in January 2020 it seems to increase largely after complete shift of CAB. From the transactions it is observed that the conditions before re-establishment started growing till date.

This growth is due to CAB but it also possesses some boost due to Krishna River Flood 2019 and 2021. Also, some reduction in number of transactions is observed due to pandemic effect but again it is regaining its original growth rate gradually and the situation seems to remain positive in coming days. A rise in rate per Sqmt. for land is increased by about 600% from 2014. A rise in rate per Sqmt. on built up area for shop is increased by about 155% from 2014. A rise in rate per Sqmt. on built up area for flat is increased by about 187% from 2014. After the commencement of construction of the Central Administrative Building, gradual changes in the area started occurring. This place started attracting many private investors. They started investing in surrounding properties. As a result, rise in property rates were observed during this period. Also, the surrounding area started to develop with the progress of construction of the Structure, large amount of development in that area is observed and there is still scope for future developments as many new

projects are getting introduced in that area. Also, it has become one of the value adding factors in the development of the Sangli City.

A study regarding sale of open land indicates that before re-establishment the documentary land rates are very near to government guideline value or there is less difference between the actual and documentary amount paid. After re-establishment, the documentary sale values are quite higher and nearer to the actual sale transactions immediately after re-establishment. The same effect remains constant upto 2021.

Hence, construction of one value adding structure in City can boost the economic, social and real estate sector prospective of the entire city and helps in enhancing the lifestyle of the community as well as give fame to the city and boost its morale.

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Effect of Partial Replacement of Fly Ash and GGBS with Cement in Concrete

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ABSTRACT

Ordinary Portland Cement (OPC) is used as a binding medium in the construction industry all over the world. The rapid infrastructure development leads to an increase in energy demand and carbon dioxide evolution in the cement manufacturing industry. In this context, it is essential to find an alternative, which reduces the depletion of natural resources, energy consumption and carbon dioxide emission. On the other hand, many industries generate wastes like fly ash, ground blast furnace slag (GGBS), silica fume, red mud, pond ash, sugarcane bagasse ash, etc. The disposal of these waste materials causes environmental waste management problems. To overcome this issue, in this paper, attempts have been made to determine the optimum percentage of fly ash and GGBS with cement in M30 grade concrete. The experimental investigations revealed that the concrete mix with 15% FA+15% GGBS+70%OPC combination results in the optimum compressive, split tensile and flexural strength.

KEYWORDS

Fly ash, Blast furnace slag, Compressive strength, Split tensile strength, Flexural strength, Concrete.

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1. INTRODUCTION

The demand for cement is always rising due to rapid infrastructure development all around the world. The manufacturing process of cement results in depletion of natural resources, energy consumption and also emit carbon dioxide into the atmosphere and evolve about 5% of the global carbon emissions. Hence, the construction industry has been in search of another alternative to cement in terms of either binding material or mineral admixture. In contrast to this, many industries generate waste ingredients like fly ash (FA), blast furnace slag which is ground and granulated in nature (GGBS), silica fume, red mud, pond ash, sugarcane bagasse ash, rubber waste, plastic waste, demolished concrete waste, etc. which is resulting to detrimental threats to the environment along with the waste disposal crisis.

Many researchers have investigated the effect of these waste materials as a partial replacement for cement. The different technologies to use the fly ash are essential in order to reduce CO_2 emissions [1]. The pozzolanic materials like GGBS and fly ash result in enhancement of the compressive strength of concrete due to

pozzolanic activity [2]. The inclusion of fly ash and GGBS in concrete improves the properties of concrete in the fresh and hardened state [3, 4]. The combined utilization of blended materials like high volume fly ash and GGBS leads to better strength, resistance to chemical attack, reduction in environmental influence and economic alternative to construction material [5]. Attempts have been made to obtain the optimum replacement percentage. The 60% replacement of pulverized fly ash and 40% replacement of GGBS improves the compressive strength, spilt tensile strength and flexural strength by 25%, 41% and 34% respectively at the end of 28 days [6]. In the M25 grade of concrete, when the portland cement is replaced by 9% GGBS and 40% fly ash resulted in maximum compressive, split tensile and flexural strength [7]. The critical research appraisal highlighted the need for further study to determine the optimum proportion of fly ash and GGBS for the partial replacement of cement.

In the present study, FA and GGBS waste by-products from thermal power plants and the pig iron industry respectively are used at different proportions as a partial replacement of cement in M30 grade concrete. The experimental investigation is carried out on concrete mixes with partial replacement of fly ash of different proportion 0%, 5%, 10%, 15%, 20%, 25% and 30% and GGBS of different proportion 0%, 30%, 25%, 20%, 15%, 10% and 5% by the dry weight of cement. The tests are conducted to determine the properties of fresh concrete in terms of workability and the properties of hardened concrete in terms of compressive, split tensile and flexural strength.

2. TESTING OF MATERIALS

The properties of cement, coarse aggregate, sand, water, fly ash and ground granulated blast furnace slag (GGBS) are obtained by performing tests in the laboratory.

Sr. No.	Characteristics	ACC Cement Experimental results	Requirements as per IS:269-2015 [8]
1	Compressive Strength		
	i. 3-Days	42.0	Not less than 27
	ii. 7-Days	52.0	Not less than 37
	iii. 28-Days	65.0	Not less than 53
2	Fineness: Specific Surface (m ² /kg)	349	Not less than 225
	Soundness:	1.0mm	Not more than 10mm
3	Setting Time (minutes):		
	i. Initial	195	Not less than 30
	ii. Final	280	Not more than

Table-1. Physical Properties.

			600
4	Specific Gravity of OPC 53 grade cement		3.15

2.1. Ordinary Portland Cement

In the present investigation work, ACC cement of 53 grade is used. The experimental results are obtained as shown in **Table-1**.

2.2. Sand

The natural fine aggregate brought from the local river not containing organic impurities is utilized in the manufacturing of concrete. The sieve analysis is performed on the fine aggregate. The physical characteristics of fine aggregate are depicted in **Table-2**.

Sr. No.	Property of fine aggregate	Requirement as per IS:2386-1963 [9]	Experimental result
1	Silt content	3%	0.88%
2	Specific Gravity	2.6-2.8	2.75
3	Fineness Modulus	2.6 -2.9	2.57
4	Water absorption	-	1.0%
5	Free Moisture content	-	Nil

Table-2. Characteristics of Fine Aggregate.

The sieve analysis of fine aggregate is performed and specified in **Table-3**.

2.3. Coarse Aggregate (C.A.)

The crushed aggregates used consisted of 10mm and 20mm nominal size and are tested as per IS: 383-2016 [10]. The features of C.A. are indicated in **Table-4**. The grading of C.A. is obtained and mentioned in **Table-5**.

Table-3. Sieve Analysis of Fine Aggregates per IS 383: 2016 [10].

Sr. No.	Sieve Size	Weight Retained in gms	% wt. Retained	Cumulative % Retained	% Passing	Cumulative percentage passing as per IS:383-2016 ZONE I
1	4.75 mm	0	0	0	100	90-100
2	2.36 mm	439	21.95	21.95	78.05	60-95
3	1.18 mm	234	11.70	33.62	66.35	30-70
4	600µ	1039	51.95	85.60	14.40	14-34
5	300µ	227	11.35	96.95	3.05	3-20
6	150μ	45	2.25	99.2	0.8	0-10

Sr. No.	Property	Test	Requirement as per
		result	IS: 2386-1963 [9]
1	Specific Gravity	2.8	2.6-2.8
2	Impact value	14.5%	30% used for concrete
			(Maximum)
3	Crushing value	18.6%	30% used for surface
			course (Maximum)
			45% used for other than
			wearing course
			(Maximum)
4	Size of Aggregates	20mm	-
5	Water absorption	0.6%	-
6	Free Moisture content	Nil	-
7	Fineness Modulus for 20mm	7.08	5.5 to 8.0
8	Fineness Modulus for 10mm	6.20	5.5 to 8.0

Table- 4. Characteristics of Coarse Aggregate.

Table-5. Gradation of Coarse Aggregate.

IS	Cumulative	Cumulative	Cumulative	Cumulative	Combined	Confirmed
Sieve	Percentage	Percentage	Percentage	Percentage	grading	Combined
(mm)	of	of	of	of	(100%)	grading
	Passing	Passing (%)	Passing	Passing		As per
	(%)		(60%)	(40%)		IS:383-
						2016[10]
	Fraction I	Fraction II	Fraction I	Fraction II		
	(20mm)	(10mm)	(20mm)	(10mm)		
40	100	100	60	40	100	100
20	100	100	60	40	100	95-100
10	0	71.20	-	28.5	28.5	25-55
4.75	0	9.40	-	3.7	3.7	0-10
2.36	0	0	-	-	-	-

2.4. Water

Potable water free from salt is used for casting and curing concrete as per IS: 456-2000 [11] recommendation.

2.5. Fly Ash

The fly ash used is obtained from Ash-tech India privet Ltd, Pune. The physical and chemical characteristics of Fly Ash are depicted in **Table-6**.

Sr. No.	Property	Fly Ash	Requirement as per IS:3812-Part 1-2003[12]
1	CaO	3.68	3 to 5
2	Silica content	60.27	70 (min)
3	Al ₂ O ₃	25.46	70 (min.)
4	Fe ₂ O ₃	6.02	
5	LOI	1.10	5 (max.)
6	Magnesia	0.29	5 (max.)
7	Alkalis	1.36	1.5 (max.)
8	SO ₃	0.12	3 (max.)
9	Specific gravity	2.20	2.10 to 2.60
10	Specific Surface m ² /kg	398	250 (min.)

Table-6. Features of Fly Ash.

2.6. Blast Furnace slag (GGBS)

GGBS TISCO 78 confirming to IS:12089-1987 [13] is used and the Physical features of GGBS are displayed in **Table-7**.

Sr.	Characteristics	Properties	Requirement as per
No.		of slag used	IS:12089-1987 [13]
1	SiO ₂	31.70	
2	CaO	32.30	
3	Al ₂ O ₃	24.00	
4	MnO	1.25	5.5 (max.)
5	MgO	5.92	17.0 (max.)
6	Sulphide Sulphur	0.80	2.0 (max.)
7	Specific gravity	2.95	2.90 to 3.10
8	Fineness, m ² /kg	330	
9	Glass content percentage	93	
10	Bulk density	1100	
11	Colour	Dull white	

Table-7. Physical features of GGBS.

3. METHODOLOGY

3.1. Trial Concrete Mixes

The seven trial concrete mixes are prepared using different proportion of fly Ash and GGBS as shown in **Table-8**.

Sr. No.	Concrete Mix	% Fly Ash + % GGBS
1	M30 (0+0)	Normal concrete (0% FA +0% GGBS)
2	M30 (0+30)	0% FA +30% GGBS
3	M30 (5+25)	5% FA + 25% GGBS
4	M30 (10+20)	10% FA + 20% GGBS
5	M30 (15+15)	15% FA + 15% GGBS
6	M30 (20+10)	20% FA + 10% GGBS
7	M30 (25+5)	25% FA + 5% GGBS
8	M30 (30+0)	30% FA + 0% GGBS

Table- 8. Concrete Mixes.

3.2. Concrete Mix Design

The data used for mix design M30 grade concrete is as described in Table-9.

Sr. No.	Data	Specification
1	Grade designation	M30
2	Type of concrete	RCC
3	Sort of cement	OPC (53 grade)
4	Nature of coarse aggregate	Crushed angular
5	Maximum nominal size of aggregate	20mm, 10mm
6	Workability	Slump = 100mm
7	Exposure environment	Severe
8	Fine aggregate	Grading zone I confirmed to
		IS: 383-2016 [10]
9	The specific gravity of cement	3.15
10	The specific gravity of C.A.	2.75
11	The specific gravity of fine aggregate	2.80
12	The specific gravity of Fly Ash	2.20
13	The specific gravity of GGBS	2.95
14	Water absorption for C.A.	0.6%
15	Water absorption for fine aggregate	1.0%
16	The moisture content of aggregate for	Nil
	coarse aggregate	
17	The moisture content of aggregate for	Nil
	fine aggregate	

Table-9. Data for Concrete Mix Design.

The proportion of ingredients of concrete is obtained by using IS:10262-2009 [14] for M30 grade concrete. The mix proportion of concrete mixes containing fly ash and GGBS is determined by considering cement content as 70% fraction of total cementitious material and pozzolanic materials as 30% fraction of total cementitious material required.

4. RESULTS AND DISCUSSION

4.1. Workability

The fresh property of concrete i.e., workability is measured by the slump cone test as shown in **Figure-1**.



Figure-1. Slump cone test on fresh concrete.

The results obtained from the slump cone test on fresh concrete are presented in **Figure-2**.





From **Figure-2**, it is observed that concrete mixes with different percentages of fly ash and GGBS show more workability than normal concrete. The workability of concrete mixes M30(0+30), M30(5+25), M30(10+20), M30(15+15), M30(20+10), M30(25+5) and M30(30+0) are increased by 28.57%, 25.71%, 20.00%, 15.24%, 12.38%, 9.52%, 4.76% w.r.t. M30(0+0). This is due to fact that the use of good quality finely divided fly ash always increases the workability. While with the

increase in the quantity of GGBS in concrete mix slump increases. This is because of the glassy surface configuration, fineness and granulated particle shape of slag, which is different from cement particles.

4.2. Compressive Strength

The compressive strength test is carried out according to IS:516-1959 [15]. The cubes of size 150mmx150mmx150mm are positioned in the compression testing machine in the way the load is exerted to opposite sides of the cubic specimens as cast, that is, not to the top and bottom. The load is applied without shock and gradually improved at a frequency of approximately 140kg/sq.cm/min until the resistance of the cubes to the ever-rising load breaks down and no larger load can be sustained by a compression testing machine of 2000kN capacity. The ultimate load applied to the cubic specimen is then noted. **Figure-3** presents the compression strength testing cube specimen.



Figure-3. Compression test of cube specimen.



Figure-4. Compressive Strength of Concrete.

Figure-4 represents a comparison of compressive strength results for 7, 14 and 28 days. From **Figure-4**, it is detected that, compressive strength of concrete mixes M30(0+30), M30(5+25), M30(10+20), M30(15+15), M30(20+10), M30(25+5) and M30(30+0) are improved by 1.58%, 3.54%, 5.71%, 16.26%, 5.39%, 3.07%, 1.62% w.r.t. M30(0+0) at the age of 7 days. The compressive strength of concrete mixes M30(0+30), M30(5+25), M30(10+20), M30(15+15), M30(20+10), M30(25+5) and M30(30+0) are increased by 2.04%, 7.31%, 11.29%, 17.45%, 11.57%, 3.74%, 3.50% w.r.t. M30(0+0) at the age of 21 days. The compressive strength of concrete mixes M30(0+30), M30(5+25), M30(10+20), M30(15+15), M30(20+10), M30(25+5) and M30(30+0) are enhanced by 0.94%, 4.41%, 8.35%, 20.07%, 12.50%, 10.78%, 2.56% w.r.t. M30(0+0) at the end of time period of 28 days.

This indicates that concrete mixes with different percentages of fly ash and GGBS result in more compressive strength than normal concrete due to the pozzolanic activity of fly ash and GGBS. The failure pattern of normal concrete mix results in many uniformly distributed cracks. However, concrete mixes with fly ash and GGBS show only a few cracks at internal transition zones.

The concrete mix with 15% fly ash plus 15% GGBS and 70% cement produces the optimum compressive strength among the trial mixes taken into consideration.

This also shows that the inclusion of fly ash and GGBS develops slower strength at an early age. Since the pozzolanic reaction proceeds slowly since fly ash is not highly reactive and surface hydration of GGBS is a little slower than cement particles. However, because of continued pozzolanic reactivity concrete with fly ash and GGBS develops greater strength at a later age, which is observed to be exceeded that of the normal concrete without fly ash and GGBS.

4.3. Spilt Tensile Strength of Concrete

Split Tensile Strength on cylindrical specimens of size 150mm diameter and 300mm height is performed according to IS:5816-1999 [16] as shown in **Figure-5**.



Figure-5. Spilt tensile strength of the cylindrical specimen.



Figure-6 depicts split tensile strength results of concrete mixes at the end of 28 days.

Figure-6. Spilt Tensile Strength of Concrete.

From **Figure-6**, it is detected that, the split tensile strength of concrete mixes M30(0+30), M30(5+25), M30(10+20), M30(15+15), M30(20+10), M30(25+5) and M30(30+0) are increased by 6.67%, 10%, 16.67%, 26.67%, 23.33%, 20.67%, 7% w.r.t. M30(0+0). The concrete mix with different percentages of fly ash and GGBS results in more spilt tensile strength than normal concrete. This is because of the increased denseness of concrete mix due to the pozzolanic activity of fly ash and GGBS. The concrete mix with 15% fly ash plus 15% GGBS and 70% cement produces the highest flexural strength among the trial mixes taken into consideration.

4.4. Flexural Strength of Concrete



Figure-7. Flexural strength of beam specimen.

The beam specimens of size 150mmX150mmX700mm are tested by using the universal testing machine as per the provisions of IS:516-1959 [15] with the rate of loading of 400kg/min as shown in **Figure-7**.



Figure-8 presents the flexural strength of concrete mixes after 28 days.



From **Figure-8**, it is observed that, the flexural strength of concrete mixes M30(0+30), M30(5+25), M30(10+20), M30(15+15), M30(20+10), M30(25+5) and M30(30+0) are increased by 8.57%, 10.57%, 12.00%, 17.14%, 14.29%, 10.57%, 10.00% w.r.t. M30(0+0). The concrete mixed with different percentages of fly ash and GGBS results in more flexural strength than normal concrete due to refinement of pore structure due to pozzolanic reaction. The concrete mix with 15% fly ash plus 15% GGBS and 70% cement produces the highest flexural strength among the trial mixes taken into consideration.

It is observed that the optimum results are obtained for the M30 concrete mix with 15% fly ash plus 15% GGBS and 70% cement in terms of compressive, split tensile and flexural strength. This is due to fact that 15% GGBS added to the concrete mix reacts on it is own. Generally, the hydration reaction is extremely slow and needs some activation. Here, this activation typically happens in the presence of 70% portland cement which produced calcium silicate hydrate (C-S-H) gel during hydration which increases in strength. 70% cement incorporated in the mix produces C-S-H gel and calcium hydroxide as hydration products. During the pozzolanic reaction, the water-soluble calcium hydroxide obtained in the hydration of portland cement reacts with 15% fly ash in presence of water to produce more quantity of solid C-S-H gel which improves the strength of the concrete.

5. CONCLUSIONS

The present work experimentally investigated the influence of fly ash and GGBS on concrete with partial replacement of cement. The properties fresh of concrete in the form of workability and the features of hardened concrete in the form of compressive, split tensile and flexural strength are studied. From the experimental analysis, the conclusions are withdrawn and enlisted as below:

- 1. The concrete mixed with different percentages of fly ash and GGBS shows more workability than normal concrete due to finely divided good quality of fly ash and glassy surface configuration, fineness and granulated particle shape of slag.
- 2. The concrete mixed with different percentages of fly ash and GGBS results in more compressive strength than normal concrete due to the pozzolanic activity of fly ash and GGBS.
- 3. The fly ash and GGBS concrete develop a slower compressive strength at early ages than normal concrete because of the slower rate of pozzolanic reaction of fly ash and a slower rate of reaction of GGBS. However, the later age strength of fly ash and GGBS concrete exceeded the strength gained by normal concrete due to continuous pozzolanic reactivity.
- 4. The concrete mix with different percentages of fly ash and GGBS results in more spilt tensile strength than normal concrete. This is because of the increased denseness of concrete mix due to the pozzolanic activity of fly ash and the reactivity of GGBS.
- 5. The concrete mix with different percentages of fly ash and GGBS results in more flexural strength than normal concrete due to refinement of pore structure due to pozzolanic reaction and the reactivity of GGBS.
- 6. The optimum results are obtained for the M30 concrete mix with 15% fly ash plus 15% GGBS and 70% cement in terms of compressive, split tensile and flexural strength. In presence of 70% portland cement 15% GGBS gets activated to produce calcium silicate hydrate. Portland cement (70%) also produces calcium silicate hydrate and calcium hydroxide. During the pozzolanic reaction, the water-soluble calcium hydroxide obtained in the hydration of portland cement reacts with 15% flyash in presence of water to produce more quantity of solid calcium silicate hydrate which improves the strength of the concrete.

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Development and Testing of Intelligent Personal Assistant

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ABSTRACT

An Intelligent Personal Assistant (IPA), Virtual Personal Assistant (VPA), or Intelligent Virtual Assistant (IVA) is nothing but a software agent, which performs tasks for each respective user, based on their commands and questions. It helps in doing the work fast, and conveniently and can reduce screen time also. The fundamental advantage of such IPA is the reduction in the cost for the human personal assistant and also reduction of the human errors. This article represents the development and testing of one such IPA named "EDI" which can have a friendly chat to do mathematical operations, just play the media, open applications/software; search on the web, Wikipedia, YouTube, etc. just by a voice giving voice commands. The newly developed EDI is programmed so that, it can interpret human speech, and also respond to individual users with synthetic voices. A python language is used for the development of EDI, which helps in easy programming and fast coding using available libraries. The testing of the developed IPA shows 95 to 100% successful execution of the given commands for various tasks. The innovative feature of the developed IPA is that it can also be used for PCs and laptops.

KEYWORDS

Virtual Personal Assistant, Intelligent Personal Assistant, Speech to Text, Text to speech, Text analyzing.

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1. INTRODUCTION

Personal assistants are the individuals, who will assist you with some amount fees. Personal assistants help you and assist you in your work. Making you and your work more efficient accurate and fast. Although having a personal assistant can be very useful, not everyone can afford to hire one as hiring one human personal assistant can be very costly. Even though, human personal assistants may be more capable and can do more work than machines they may still do human errors, which may affect your work accordingly. Also, as human beings, they cannot be as perfectly accurate. However, intelligent personal assistant, may not be as capable as humans but is more accurate, fast, and costs very less. Millennial consumers are looking for more comfortable technology. In this era where speed, efficiency, accuracy, and convenience are constantly being challenged and optimized and it's very clear that humans are moving towards less user-screen interaction.

The purpose of the development of intelligent personal assistants is to do voice recognition and speak human languages by taking users' commands. Personal intelligent assistants improve the Internet of Things (IoT).

Therefore, this study is aimed to develop an intelligent Personal Assistant that supports speech recognition and text-to-speech (gTTS), which can be very useful and convenient for users. The developed intelligent personal assistant is named 'EDI' inspired by a game character. The fundamental purpose of EDI is to be capable of voice and speech interaction, and music playback, EDI enables operation of gadgets PCs, laptops, and their applications. The users can utilize conversational and spoken speech voice instructions. The motivation behind the development of the IPA application is to provide several useful features of a virtual personal assistant VPA to aid task completion. The intelligent personal assistant's primary function is to respond to the user's instructions.

2. LITERATURE REVIEW

Di Prospero et al. (2017); Gnewuch et al. (2017) concluded that for chatbots utilization in voice-supported intelligent personal assistants (IPA) and its popularity, the newly designed smart assistants, such as Cortana, Alexa, Google Assistant, and Siri are very useful tools. The domain-specific IPAs are also getting smarter than earlier [1, 2]. Kepuska and Bohouta (2018) concluded that the controversies regarding the similarities and differences between the various IPAs for different applications are still going on. The IPAs are currently installed by the manufacturers of smart devices directly to help users directly [3]. The research shows that using artificial intelligence (AI) and natural language processing (NLP), for different applications, the chatbot form of conversation agents is developed by Nguyen and Sidorova (2018); Jain et al. (2018) [4, 5]. Further, in the next year, Bittner et al. (2019) showed that chatbots can become more professional by improving text-to-speech and speech-to-text communication [6]. There is major competition between intelligent personal assistants is looking for more users now and then.

Below are some examples of well-known intelligent assistants.

1.1. Google Assistant

Google Assistant is an intelligent assistant application developed by Google Inc. It has artificial intelligence making it possible to have a two-way conversation.

• Initially released on 18 May 2016.

- Written in C++ language Supported operating systems: Android, chrome os, kaios, Linux, IOS
- mobiles and automation devices are the primary use of Google Assistant.

1.2. Siri

Siri is an intelligent personal assistant program created by Apple Company. Siri also has artificial intelligence.

- Initially released on 4 October 2011
- Written in swift language.
- Supported platforms are iPhone, iPad, apple watch, and iPod touch as mobile devices, and Apple TV as a stationary device. etc.
- Supported OS is IOS 5 onwards for iPhone mobile devices, watch OS for Apple watches, tv OS for apple tv, macOS Sierra for Mac, iPad, etc.

1.3. Cortana

Cortana is an intelligent assistant software developed by Microsoft. Cortana uses the Bing search engine to perform tasks given by its users.

- Initial release date: 2 April 2014
- Written in C# and some advanced points in c/c++
- Supported platforms: Windows 10, Windows 11, Windows Mobile, Windows Phone 8.1, Microsoft Band 2, Surface Headphones, Harman Kardon Invoke, Skype, Microsoft Band, Cyanogen OS, Windows Mixed Reality, and Amazon Alexa. etc.
- Supported operating systems: Windows, iOS, Android, Xbox OS

The EDI is highly inspired by the above intelligent personal assistants. However, EDI is programmed using Python language, which is very new in the market, and trending EDI are more capable to update with technology. Python language is used for developing EDI, which has very good APIs. It is very easy to create better-looking software/applications from it.

- Friendly chat
- Simple Mathematical Operation
- Complex Mathematical Operations,
- Open the Application by voice
- Internet Applications.

3. SYSTEM ARCHITECTURE

For a better understanding of the architecture and workings of EDI, the following diagrams are represented.

1.4. Activity Diagram

The EDI system is initially in standby mode. It starts processing as soon as it receives any wake-up calls. The following **Figure-1** shows the activity diagram of EDI.



Figure-1. Activity diagram of EDI.

The received command is identified whether the user is asking questions or giving tasks. Following the identification of the query or assignment, appropriate action is taken. The EDI pauses for more commands from the user after the question or task has been answered. This loop will run until the quit command is issued.

1.5. Use case Diagram



Figure-2. Use case diagram of EDI.

EDI can handle only a single user at a time. The user gives commands or asks questions to the EDI. EDI then processes it and answers. The response is sent back to the user. The following **Figure-2** represents the use case diagram of EDI.

1.6.Dataflow Diagram

The following **Figure-3** represents the flow of data/information through the whole user EDI interaction. Also, the subsequent **Figure-4** shows the various component diagram and their connections used in EDI.







Figure-4. Component diagram.

4. HARDWARE AND SOFTWARE

4.1. Hardware

- A working computer that is capable of running Windows OS
- It should be able to run PyCharm and PyCharm libraries.

4.2. Software

- OS which can run PyCharm software, and gives access to its libraries.
- A web browser so EDI can access the internet
- And if the user asks EDI to open software, it should be installed on the computer first

5. PROPOSED TECHNOLOGY APPROACH

5.1. Python

Python is a class-based high-level, instructive programming language. Python is a powerful, healthy, and extremely useful programming language that is mostly used for Rapid Application Development (RAD). Python Language is very easy to write as well as it is very easy to execute its codes. In comparison to certain other object-oriented programming languages (OOPs), Python may express similar reasoning with as little as nearly one-fifth of the code.

Python has a huge list of advantages over other programming languages. Python programming language has so many applications that it can't be confined to one. Python's popularity has empowered it to participate in a variety of well-known and globally recognized processes, such as data science, AI, ML, and so on. Python has a plethora of libraries to meet this project's needs. In EDI, packages such as speech recognition, gTTs enabling text-to-speech, selenium for online automated processes, and others are utilized.

Python is indeed a proper and systematic programming language. For small cases, efficiency is usually not a hindrance. If current Python code is not effective sufficient, a typical approach to improving it would be to figure out, what is consuming the most duration and re-implement it in a lower-level language. When compared to coding it all in low-level programming, it will result in far less programming and a much more effective program [7].

The intelligent Assistant is indeed the component in this case. It offers two distinct services: Task execution and inquiry answering, among other things.

5.2. PyCharm Libraries Used for EDI

5.2.1. gTTS
Google Text-to-Speech (gTTS) is a Python library and command-line interface (CLI) utility. It writes human language to a file, byte strings, or stdout and saves it as digital audio data. Alternatively, one may pre-generate gTTS request URL's to input into an external software such as an internet browser. Many human-spoken languages are supported by the gTTS-API and python library. The voice could be provided in either of the two audio speeds available: rapid or slow. **Figure-5** below represents the working of gTTS [8].



Figure-5. Working of gTTS.

5.2.2. Speech Recognition

The ferry's first component, which is required for speech recognition is spoken words i.e., Speech itself. Via a microphone, the actual sound is turned into an electric or digital signal, which is then converted to digital data with an analog-to-digital processor. Many models can then be used to convert speech into text once it has been converted to digital data.

Speech-to-text conversion, in layman's terms, means that an app recognizes the words spoken by a person and converts the voice to written text. There are lots of reasons one would want to use Speech-to-Text conversion.

Nowadays, Speech Recognition is a very useful feature in several applications used like home automation, AI, and much more. Speech Recognition can also be used on microcontrollers such as Raspberry Pi provided with a microphone. Following **Figure-6** shows the working of speech recognition.



Figure-6. Working of Speech recognition.

Speech Recognition has all the scripts required for recognition of speech and accessing the microphone. The Speech Recognition library is very flexible and thus is included and supported in a huge list of APIs. The Google Web Speech API supports a Speech Recognition library's hard-coded default key. Due to the flexibility and usability of the Speech Recognition library, it is used in a high number of Python projects.

Selenium: Selenium Python bindings library provides a simple API to write functional/ acceptance tests using Selenium WebDriver. Using Selenium Python API, one can have access to all functionality of Selenium WebDriver; it also provides an API to pierce Selenium Web motorists like Firefox, Chrome, Remote, etc. Selenium is only supported in the3.5 or advanced performances [9].

- Open Source and Movable
 Combination of tool and DSL
- Easier to understand and apply Lower burden and stress for testers
- Cost reduction for the Business Guests
- WolframAlpha: The WolframAlpha Webservice API provides a webgrounded API allowing the computational and donation capabilities of Wolfram Nascence to be integrated into the web, mobile, desktop, and enterprise operations. WolframAlpha is an API that uses Wolfram's techniques and knowledgebase to cipher expert positional replies. This component explains how to create a basic Python auxiliary operation that can respond to simple inquiries such as the ones stated below [10].

5.2.2. Pyaudio

PyAudio is a Python audio library that works across platforms. It offers more features than ordinary audio libraries, such as recording and continuous audio streaming, but it is heavily reliant on PortAudio, resulting in a more difficult installation. It also includes Python cassettes for PortAudio, a cross-platform audio I/O library, as well as python-sound. Using PyAudio, one will be capable of playing

and audio input on a variety of platforms using Python following **Figure-7** depicts the working of Pyaudio [11, 12].



Figure-7. working of Pyaudio.

6. FEATURES OF EDI

6.1. Tasks

Tasks are nothing but the desired work given by the user of an intelligent assistant. As EDI is an intelligent assistant, it should also be able to perform various tasks given by the users. EDI should be able to take proper input from the user and perform them and give proper output as well. Voice reorganization and text-to-speech utilities are added for less screen interaction with the user. As, for windows, our intelligent personal assistant is capable of the following tasks.

6.1.1. Friendly chat

EDI :	Hello, Sir.
EDI :	What can i do for you?
Speak.	
Stop.	
You :	who are you
EDI :	Hello, I am EDI. Your personal Assistant.
	I am here to make your life easier.
	You can command me to perform various tasks such as calculating sums or opening applications
EDI :	What can 1 do for you?
Speak.	
Stop.	
	who created you
EDI :	I have been created by DOT Student.

Figure-8. Friendly Chat conversation.

EDI is programmed so that it can have a simple friendly conversation with the user which includes greeting the user and giving self-information the user. Following **Figure-8** depicts the friendly chat conversation of EDI.

6.1.2. Simple Mathematical Operation

EDI is programmed so that it can do both simple as well as complex mathematical operations. **Figure-9** shows the conversation between the user giving mathematical operation commands to EDI and how EDI responds to the user.

EDI :	Hello, Sir.
EDI :	What can i do for you?
Speak.	
Stop.	
You :	calculate 20 + 35
EDI :	The answer is 55
EDI :	What can i do for you?
Speak.	
Stop.	
You :	calculate 20 X 35
EDI :	The answer is 700
EDI :	What can i do for you?
Speak.	
Stop.	
You :	exit
EDI :	Ok bye, Sir.

Figure-9. Mathematical operation (Simple)

6.1.3. Complex Mathematical Operations

Subsequently, the **Figure-10** shows the conversation between the user giving complex mathematical operation commands to EDI and how EDI responds to the user.



Figure-10. Mathematical operation (Complex).

6.1.4. Open the Application by voice

Google Chrome

The following **Figure-11** shows the conversation of the user giving open chrome command to EDI and how EDI responds to the user, and **Figure-12** shows the Google Chrome opened by EDI after receiving a command from the user

EDI :	Hello, Sir.
EDI :	What can i do for you?
Speak.	
Stop.	
You :	open Google Chrome
EDI :	Google Chrome
EDI :	What can i do for you?
Speak.	
Stop.	
You :	exit
EDI :	Ok bye, Sir.
Proces	s finished with exit code 0

Figure-11. Open application command to open Google chrome.



Figure-12. Google application opened by EDI.

Microsoft Word

Figure-13 shows the conversation between the user giving an open Microsoft Word command to EDI and how EDI responds to the user. Simultaneously, **Figure-14** shows the Google Chrome opened by EDI after receiving a command from the user.

```
EDI : Hello, Sir.
EDI : What can i do for you?
Speak...
Stop.
You : open Microsoft Word
EDI : Opening Microsoft Word
EDI : What can i do for you?
Speak...
Stop.
You : exit
EDI : Ok bye, Sir.
Process finished with exit code 0
```

Figure-13. Open application Command to open Microsoft Word.



Figure-14. Microsoft Word opened by EDI.

6.2. Internet Application

VPA is programmed to use the internet to help them access data from all other the world uploaded on the internet. Using VPA, users can easily access, engage and customize, the data on the internet. It can be news, weather information, using Wikipedia, voice search on google or playing videos on YouTube.

The developed EDI is programmed as it should perform various tasks regarding the internet. EDI can access the voice web, where the contents of the internet can be accessed using a human voice. EDI uses synthetic voice for human output voice. Using a web browser EDI can access the internet and perform various tasks on the internet.

6.2.1. Web search by voice

Google search

Figure-15 shows the conversation between the user giving web search on chrome command to EDI and how EDI responds to the user, and Figure-16 shows the web search done by EDI after receiving the command from the user.

EDI	\$	Hello,	Sir.	un de la compañía			
EDI		What c	an i do f	for you?			
Spea	ik.						
Stop	ί.						
You		search	Shivaji	University	on	Google	
EDI		search	shivaji	university			

Figure-15. Google web search command.



Figure-16. Google web search result.

Wikipedia search

Following **Figure-17** shows the conversation between the user giving the Wikipedia web search command to EDI and how EDI responds to the user, and similarly, **Figure-18** shows the Wikipedia web search done by EDI after receiving the command from the user.



Figure-17. Wikipedia web search command.

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Figure-18. Wikipedia web search result

YouTube search

Figure-19 shows the conversation between the user giving the YouTube web search command to EDI and how EDI responds to the user, and **Figure-20** shows the YouTube web search done by EDI after receiving the command from the user.

EDI : Hello, Sir.	
EDI : What can i do for you?	
Speak	
Stop.	
You : search Shivaji University on YouTub	
EDI : Opening in youtube	
EDI : search shivaji university	

Figure-19. YouTube web search command.



Figure-20. YouTube web search result.

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7. RESULT OF TESTING

After testing EDI on different machines, different users, different devices, and different OS devices, the results are shown below. The error found is only related to voice recognition and text-to-speech. There is no problem found with the execution of given commands. All tasks are tested and results are given.

7.1. Offline tasks

These tasks are tested without the need for the internet.

7.1.1. Friendly chat

Following **Table-1** represents the friendly chat command results and **Figure-21** shows the accuracy plot of comparison between the success and failure of friendly conversation. It is found that friendly chat with user 1 was 96%, user 2 was 92%, and user 3 was 80% successful.

Command: Friendly Chat	Success	Failure
User 1	96%	4%
User 2	92%	8%
User 3	80%	20%

Table-1. shows the results of the friendly chat commands.





7.1.2. Simple mathematical operations

Following **Table-2** depicts the results of our testing of simple mathematical operations, and **Figure-22** depicts the comparison plot of the accuracy result of success and failure of simple mathematical commands testing. It is found that

addition was 100%, subtraction was 100%, multiplication was 98% and division was 95% successful.

Command: Mathematical Operations (Simple)	Success	Failure
Addition	100%	0%
Subtraction	100%	0%
Multiplication	98%	2%
Division	95%	5%

Table-2. shows the results of simple mathematical operation testing.



Figure-22. Plot showing a comparison of the accuracy of simple mathematical operation.

7.1.3. Complex mathematical operations

Following **Table-3** reveals the result of our testing of complex mathematical operations, and **Figure-23** reveals the plot of comparison of the accuracy result graph of success and failure of complex mathematical commands testing. It is found that derivation was 96% and integration was 99% successful.

Table-	3. shows	the result	ts of com	plex mather	natical ope	ration comm	ands.
					1		

Command: Mathematical Operations (Complex)	Success	Failure
Derivation	96%	4%
Integration	99%	1%





7.1.4. Open applications by voice

Following **Table-4** depicts the result of our testing of the open application by voice commands on various applications, and **Figure-24** depicts the accuracy result plot of the success and failure of open applications by voice commands testing. It is found out opening chrome was 94%, MS WORD is 92%, and excel was 95% successful.

Command: Open Application	Success	Failure
Google Chrome	96%	6%
Microsoft Word	99%	8%
Microsoft Excel	96%	5%

Table-4. shows the results of open application commands.



Figure-24. Plot of comparison showing accuracy of open application Internet application.

7.1.5. Web search by voice

Following **Table-5** represents the result of our testing of web search by voice commands on various applications, and **Figure-25** represents the comparison plot of the accuracy result of success and failure of Web search by voice commands testing. It is found web search by voice in chrome is 96%. Wikipedia was 93%, and YouTube is 98% successful.

Command: Open Application	Success	Failure
Chrome	96%	4%
Wikipedia	93%	7%
YouTube	98%	2%

Table-5. Represents the results of our t	testing of web search by	voice commands
on various	applications.	



Figure-25. Plot of comparison showing accuracy result of success and failure of Web search by voice commands testing.

8. CONCLUSION

This paper represents the development and testing of an intelligent personal assistant or virtual personal assistant named EDI after a video game character. EDI is developed using the python language and executed on PyCharm an Integrated Development Environment IDE in short using its libraries. The EDI can have friendly chat, do mathematical operations, open software installed on a PC, do a web search, do a Wikipedia search, and do a YouTube search. The EDI is tested several times and found almost no errors showing accuracy and reliability. The real-time intelligent personal assistant EDI is a very useful tool for various operations not only on mobiles and gadgets but also on PCs and laptops. The newly developed EDI is programmed so that, it can interpret human speech, and also respond to individual users with synthetic voices. A python language is used for the development of EDI, which helps in easy programming and fast coding using available libraries. The testing of the developed IPA shows 95 to 100% successful execution of the given commands for various tasks.

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A Development of Web Based Placement Management System

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ABSTRACT

Placement is an important part of professional institutes. There is huge data collecting and handling is involved in such placement activities. Manual handling of data may lead to issues like error, data security and delay. In this paper we presented a web-based application to collect and handle large students' data required for placement. The proposed web-based application is build using MySql and Django platform. This application is easy to handle and can be access anywhere by students and faculty.

KEYWORDS

Web application, Placement, MySQl, Djang.

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1. BACKGROUND

In recent years Professional Education had experience a massive transformation. The government of India and also governing bodies are emphasis on quality of professional education in India. The quality Placement plays the critical role in the Professional Education system. Quantitative and quality Placement of the institute become one of the important metrics to showcase institute is well performing. Also, placement is key highlight to attract good merit students towards admission.

Placement is the outcome of team work. Placement of the student not only depends upon his academic performance. There are several other factors that contributed lot in student's placement such as presentation and communication skills, general aptitude and reasoning ability, soft skills, coding skill etc. These skills are priority demand for hiring fresher professionals. Imparting these skills in students is an important challenge in front of professional institutions.

So, every professional institution has a dedicate team called Training and Placement Cell which looks after all training needs of the student. This cell also has responsibility to provide good number of placement opportunities to students so that students can have their jobs in hand not after graduation but well before they graduate from institute.

2. INTRODUCTION

In present situation, work of Training and Placement Cell is done manually in professional institutes. In such manual working Training and Placement cell, every work has involvement of human hand. Company needs aspiring student's data in specific format prescribed by them. Even if some fields are common in student's data, we found deviation of the data and data format for company by company. For example, the eligibility criteria of companies may change with percentages, number of backlogs, year gap etc. So, there is need to have database of each student at each institute with inclusion all micro fields necessary for company eligibility, Skill sets and achievements.

Also, there is need of sorting of available student's database as per requirements of the company. This sorted database having specified format can be shared with companies whenever needed. This job is tedious and time consuming. Involvement of human in said work may lead to errors.

Nowadays use of Excel, google form and social media have made this task easy. Institutes can collect the student's data from anywhere and anytime. But still there are certain questions still unanswered. First the authenticity of data received from social media. It has been observed that students many times does not fill the data own their own responsibility. Second the security of the students data. As student sharing academic data as well as personal data it should be secured and should not altered by any unauthorized access.

The Proposed System is a web-based application that aims to overcome the drawbacks of the traditional Training and Placement Management system. This application establishes linkage between placement officers and students. Every placement officer and student will allocate login and password. Placement officer can update training events and schedule to the students. Placement officer can post different campus drive and their registration link to each student. This application compromises with features, by which placement officer can sort students as per company criteria, can create list of students in any required format and generate different reports for purpose of record in easy manner. Students can receive information about training and campus drive in their login. Students can update their credentials or information like marks, achievements, certification etc through their login. All parental control is available to admin login.

3. RELATED WORK

The undertaking goals of work in [1] is to make documentation of student's placement and automation of documentation. But lacks in feature of Event

Management System also generation of reports. The work presented in [2] notable capabilities of online registration, security, computerized percent calculation, information sorting and notification services. But there is a missing of Event Management System' and record generation.

In reference [3] author have emphasized the employment and therefore technique to the importance of the open search maximize the use of controllers, Author also offered an alternate search technique those for scenarios during which the open search technique isn't applicable. Where application system system proposed in [4] is used as an for the placement Officers within the college to manage the student information with respect to placement. Student logging should be able to upload their personal and academic information within the variety of a resume.

The framework for the cloud is proposed such that it consists of the Resource Management and Resource Placement modules of cloud to resolve global most beneficial problem of untimely convergence confronted through different swarm sensible set of rules for Resource Placement within side the PaaS layer of the Cloud presented in [5].

4. PROBLEM FORMULATION

After literature survey we have identified that training and placement authority of every institute has lot of data and activities to process if the data is not processed or handled properly problems like miscommunication, data loss, improper execution of placement process and ineffective reporting may happen. Also, we have realized after our survey the current system adapted by many of the institutes has very limited functionality and doesn't allow any kind of automation and resume building.

The placement activities play very important role in student career and building college reputation. In our college training and placement activities are done manually, there are more chances of error. It is very time-consuming activity for collecting, managing, updating student data as number of student increases. The training and placement officer need to short list according to company requirement. It is required to design of a computerized student automation module to speed up capabilities. Also, there were no records kept of the past students so there is less communication between pass students with training and placement department.

The aim of the proposed system is to develop a modified system with improved facilities that are important for placement officers and students. The proposed system can overcome all the limitation of the existing systems, such as student's information is maintained in the database, it offers more security to data, ensures data accuracy, reduces massive paper work and save lot of time and effort.

The objectives of the system are: -

- To reduce paperwork.
- Reduced operational time.
- Increased accuracy and reliability.
- Increased operational efficiency.
- Data security.

5. METHODOLOGY

Figure-1 shows the proposed T & P Management System.



Figure-1. Proposed T & P Management System.

5.1 Admin Section

Login

1. Admin will login through provided login credential.

2.Admin can create TPO account only admin have rights to create TPO.

5.2 TPO Section

Login

- 1. After confirmation by admin TPO will receive email having login credential.
- 2. TPO uses that username and password to login as staff account.
- 3. Email and password is verified using Staff Credentials database.
- 4. After successfully verification, user will login and he/she redirect to dashboard.
- 5. If User forgot his/her password then he/she can use forgot password option.

Forgot password

- 1. It is used to reset the password.
- 2. It is useful in the case of users forgot password.
- 3. User must know the email address which is used while registration.
- 4. The password reset link will be sent to his email address.

Dashboard of staff

- 1. Dashboard contains all students' records.
- 2. Staff member have access to all data of students.
- 3. Staff Member can filter out specific student details.
- 4. Data can be export as PDF file format.
- 5. Filter Students Data by:
 - Marks/Percentage
 - Name/Roll Number/PRN Number
 - Placed Company Name
 - Check Placed and Non-Placed Students

Webserver

- 1. This is backend of our Project
- 2. We are using Django web Framework which is written in python.
- 3. Where we are storing all credentials of all users.
- 4. Write down here which server we are going to use
- 5. Webserver contain the all-students data; The data is stored in the format of Tables. We are using MySQL database to store data.

5.3 Student Section

Register

- 1. User needs to Fill the Registration form.
- 2. After Registration process student will verify by TPO.
- 3. After verification by TPO, an email will send to students which include link, using that link student will redirect to dashboard page.

Login

- 1. Use username and password to login as student account.
- 2. Email can be username.
- 3. After successfully login, User will be redirect to dashboard.
- 4. If User forgot his/her password then he/she can use forgot password option.

Forgot Password

- 1. It is used to reset the password.
- 2. It is useful in the case of users forgot password.
- 3. User must know the email address which is used while registration.
- 4. The password reset link will be sent to his email address.

Dashboard For Student

- 1. Student Dashboard is used to show the user's personal details.
- 2. All student's related settings are available in this dashboard.
- 3. Student can update and modify his personal details.
- 4. Facility for student to apply for various drives.

Webserver

- 1. Students have limited access to database
- 2. Students can fetch only his/her personal details
- 3. He/She can update and modify only his/her data

5.4 Back-end Technology

One shoud need a strong technological stack to power your web application. Two of these open-source frameworks, Node.js and Django, have received a lot of attention for their overall performance.

A cross-platform runtime environment called Node.js is used to create effective and quick web applications. It is built on Javascript and works on both the client and the server. Because it is a simple tool that can be used to run Javascript outside of the browser, Node.js has become very popular. Django, on the other hand, is a high-level, cross-platform Python framework. It focuses on getting rid of tedious procedures and laying the groundwork for quick application development [6].

5.5. Database

Support for the ORM framework exists in Django. The ORM framework's benefits include: The ORM framework can be used by developers to interact with a variety of databases, including PostgreSQL, SQLite, Prophet, MySQL, and more.

For common database activities, developers don't need to create lengthy SQL queries. The ORM framework is not supported by Flask. To conduct common database operations, designers must enter SQLAlchemy (Protest Social Mapper and SQL toolkit for Python). **Table-1** shows the database comparison.

Node	Django	РНР
Based-on: C, C++, and JavaScript Architecture: Run-time environment.	Based on: Python	Based on: C Pre-written Scripts- Comes with prewritten.
Performance:Lesscomplicated system,moreflexibility to developers	Faster development: reduce the development time and shorten the time-to-market.	Learning Curve- An easy-to-learn language with a consistent and logical syntax.
Scalability: Advanced scalability Popularity and Utilization: Most popular JavaScript framework.	Scalability: Presents a lot of opportunities to scale seamlessly and keep up with the growing needs.	Database Connection- Compatible with popular database services like MySQL or Maria.
Development Speed: More operating time but helpful if developers are effective.	Machine learning- friendly: Preferred for machine learning.	Speed- Boosts user engagement and SEO rankings
Security: Comparatively comes as less secure built-in tool, but manual operations covers the security deficiency	Secure: Facilitates the creation of secure websites and applications and protects them against common attacks such as cross-site request forgery etc.	Cross-Platform- Supported by major operating systems including Linux, Solaris, UNIX, MAC OS, and Windows.
Flexibility : More flexibility due to rich ecosystem, giant	Flexibility: Supports rapid changes during	

Table-1. Database Comparison.

JavaScript	library,	development	
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6. **RESULTS**

Figure-2-6 show the results related to present work.

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Figure-2. Login Page

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Figure-3. Students' dashboard

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Figure-4. Students Sorting

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Figure-5. TPO dashboard and Profile

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Figure-6. TPO post of Event or Campus Drive

7. CONCLUSION

'Placement Management System' is a web-based application developed on the windows platform for the Training and Placement Cell of Department of Technology, Shivaji University, Kolhapur. The proposed work provides a platform to the students and faculty members for updating, handling and sharing students data for campus drive and placement. The proposed system also able to handle record of the students placement. The proposed system enables faculty members to generate students data in form required by campus drive. The personal and academic data of the students Department of Technology, Shivaji University, Kolhapur can be

maintained in the database and can be retrieve from system at any time anywhere and any required format.

The proposed Placement Management System contains all kinds of information about the students. The system includes the personal information and academic information of the students. It also takes data of student's participation in the co-curricular activities and extracurricular activities. Skill sets of the students can also be added into system database. Systems also allow to record achievements of the students. The system is an online web-based application that can be accessed by students and faculty members anywhere and anytime.

It facilitates Training and Placement Officer (TPO) to sort list of students as per criteria demanded by campus drive. It helps to keep track of the student's placement. This system can be used as an application for the Training and Placement Officer (TPO) of the college / Department to manage the student information with regards to placement. Database of the students can be viewed by all the users. Data security is maintained so that unauthorized user cannot modify and access data of the students. The students can update their own information anytime. Campus Drives or Events in the organization can be informed to students using dashboard provided to training and placement officer (TPO). Students can view and apply to campus drives using link mention in the dashboard.

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