Nanomaterials Use in Wastewater Treatment

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Abstract—Adequate supply of clean, safe and potable water on a regular basis, are the main issues faced by the people nowadays. To achieve this objective wastewater should be treated so that it can be reused as well as environment should be saved by the negative effect of the untreated wastewater. This paper has focused on the different types of nanomaterials used by nanotechnology that can help in wastewater remediation. It is evident from the literature that this technology is having lots of advantages over conventional methods but still needs lots of research before the successful industrial application.

Keywords—Waste water treatment, ETP, sewage management, environment

I. INTRODUCTION

Water containing unwanted substances which adversely affect its quality and thus making it unsuitable for use is termed as wastewater. Wastewater is generated from various sources such as residential areas, commercial/industrial properties, agriculture etc. Composition of wastewater varies widely and depends upon the source from which it is generated. Common constituents of wastewater are pathogenic and non-pathogenic microorganisms, organic substances such as excreta, plants material, food, protein, and inorganic substances like metal particles, ammonia along with gases. When left untreated these constituents may pose threat to living beings and the environment, which makes it essential to treat wastewater before disposal. Various physical, chemical and biological treatment processes are used for wastewater treatment. Among these methods, currently, nanotechnology has been extensively studied by researchers as it offers potential advantages like low cost, reuse and highly efficient in removing and recovering the pollutants.

II. NANOTECHNOLOGY

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As defined by the National Science, Engineering & Technology (NSET) Initiative, nanotechnology is ¹Research and technology development at the atomic, molecular or macromolecular levels, in the length scale of approximately 1 - 100 nanometer range, to provide a fundamental understanding of phenomena and materials at the nanoscale and to create and use structures, devices and systems that have novel properties and functions because of their small and/or intermediate size.

When modified at nanoscale, matter can exhibit certain extraordinary and useful properties, which are not observed before [1]. Research in nanotechnology promises breakthroughs in areas such as medicine [2]-[4] data storage [5], [6] food industry [7], molecular biotechnology [8], computing [9], defence [10], robotics [11], textiles [12], [13] environment and sanitation [14], [15]. Another exciting and promising application of nanotechnology in water purification seems to be in desalination of water [16]. Despite its lucrative applications in various fields, certain environmental and ethical concerns cloud the celebration of nanotechnology as the next technological boom [17].

III. NANOTECHNOLOGY APPLICATIONS IN WASTEWATER TREATMENT

In terms of wastewater treatment, nanotechnology is applicable in detection and removal of various pollutants. Heavy metal pollution poses as a serious threat to environment because it is toxic to living organisms, including humans, and not biodegradable.

Various methods such as Photocatalysis, Nanofiltration, Adsorption, and Electrochemical oxidation involve the use of TiO2, ZnO, ceramic membranes, nanowire membranes, polymer membranes, carbon nanotubes, submicron nanopowder, metal (oxides), magnetic nanoparticles, nanostructured boron doped diamond are used to resolve or greatly diminish problems involving water quality in natural environment [18], [19]. Nanoparticles when used as adsorbents, nanosized zerovalent ions or nanofiltration membranes cause pollutant removal/ separation from water whereas nanoparticles used as catalysts for chemical or photochemical oxidation effect the destruction of contaminants present [20]. Scientists classified nanoscale materials that are being evaluated as functional materials for water purification into four classes namely, dendrimers, metal-containing nanoparticles, zeolites and carbonaceous nanomaterials [21]. Following are the different types of
materials that are or can be used in wastewater treatment and purification by nanotechnology.

Dendritic polymers include random hyperbranched polymers, dendrigraft polymers, dendrons and dendrimers. They are symmetrical and spherical macromolecules, comprising a relatively dense shell composed of a core, branching sites and terminal groups that usually form a well-defined surface [22]. Dendrimers are available in different shapes such as cones, spheres, and disc-like, generally in the size range of 2 to 20 nm [23]. A dendrimer structure is obtained by reaction of several dendrons with a multifunctional core. Over one hundred compositionally different dendrimer families have been synthesized and over 1000 differentiated chemical surface modifications have been reported [24]-[26]. Diallo and his coworker recovered Cu (II) ions from aqueous solutions using dendron-enhanced ultrafiltration (DEUF) and poly (amidoamine) (PAMAM) Dendrimers with Ethylene Diamine (EDA) core and terminal NH2 groups [27]. Dendritic polymers can be used as high capacity and recyclable water soluble ligands for toxic metal ions, radionuclides and inorganic anions and recyclable unimolecular micelles for recovering organic solutes from water [28]. These features popularized the application of dendritic polymers in water purification [29]. Poly (amidoamine) dendrimer (PAMAM) based silver complexes and nanocomposites have been used as antimicrobial agents in vitro. The protected silver and silver compounds showed high antimicrobial activity against S. aureus, P. aeruginosa and E. coli without the loss of solubility [30].

Metal oxide (Natural or Engineered) nanoparticles include Titanium dioxide (TiO2); zinc oxide (ZnO); cerium oxide (CeO2). They have high reactivity and photolytic properties [31]. They are considered good adsorbent for water purification because they have large surface area and their affinity can be increased by using various functionalized groups. Effectiveness of MgO nanoparticles and magnesium (Mg) nanoparticles as biocides against Gram-positive and Gram-negative bacteria (Escherichia coli and Bacillus megaterium) and bacterial spores (Bacillus subtillis) was demonstrated by Stoinov and his colleagues in 2002 [32]. Nano TiO2 and Cu2O electrodes were used for electrocatalytic oxidation of organic components and COD removal was observed to be high [33]. Silver loaded nano-SiO2 composite coated with crosslinked chitosan has high biocidal activity against Escherichia coli and Staphylococcus aureus [34]. Zinc oxide nanoparticles have been used to remove arsenic from water. Some adsorption processes for wastewater treatment have utilized ferrites and a variety of iron containing minerals, such as akaganite, feroxyhyte, ferrihydrite, goethite, hematite, lepidocrocite, maghemite and magnetite [35]. Magnetic nanoparticles, 2-3 orders of magnitude smaller than a bacterium, are reported to be beneficial when compared to magnetic beads. Iron oxide and titanium dioxide are good sorbents for metal contaminants. Hildebrand and his co-workers in 2009, tested Pd/Fe3O4 nano catalysts for selective dehalogenation in wastewater treatment process [36]. The catalyst was found to be highly active, magnetically re-extractable and high organic solvents concentration tolerant; however, it was found to be sensitive to the presence of heavy metals (Pb, Hg).

Zeolite nanoparticles can be prepared by laser-induced fragmentation of zeolite LTA microparticles using a pulsed laser or by hydrothermal activation of fly ash. Zeolites are used as an ionexchange media for metal ions and effective sorbents for removal of metal ions. Zeolites have been reportedly used in the removal of heavy metals such as Cr(III), Ni(II), Zn(II), Cu(II) and Cd(II) from metal electroplating and acid mine wastewaters [37]. Carbon-based nanoparticles act as sorbents because they have high capacity and selectivity for organic solutes in aqueous solutions. Few examples of carbonaceous nano particles are Fullerenes/Buckyballs (Carbon 60, Carbon 20, Carbon 70); carbon nanotubes; nanodiamonds; nanowires. They exist as hollow spheres (buckyballs), ellipsoids, tubes (nanotubes); 1nm wires (nanowires) or hexagonal structures (nanodiamonds). They exhibit excellent thermal and electrical conductivity. Carbon-based NMs are stable, have limited reactivity, are composed entirely of carbon, and are strong antioxidants [38]. Acid treated, surface modified CNTs with improved colloidal stability were successfully tested for U (VI) adsorption [39]. Multi walled CNTs have been tested for the adsorption of coexisting contaminants viz. 2,4,6-trichlorophenol and Cu(II) [40]. Chitosan nano particles are used to enhance the absorption capacities for the acid dyes removal [41]. Also ZVI chitosan nanoparticles removes Cr (VI) from water by adsorption followed by reduction to Cr(III) [42].

Metal nanoparticles include nanosized silver, gold, palladium etc particles. Nanosilver (Engineered) forms include colloidal silver, spun silver, nanosilver powder, and polymeric silver. They are typically 10 to 200 nm in size. Being made up of many atoms of silver in the form of silver ions, they have high surface reactivity and strong antimicrobial properties. Medicine applications, water purification, and antimicrobial uses. They are used for a wide variety of commercial products [43]. Nanomaterials can also be used for biomolecular detection for example gold nanorods have been used for colorimetric low-concentration detection of polynucleotides such as cytome and glutathione [44]. Ag (I) and silver compounds have been used as antimicrobial compounds for coliform found in waste water [45]. Nanoparticles of gold coated with palladium are very effective catalysts for removing tri-chloroethane (TCE) from groundwater 2,200 times better than palladium alone.

Zero-Valent Metals (Engineered) nanoparticles include nanoscale zero-valent iron (nZVI), emulsified zero-valent iron (EZVI), and bimetallic nanoscale particles (BNPs). BNPs include elemental iron and a metal catalyst (such as gold, nickel, palladium, or platinum). Their size depends on the nanomaterial containing the zerovalent metal and is generally between 100-200 nm. They have high surface reactivity which can be controlled by varying the reducant type and the
reduction conditions. Different materials which can be used for their production are ferric (Fe [III]) or ferrous (Fe [II]) salts with sodium borohydride. Mechanism of reactivity for ZVI is similar to the mechanism of corrosion. They bring about remediation of waters, sediments, and soils by reducing contaminants such as nitrates, trichloroethene, and tetrachloroethene [46], [47].

Quantum Dots (Engineered) are made from cadmium selenide (CdSe), cadmium telluride (CdTe), and zinc selenide (ZnSe). Their size ranges from 10 to 50 nm. They have a reactive core controls which controls their optical properties. For the core possible metal structures include: CdSe, CdTe, CdSeTe, ZnSe, InAs, or PbSe, and for the shell possible metal structures are CdS or ZnS. Composite nanomaterials (Engineered) are made with two different nanomaterials or nanomaterials combined with nanosized clay. They can also be made with nanomaterials combined with synthetic polymers or resins. They have multifunctional components which exhibit novel electrical, magnetic, mechanical, thermal, imaging or catalytic features [48].

IV. CONCLUSION

Industrialization and population are the main reasons for increase in amount wastewater. These are also the main areas which require regular supply of clean water. Several methods are employed to ensure a sustained supply of water for the requisite purposes. Nanotechnology is also being looked upon to provide an economical, convenient and ecofriendly means of wastewater remediation. Different types of nanoparticles such as nanosized metals, metal oxides, zerovalent ions, nanofiltration membranes have proven effective in detection, removal and/or destruction of contaminants.

ACKNOWLEDGMENT

Authors are also highly thankful to reviver of this paper for support and guidance. We also wish to thank Chairman, Director General, Director, HOD and Faculty members of Department of Biotechnology, Meerut Institute of Engineering Technology for their continuous encouragement and problem solving assistance.

REFERENCES

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Energy requirements for vegetable oils to hydrogen process

Kalala Jalama

Abstract—This study has estimated the process energy requirements for producing H$_2$ from vegetable oils by steam reforming and has identified the most energy intensive step in the process in order to exploit opportunities for reducing energy requirements. A flowsheet was developed in ChemCad 6.4 and comprised three major steps: i) Steam reforming of vegetable oil, ii) Water-gas-shift (WGS) reaction and iii) CO$_2$ removal from the produced H$_2$. The vegetable oil was modeled by triolein and steam-to-carbon (S/C) ratios of 3, 6 and 9 were considered. The energy required for H$_2$ production was estimated as ca. 111, 112 and 114 MJ/Kg for S/C ratios of 3, 6 and 9 respectively. The CO$_2$ removal process was found to be the most energy intensive accounting for ca. 60% of the process energy requirements. The major contributor to the high energy requirement for this section is CO$_2$ stripping.

Key words— Energy requirements, H$_2$ production, steam reforming, vegetable oil

I. INTRODUCTION

Production of H$_2$ from renewable sources currently receives more interest. H$_2$ derived from renewable sources is a cleaner energy source and can be used in fuel cells for electric power generation to meet future global energy needs [1]. Recent studies on H$_2$ production by reforming of glycerol [2-6] and vegetable oils [1, 7, 8] have been reported in literature. Interest in glycerol as a feedstock for H$_2$ production is mainly explained by the fact that it is a waste product of a biodiesel production plant. It is usually purified to some degree and sold to various refiners in order to improve the process economics but with more biodiesel production facilities coming on stream, glycerol price will continue to decrease. Marquevich et al. [8] reported H$_2$ production by steam reforming of vegetable oils using Ni-based commercial and research catalysts. Their experimental results showed that oil conversion to gases and H$_2$ yields do not depend on the type of vegetable oil and hence indicated that the process might be suitable for producing H$_2$ from residual oils and fats from food processing in favour of the process economics. Pimenidou et al. [7] used NiO/Al$_2$O$_3$ catalyst system for chemical looping reforming of waste cooking oil in packed bed reactor and reported a repeatable synthesis gas composition with H$_2$ selectivity very close to the equilibrium. Yenumala et al. [1] performed a thermodynamic analysis of the reforming of vegetable oil for H$_2$ production. They modeled the vegetable oil as a mixture of tripalmitin, tristearin and trioleate, and reported optimum conditions for H$_2$ yield with very low methane selectivity. In another study [9] we have determined the effect of operating temperature, pressure and S/C ratios on H$_2$, CO, CO$_2$, CH$_4$ and carbon formation during vegetable oil steam reforming for H$_2$ production.

Most studies on vegetable oils reforming for H$_2$ production focused more on kinetics and thermodynamic aspects and very little is known on the process energy requirements. Hence this study aims at i) estimating the process energy requirements for producing H$_2$ from vegetable oils by steam reforming; ii) identifying the most energy intensive step in the process in order to exploit opportunities for reducing energy requirements.

II. METHODOLOGY

A process flowsheet was developed and simulated using ChemCad 6.4 simulation package to estimate the process energy requirements for producing H$_2$ from vegetable oils by steam reforming. The simulated flowsheet comprised three major steps: i) feed preparation and steam reforming of vegetable oil; ii) WGS reaction and iii) gas purification. The feed to the reforming reactor was chosen as 1 000 Kg/h of vegetable oil and mixed with steam to achieve S/C ratios of 3, 6 and 9. The vegetable oil was modeled by triolein and the reforming process was modeled by Gibbs free energy minimization in ChemCad. The Gibbs reactor model is based on the principal that at chemical equilibrium the total Gibbs energy of the system has its minimum value. By attempting to minimize the total energy of the system, individual equilibrium constants are not considered. Rather, the possible reaction species are noted, and the distribution of these species is established using a general mathematical technique to give a minimum free energy for the system [10]. The selected possible components in the predicted equilibrium product included H$_2$, CO, CO$_2$, alkanes (C$_1$ to C$_{15}$), olefins (C$_2$ to C$_{15}$), cyclic hydrocarbons, aromatic compounds, light ketones, alcohols, carboxylic acids and carbon. All the selected components with their physical and chemical properties were available in ChemCad 6.4 components database. Operating conditions that minimize the formation of CH$_4$ and carbon determined in another study [9] were used: operating pressure of 1 bar and operating temperatures of 800, 900 and 1000°C for S/C ratios of 9, 6 and 3 respectively. The WGS reaction was used to convert the CO formed in the reforming reactor into more H$_2$. This process was modeled by equilibrium conditions at high temperature (350°C) and low temperature (200°C). The gas from the WGS step was purified by condensing the unreacted steam out and by absorbing CO$_2$ using selexol. The property model used for the simulation