Sorption applications of nanomaterials for the removal of heavy metals from water and waste waters

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ABSTRACT - The presence of heavy metal ions in the water or waste waters has become one of the serious problems in the world. The development of nanotechnology has offered a variety of nanomaterials for the removal of heavy metals from the waste waters. The adsorption dependent removal of heavy metal ions using nanomaterials is based on the physical interactions between metal ions and adsorbents. Nanomaterials are cost effective and environmentally safe and they have specific physical and structural properties and such properties make them very efficient adsorbents. Nanomaterials show better performance than other adsorbents due to larger surface areas. Recently, various nanomaterial adsorbents have been developed for the advancement of efficient waste water treatment technologies. In future, chemists will have to be developing more efficient, low cost and very low environmentally impact nanomaterials for the waste water treatments.

Keywords: Heavy metals, Nanotechnology, Nanomaterials, Adsorption, Waste water treatment.

I. INTRODUCTION

Water is an important part of the all physiological activities of living organisms. The harmful contaminants in the fresh and saline water have increased worldwide due to the revolution of industrial and agricultural activities. A rapid increase in human population from last three decades has also a major role in the water pollution [1]. The presence of hazardous contaminants in the fresh or saline water leads many life time threatening diseases. The contaminations due to heavy metals in the water are very serious problem specifically in developing or highly dense populated countries like India and China [2,3]. Heavy metals are known for their toxicity to human and other living forms. They are the metals with high atomic numbers, atomic weights and a potential toxicity. Most of them involve in some important physiological activities in the living organisms under concerned limits but some are very harmful at very low concentrations. Due to non-biodegradability, they are consistently flow in the water and life forms. The common heavy metals are copper (Cu), lead (Pb), cadmium (Cd), zinc (Zn), nickel (Ni), iron (Fe), chromium (Cr), cobalt (Co), manganese (Mn) and mercury (Hg). The release of heavy metals in the water bodies may due to natural or manmade. The natural and anthropogenic activities for the exposure of heavy metal ions in aquatic bodies are metal corrosion, soil erosion, volcanic eruption, mining, smelting of ores, chemical industries, domestic and agricultural activities, refineries, fossil fuel combustion, nuclear plants, high tension lines, polymer, textiles etc [4,5].

Various methods such as photocatalytical oxidation, coagulations, electrochemical, pre-concentrations, phytoremediation, biosorption, ion-exchange, reverse osmosis and adsorption have been used in the removal processes [6-9]. Among these the adsorption based on nanomaterials is more efficient and convenient for the removal of heavy metals from water or waste waters[17-28]. Nanotechnology offers a variety of nanomaterials as adsorbents in the nano level (particle sizes 1-100nm). As compared with other traditional adsorbents, nano based adsorbents have unique shape and size properties and have high adsorption capacities to remediate metal ions from aqueous systems [10,11].

COMMONLY USED NANOSORBENTS FOR THE REMOVAL OF HEAVY METALS:

The nanomaterial sorbents show unique shape and sizes and known for their significant role in the water treatments. A good nano based sorbent should fulfill the following characteristics:

1. The selected nonosorbents for the removal processes should be environmentally friendly.
2. No harmful chemicals or sludge generating.
3. Not much expensive and applicability of nanosorbents at large scale operations.
4. The sorbents should posses' high sorption capacity and even efficient at very low concentrations of heavy metals present in waste water.
5. After the adsorption, the metal ions can easily be removed from the surface of metal loaded nanosorbents.
6. All the nano based adsorbents should be recycled.

 DOI : 10.18231/2454-9150.2019.0185

Nanosorbents

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Carbon, Polymer and Metal oxide based nanomaterials

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Sorption of copper, lead, cadmium, iron, zinc, arsenic, nickel, cobalt, chromium and mercury from water or waste waters

Fig. 1 Nanosorbents for waste water treatment

1) Carbon based nanomaterials: In general, the carbon based nanomaterials like carbon nanotubes, fullerene and graphene have been used for the removal of heavy metals from waste waters. These all are the allotropes of carbon and show good adsorption capacities.

Carbon nanotubes: The carbon nanotubes have tube shaped structures and are made up of carbon atoms. The carbon atoms are linked to each other by strong chemical bondings and arranged in layerd form of hexagonal rings. Carbon nanotubes are differing in structure, length, thickness and number of layers. They are of many types but usually categorized in to single walled and multiwalled nanotubes. A single-walled carbon nanotube is like a definite straw and has a single layer. Multi-walled carbon nanotubes are a combination of nested tubes and usually have 2 to100 or more walls or tubes. Farghali and coworkers [12] have developed acidified functionalized multi-walled carbon nanotubes by the oxidation of multi-walled carbon nanotubes in the presence of hydrogen peroxide and nitric acid. This nanosorbent show a good adsorption capacity for the removal of Pb (II), Cu (II), Ni (II) and Cd (II) ions from contaminated waste water. The percentage adsorption was recorded for Pb (II), Cu (II), Ni (II) and Cd (II) ions are 93, 83, 78 and 15%, respectively.

The modified Multi-walled carbon nanotubes with 8-hydroxyquinoline for the removal of copper, lead, cadmium and zinc metals from metal containing aqueous solution was used by Kosa and Zhrani [13]. The adsorption study has been carried out under batch operation including dosage, temperature, pH, ionic strength, metal ion concentration, and competition among metal ions, respectively. The experimental results show that the almost all metal ions have removed from aqueous solution at dosage of sorbent 250 mg, pH 7.0 and temperature 298 K. Sulfonated magnetic multi-walled carbon nanotubes have used in the adsorption of cobalt from aqueous solutions by Yang et al.]14] and found this adsorbent is efficient for the selective removal of cobalt. The equilibrium data of adsorption was best fitted to Freundlich, Langmuir isotherm models, pseudo unimolecular and pseudo bimolecular isotherm models. Surface-modified carbon nanotubes have been used remove lead ions from waste water by Quyen et al. [15]. The adsorption capacity was of the adsorbent was found to be 100mg/g as evaluated by Langmuir isotherm model. The equilibrium data of adsorption were best fitted to pseudo second order kinetic model rather than pseudo first order kinetic model.

Fullerenes: Fullerenes are ball shaped structure and made up of carbon atoms. They have very low density as compared to graphite and diamond due to a hollow ball shaped structures. Fullerene nanomaterials are consisted of fullerenes and surface functionalized fullerenes. These are used in optic, medical, cosmetic and electronics uses [16]. The fullerenes show closed cage of carbons containing hexagonal and pentagonal rings. Their general formula is C_{20+X}, where X is an integer number. Due to high electron affinity, hygroscopic nature and larger surface area, they are used in extraction of different chemical species from the aquatic systems [16,17]. Fullerenes have low affinity for the metal ions are present in waste waters due to surface defect or escaping of metal ions into the crystal or tendency of fullerenes for aggregations. The addition of fullerenes in other adsorbent makes them porous, enhance adsorption capacity for metal ions and improves hydrophobic nature [18-21].

Graphenes: Graphene is also a unique allotrope of carbon and it consisting of a single layer of carbon atoms to form a hexagonal lattice. Graphene is known for its specific properties and used in the optics, sensors, and biodevices. It is nearly related to graphite which is ingredient of pencil lead. Graphite is made up of a three dimensional layered structure and a proper gape is found between the layers. Graphene gives graphene oxide by the treatment with graphite and oxide. Graphene oxides can undergo functionalization with other reagents. The graphene based materials includes graphene and graphene oxides and have excellent properties in different ways [22,23]. The novel graphene oxide and silica materials for the removal of arsenic, cadmium, chromium, mercury and lead from waste water have reported by Wang et al. [24]. The low cost and environmentally safe material was found a promising adsorbent and the removal efficiencies for arsenic, cadmium, chromium, mercury, and lead recorded 97.7, 96.9, 96.0, 98.5, and 78.7 %, respectively. Zhang et al. [25] reported the reduced graphene oxide with poly vinyl pyrrolidine is a promising sorbent for the removal of copper from waste water. The adsorption capacity of the material was found to be 1689 mg/g at an initial pH value of 3.5 and contact time 10 minutes. Pourbeyram [26] was introduced graphene oxide (functionalized by zirconium and phosphate) for the removal of Pb (II), Cd (II), Cu (II), and Zn (II) from aqueous solutions. The adsorption study was carried out by batch system that included pH, contact time, and initial concentration of metal ions. The maximum adsorption capacity of the sorbent at pH 6 for Pb (II), Cd (II), Cu (II), and Zn (II) was found to be 363.42, 232.36, 328.56, and 251.58 mg g–1, respectively.

 DOI : 10.18231/2454-9150.2019.0185

2) Polymer based nanomaterials: Polymer based nanomaterials are solid colloidal particles with particle sizes 10 to 500nm. These are very sensitive, bioactive and show adsorptive and adhesion properties. They may be obtained from naturally, biosynthetically and chemically [27]. Piri [28] has considered the nanocomposites made from clay coated with polyaniline and used to remove lead and cadmium from contaminated water. The sorption of metals has been carried out under the batch conditions i.e. contact time, pH and concentrations. The maximum removal of lead and cadmium was found to be 90% and 20% after agitation time 90 minutes. The physic-chemical process during adsorption was confirmed by pseudo second order kinetic and Temkin isotherm models. A modified polyamine-polyurea polymer with pyromellitic diaanhydride nanosorbent was studied by Ozer et al. [29] for the adsorption of Cu (II), Ni (II), and Pb (II) ions under the batch conditions i.e. pH, contact time, amount of adsorbent, temperature, and initial concentrations. The adsorption capacity of the material for Cu (II), Ni (II), and Pb (II) ions was found to be 73.5, 81.3, and 109.9 mg g^{-1}, respectively. The suitability of adsorption mechanisms was confirmed by infra particle diffusion model.

3) Metal oxide based nanomaterials: The nanosorbents prepared from metal or metal oxides are showing very low environmental impact, low solubility and no secondary pollutants generating. The common sorbents like iron oxides, zinc oxides, copper oxides, titanium oxides, magnesium oxides, nickel oxides, aluminium oxides, cerium oxides, silver nanoparticles, manganese oxides etc [30-37] have been used for waste water treatments. Tamez and coworkers36 has used the nano-sized Fe_3O_4 and Fe_2O_3 for the removal of Cu (II) and Pb (II) ions from aqueous solution under the batch system. The adsorption capacity of Fe_3O_4 for Cu (II) and Pb (II) were found 37.04 mg/g and 166.67 mg/g and adsorption capacity of Fe_2O_3 nanomaterials for Cu (II) and Pb (II) ions were evaluated to be 19.61 mg/g and 47.62 mg/g, respectively. A nanomaterial copper oxide has used by Taman and coworkers [37] for the adsorptive removal of Fe (III) and Cd (II) ions under batch experiments i.e. contact time pH, initial metal ion concentration and dosage. The equilibrium data of adsorption were best fitted to pseudosecond-order kinetics. The suitability of experimental data with Langmuir isotherm model indicates monolayer coverage of metal ions on the surface of sorbent. Mahdavi [38] has used modified Al_2O_3 nanoparticles with humic acid, extract of walnut shell and 1,5-diphenyl carbazon for the sorption of Cd (II), Cu (II), and Ni (II) ions from aqueous solutions. The maximum adsorption capacities of modified Al_2O_3 for Cd (II), Cu (II), and Ni (II) were recorded 92.0, 97.0, and 63.8 mg g^{-1}, respectively. The equilibrium data of adsorption has been well explained by Langmuir isotherm model.

CONCLUSIONS AND FUTURE ASPECTS OF NANOMATERIALS AS NANOSORBENTS:

The rapid industrializations and human populations have increased the exposure of heavy metals in the fresh, saline and waste water. Most of conventional methods are suffering with early saturation, poor performances, lack of specificity, takes longer time for the removal etc. The use of nanomaterials in the water purification techniques is better alternative over the conventional methods. In the present review article, we have highlighted some most important nanomaterials for the removal of different heavy metals and an adequate coverage of the methodology involved in the removal techniques. It will be definitely needful to all academic researchers and students for the development of efficient, eco-friendly and specific nanomaterials for the waste water treatments. In the view of commercialization, the very important point is the low production cost of nanomaterials and their efficiency for large scale operations. Some basic problems of nanosorbents are their toxicity and sludge generation. The competitive performances of nanosorbents are very difficult till now and it is very crucial to develop highly efficient and promising nanosorbents in future for the removal of heavy metals from waste water in large scale.

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ISSN : 2454-9150 Vol-04, Issue-12, Mar 2019

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