Ranking of Nanosorbents for Removal of Mercury Ions from Water/Wastewater Samples

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ABSTRACT

Water pollution by heavy metals is of great concern to government, policy makers and researchers due to their negative effects on living species. Heavy metal ions such as Pb^{2+}, Cd^{2+}, As^{3+}, Ni^{2+} and Hg^{2+} are toxic, non-biodegradable and can cause severe health problems. Mercury is highly toxic and its chronic exposure affects the nervous system and other vital organs. Pollution due to mercury even at very low concentration is worldwide problem. No biological function in the human body requires mercury and it gets biomagnified within the food chain. The removal of mercury from environmental water samples is an essential concern. Adsorption is a very efficient and economical process for metal ion removal from water. This study provides a systematic ranking of nanosorbents for removal of maximum mercury ions from water on the basis of adsorption capacity, cost, toxicity and regeneration. This study also identifies the knowledge gaps and research needs of the area and discusses the environmental impact and human safety issues of these sorbents.

Keywords: Water purification, nanomaterials, adsorbents, mercury removal and health effects

1. INTRODUCTION

In the recent year's water pollution by heavy metals such as mercury, lead, arsenic, chromium, manganese, cadmium and copper due to industrial waste and any other mediums is worldwide environmental concern. These heavy metals are toxic because of their non-biodegradable and bio-accumulative properties. Mercury metal has been considered non essential and non beneficial element for living organisms. Mercury is released in water through various industrial applications such as mercury mines, gold mining areas (Hg is used in the amalgamation process), battery manufacturing, pulp and plastic production, the electrochemical separation of chlorine from sodium at chlor alkali plants, coal combustion and oil refining process [1,2].

The European Union (EU) maximum permissible concentrations for mercury in potable and wastewater are 0.001 and 0.005mg/L respectively. The maximum concentration of mercury recommended by the World Health Organization (WHO) is 1 ppb. Mercury is predominantly hazardous once it gets into aqueous system as it gets converted into more toxic form methyl mercury which is a neurotoxicant.

A number of advanced technologies have been applied for removal of toxic metals ions from water/wastewater. Among them adsorption is the most economical and widely used technique for removal purpose. Water treatment by adsorption involves the use of different materials such as natural products, activated carbon, zeolites, clay, nanosorbents etc. Nanotechnology offers new opportunities and advantages in the field of water purification. Recently nanosorbents are most widely used materials for removal of heavy metal ions from water because of their large surface areas and large surface to volume ratio compared with conventional sorbents. Several nanosorbents such as nano-metal oxides, carbon nanotubes (CNT), magnetic nanosorbents, nano composites, modified carbon nanotubes etc. have been identified for the removal of heavy metal ions from water [3,4]. This study provides a systematic ranking of nanosorbents for removal of maximum mercury ions from water. This study also discusses the environmental impact and human safety issues of these sorbents.

2. METHODOLOGY

The study comprises of comprehensive review on nanosorbents used for removal of mercury from water/wastewater samples. The sorption mechanism has also been discussed. The nanosorbents reported till date have been ranked on the basis of adsorption capacity, cost and toxicity. The review aims to give a comprehensive picture on the different type of nanosorbents reported till date for the removal of mercury from water and helps to choose low cost and more efficient sorbents. The ranking of nanosorbents will motivate the development of low cost and more efficient adsorbents for removal of mercury from water/wastewater. This study also identifies the knowledge gaps and research needs of area.

3. DISCUSSSION

Review on nanosorbents used for removal of mercury from water/wastewater samples

The maximum adsorption capacities of different nano based sorbents under a given set of conditions are listed in Table 1. The maximum adsorption capacities have been compared for different sorbents. It is clear from the compiled data that adsorption capacity of sorbents thiol-functionalized magnetic silica nanocomposite (TF-MSNC) and nano-barium-strontium titanate coated by dithizone(BST- dithizone) are minimum and less than 20 mg/g. Wang et al. prepared a novel photo-cross-linkable nanofiber based on a uracil functionalized polymer, poly[1-(4-vinylbenzyl uracil)] (PVBU) and reported maximum Hg^{2+} adsorption capacity equal to 543.9 mg/g which is maximum among all reported values [5]. The comparison of all sorbents in terms of adsorption efficiency is depicted in Fig. 1. The Langmuir isotherm gives high correlation coefficients as compared to Freundlich isotherm which suggests that sorption occurs homogeneously on the active sites of the sorbent, and monolayer sorption is there. Removal of mercury ions may be attributed by complex mechanism which comprises a number of mechanisms such as adsorption, ion-exchange, surface precipitation, chelation and complexation.

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Modified polymer nanofibres appear to be most promising because of high specific surface areas and size of the pores on the surface. It is further noticeable that modification on the carbon nanotubes increases adsorption capacity because of surface areas and functionalized/modified groups. Functionalization on the surface plays a key role for removal of mercury ions from water. Specific functionalization on the surface increases the ions exchange capability of the adsorbents. The maximum adsorption capacity of the all reviewed nanosorbents follows the order; modified polymer nanofibres >surface functionalized nano-magnetic particles >manganese dioxide nanowhiskers > MWCNT-COOH-impregnated CS beads > SWCNT-impregnated CS composite beads > MWCNT-impregnated CS beads > Fe_3O_4@-SiO_2–SH > composite beads composed of chitosan (CS) >thiol-derivatized SWCNTs > jute nano fibres > novel zonal thiol-functionalized silica nanofibers > pristine SWCNTs.

The other sorbents listed in table have very low adsorption capacity. On the basis of starting material cost and availability of the material the approximate order of cost of reported sorbents follows the following order; jute nano fibres< novel zonal thiol-functionalized silica nanofibers< uracil-functionalized polymer nanofibres< surface functionalized nano-magnetic particles< Fe_3O_4@-SiO_2–SH< MWCNT-impregnated CS beads < MWCNT-COOH-impregnated CS beads< SWCNT-impregnated CS composite beads< thiol-derivatized SWCNTs< pristine SWCNTs. It is also very important to evaluate other aspects such as toxicity of nanomaterial and regeneration in order to rank the nanosorbents. The increasing use of nanomaterials in different applications has also raised several questions about their probable effects on human health and the environment due to their reported occurrence in environment. Regeneration studies of reported sorbents gives satisfactory results. If we analyze the toxicity of used nanomaterials as sorbents there are certain knowledge gaps as for all materials listed in table, toxicity studies are available only for few of them.

4. CONCLUSION

Heavy metals in water or wastewater due to growing industrialization are in their alarming conditions especially for mercury. A number of materials have been applied as adsorbent for their removal from water. From the survey it was observed that nanomaterials have very high sorption capability compared to other materials. This review reports maximum adsorption capacity and other issues such as cost and toxicity of different nanomaterials for removal of mercury from water. On the basis of all observation it can be concluded that

1. Polymer nanofibres offer maximum adsorption capacity for removal of mercury from water and they can be further modified to obtain better results.
2. Pristine nanotubes when used as sorbents do not give good adsorption efficiency for removal of mercury.
3. Toxicity studies have been reported only for few sorbents such as carbon nanotubes and magnetic iron oxides.
4. Toxicity of nanomaterials depends on their physical form, diameter, length and the nature of attached molecules on the surfaces or sidewall.
5. Toxicological studies of these nanomaterials are in early stage and no conclusion has been made regarding their effects
6. Toxicity studies should be analyzed thoroughly before tailoring new nanosorbents to avoid any hazards to environment and human health.
7. Cost of the used nanomaterials can be reduced by regeneration of the sorbents

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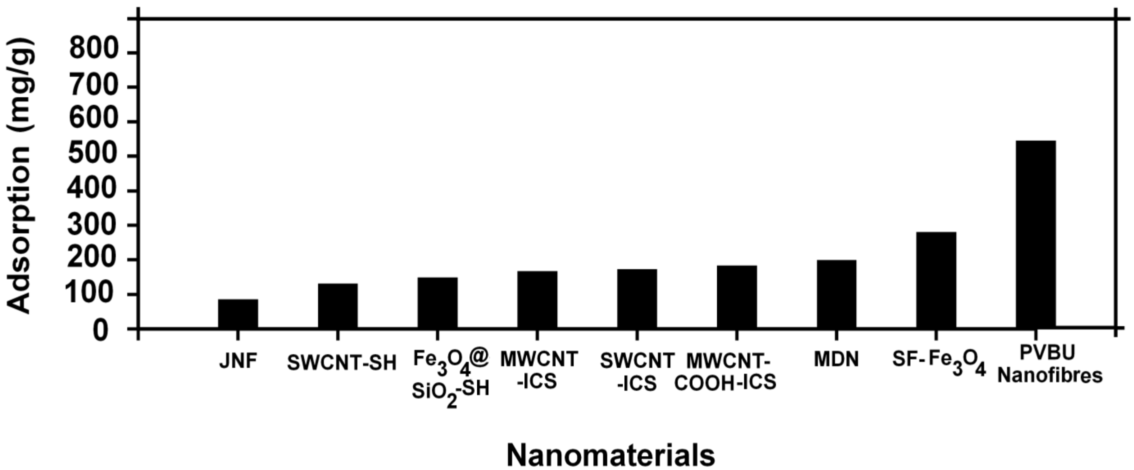

Fig.1. Adsorption of mercury by different nanomaterials from water samples at pH 4.0–7.5 and the temperature range of 25–30°C.

Table 1: Nanomaterials for removal of mercury ions from water

Sorbent	Conditions/Requirements/Properties	$Q_{max.}$ mg/g	pH	Model	Ref.
Surface functionalized	Coating the surface with polymer (vinylpyrrolidone) with	280	7.5	–	[6]

nano-magnetic particles (SF-Fe_3O_4)	thiodiglycolic acid as the primary surfactant and 4-vinylaniline as the secondary surfactant.				
Thiol-functionalized magnetic silica nanocomposite (TF-MSNC)	Surface of the magnetic silica nanocomposite was functionalized with thiol group	19.79	5.5	–	[7]
Nano-barium-strontium titanate coated by dithizone(BST-dithizone)	In the medium of pH 3–8, the adsorption time was more than 15 min. Adsorbent could be completely regenerated using 2 mol/L HNO_3.	15.3	3–8	–	[8]
Jute nano fibers (JNF)	The surface area, pore volume and pore diameter of the JNFwere found to be 15.48 Sq. m/g, 0.075 cc/g and 7.42 nm, respectively.	85.5	6	Langmuir model	[9]
Novel zonal thiol-functionalized silica nanofibers (TF-SiNF)	Fabricated by 3-mercaptopropyl trimethoxysilane on the electrospun polyacrylonitrile (PAN) nanofibers	57.49	Waste water	–	[10]
Uracil-functionalized polymer, poly[1-(4-vinyl benzyl uracil)] (PVBU)	Nanofiber can be converted into a covalent network nanofiber through exposure to UV light at a wavelength of 254 nm	543.9	7	–	[5]
Pristine SWCNTs	First-order rate model was employed to describe the kinetic adsorption	40.16	5	Langmuir model	[11]
Thiol-derivatized SWCNTs (SWCNT-SH)	Synthesized by reacting acid-cut SWCNTs with cysteamine hydrochloride using carbodiimide coupling. Desorption could be easily done by altering the pH	131.5	5	Langmuir model	[11]
Thiol-modified Fe_3O_4@ SiO_2 (Fe_3O_4@ SiO_2 -SH)	Thiol groups were modified on the Fe3O4@SiO2 through silanization reaction	148.8	6.5	Langmuir model	[12]

Manganese dioxide nanowhiskers (MDN)	Prepared by the reduction of potassium permanganate by ethyl alcohol	199.5	6-9	Langmuir model	[13]
Composite beads composed of chitosan (CS)	Protected crosslinking technique removed 2.5 times more Hg(II) from solution than beads prepared by normal crosslinking.	148.7	4	Langmuir model	[14]
Composite beads composed of chitosan (CS) with SWCNTs(SWCNT–ICS)	A protected crosslinking method was used for the preparation of the CS/CNTs beads	172.7	4	Langmuir model	[14]
Composite beads composed of chitosan (CS) with MWCNTs(MWCNT–ICS)	The optimum removal conditions were pH = 4, contact time = 40 min, and temperature = 70°C.	167.5	4	Langmuir model	[14]
Composite beads composed of chitosan (CS) with MWCNT–COOH (MWCNT–COOH–ICS)	Adsorbent can be regenerated and reused	183.2	4	Langmuir model	[14]