THOMSON REUTERS ENDNOTE

[Xavier*, 5(3): March, 2016] ISSN: 2277-9655
(I2OR), Publication Impact Factor: 3.785

IJESRT

INTERNATIONAL JOURNAL OF ENGINEERING SCIENCES & RESEARCH TECHNOLOGY

REMOVAL OF TOXIC METALS FROM AQUEOUS ENVIRONMENT USING VARIOUS ADSORBENTS: A REVIEW

R. S. Dubey and R. Xavier*

Department of Applied Chemistry, Amity Institute of Applied Science, Amity University, NOIDA-125, G. B. Nagar, UP, India

*Department of Chemistry, Mewar University, Gangrar, Chittorgarh, Rajasthan, India

ABSTRACT

In Recent decades, there has been an increasing public awareness of the long-term effect of water containing dissolved toxic metal ions. Toxic metals are known to be detrimental to plants, animals and humans. Even at very low concentration they adversely impair the nervous, digestive and skeletal system. Toxic metal contamination has been a crucial issue because these metals tend to persist and accumulate in the environment. Aquatic environment are particularly sensitive to toxic metal contamination possibly due to the structure of their food chain. This is because toxic pollutants are directly or indirectly introduced into aqueous environment significantly as a result of various industrial effluent injections in natural water bodies. In this review, presence of heavy metals in aqueous environment, its non bio-degradable properties, its high toxicity, followed by removal of these toxic metals using different techniques are discussed.

KEYWORDS: Toxic metals, adsorbents, adsorbate, aqueous environment

INTRODUCTION

The past century has seen rapid and uncensored industrialization of the human society. The natural outcome of this rapid expansion of industries is the generation of metal containing wastes which are directly or indirectly injected into the water bodies. The discharge of heavy toxic metals into aquatic ecosystems has become a matter of great concern in India over the past few decades. These heavy toxic metals are generated by dental operations, electroplating industries, leather tanning, textiles, paper and pulp industry and are potentially toxic to humans [1]. These kind of metals are directly related with environmental pollution and biological toxicity problems [2]. Some examples of these metals include mercury, lead, zinc, arsenic, copper, nickel and cadmium etc. These metals and their ions have high toxicity, non-biodegradable properties which cause severe health problems in animals and human beings. It is well known that chronic cadmium toxicity is the cause of Itai-Itai disease in Japan. The harmful effects of cadmium also include renal damage, emphysema, testicular atrophy, skeletal and malformation of the fetus [3, 4]. Similarly lead has environmental impact due to its well known toxicity [5] and wide spread use in industries, metal processing industries, storage battery manufacturing, printing, pigment manufacturing and petrochemicals etc. Intense exposure to high Pb (II) levels (from 100-200 gm/day) causes encephalopathy with the following symptoms like vertigo, insomnia, migraine, seizures and coma [6, 7]. The current annual world production of Pb (II) is approximately 5.4 million tons and continues to rise. Such industries thus continue to pose a significant risk to workers as well as the surrounding communities. Therefore it becomes all the more important that these industrial effluents, which are rich in heavy metals, should be treated before being discharged into aqueous environment. This is because aquatic systems are particularly sensitive to pollution possibly due to the structure of their food chain. As harmful substances like heavy metals and other contaminants enter into the food chain, they are ultimately accumulated in fish and other edible organisms. As they move from one ecological tropic level to another, metallic species start damaging the ecosystem. As they move up in the tropic levels, tracking these harmful substances is difficult and thus increases in concentration in living tissues throughout the food chain. Due to biomagnifications, humans receive the maximum impact, since they are at the top of the food chain. Hence, heavy metal contamination has been a critical problem [8].

METHODS OF REMOVAL

The efficient removal of toxic metals from wastewater is an important matter and is being widely studied. A number of technologies have been developed over the past years to remove toxic heavy metals from wastewater. Where small concentrations of hazardous substances dissolved in water are concerned, physical treatment can be used. Heavy metal ions can also be eliminated by several traditional techniques [9] including chemical precipitation [10], reverse osmosis [11], electrochemical treatment techniques [12], ion exchange [13], membrane filtration [14], coagulation [15], extraction [16], irradiation [17] and adsorption [18]. The basic treatments of industrial effluents include, (a) Primary treatment; which aims at removing large particles in the sewage by means of grids on sedimentation. (b) Secondary treatment: which aims at reducing the biochemical oxygen demand (BOD) in the waste water by oxidizing organic compounds and ammonium ion? This process is most of the time carried out in aerated tanks with the activated sludge. It also involves both heterotrophic bacteria and protozoa. The bacteria degrade the organic material and the protozoa graze the bacteria and in both cases organic material is converted to CO_2 and water. In addition to activated sludge, secondary treatment may also be performed with trickling filters or oxidation ponds. (c) Tertiary waste water treatment mainly aims at removing the plant nutrients nitrogen and phosphorous. Some of the other techniques are chemical precipitation, reduction, ion exchange, distillation, or other ways of extraction. The currently used above mentioned physico-chemical processes for heavy metal removal are expensive and inefficient in treating large quantities. They also cause metal bearing sludges which are difficult to dispose off. This has directed the attention towards the technology of biosorption, based on metal binding capacities of various biological materials which is an attractive alternative to physico-chemical methods.

BIOSORPTION OF METALS

Biosorption can be defined as the ability of biological materials, to accumulate heavy metals, from wastewater through metabolically mediated or physico-chemical pathways of uptake [19]. Microorganisms take up metal either actively i.e. bioaccumulation and/or passively i.e. biosorption. Algae, bacteria, fungi and yeast have been proved to be potential metal biosorbents (Table 1).

Table 1: Heavy metal uptake capacities of different microalgae:

Microalgae as absorbents	Lead (mg/g)	Zinc (mg/g)	Copper (mg/g)
M. spicatum	46.69	15.59	10.37
P. lucens	141	32.4	40.8
S. herzegoi	----	18.1	19.7
E. crassipes	----	19.2	23.1

It is demonstrated that for large scale applications, the biosorptive process are more efficient than the bio-accumulative processes because living system (active uptake) often require the addition of nutrients and hence increase BOD or Chemical oxygen demand (COD) in the effluent. The major advantages of biosorption over conventional treatment methods include low cost, high efficiency, minimization of chemical and biological sludge, no additional nutrient requirement, regeneration of biosorbent and possibility of metal recovery. The biosorption process involves a solid phase (sorbent or biosorbent, biological material) and a liquid phase (solvent normally water) containing a dissolved species to be sorbed (sorbate, metal ions). Due to higher affinity of the sorbent for the sorbate species, the latter is attracted and bound by different mechanisms. This process continues till equilibrium is established between the amount of solid-bound sorbate species and its portion remaining in the solution. Other types of materials acting as adsorbants include activated carbons [20], clay minerals [21], chelating materials [22] and chitosan / natural zeolites [23] which are known to adsorb metal ions from aqueous solution.

Complexation-ultrafiltration technique

In the recent years, the complexation-ultrafiltration technique has shown to be a promising technique for removal of heavy metals in solution. Toxic heavy metals like Cu(II), Ni(II) and Cr(III) can be removed using this method. Carboxymethylcellulose (CMC) as a water soluble polymer was used for complexing the cationic forms of the heavy metals before filtration. The function of the metal-CMC complex is to increase the molecular weight and size. The size of the complex has to be larger than the pore of the selected membranes so the complex can be retained. Permeate water is then purified from heavy metals [24]. This method proves to be a new promising technology for separation of heavy metals from effluents because of low energy requirements, very fast reaction kinetics and high selectivity of separation.

Electrochemical techniques

Various electrochemical techniques are available for effluent treatment [25]. Titanium can be used as a working electrode which is stable, energy efficient and can effectively treat variety of effluents. In the electrochemical removal of Pb, $Pb(NO)_3$ solution is used as an electrolyte. The mechanism of electrochemical removal of lead can be shown by the following reactions:

$$Pb(NO_3)_2 \longrightarrow Pb^{2+} + 2NO_3^-$$

The reaction at anode is:

$$Pb^{2+} \longrightarrow Pb^{4+} + 2e^- \quad E = -1.6 \text{ volts}$$

Then Pb^{4+} ion is further oxidized to hydrated lead dioxide ($PbO_2.xH_2O$)

The reaction at the cathode is:

$$NO_3^- + 2e^- \longrightarrow NO_2^-$$

Nitrate ions are reduced more easily than Pb^{2+} ions and thus function as cathodic depolarisers to maintain the cathode potential below the value required for the reduction of Pb ions. As a result Pb gets deposited on electrode as hydrated lead oxide. This technique can be used to remove Ni, Cr, Cd, Hg etc.

Use of nano-materials for removal of heavy metals

Although traditional sorbents can remove heavy metal ions from waste water, the low sorption capacities and efficiencies limit their application deeply. To solve these defects of traditional sorbents nanomaterials are used as the novel ones to remove heavy metal ions in waste water. Materials with the particle size between 1nm to 100 nm are defined as nanomaterials. These are extensively being investigated because of recent developments in nanosciences and nanotechnology which has potential remedies of environmental problems [26, 27]. Compared with traditional materials nano-structure adsorbents have exhibited much higher efficiency and faster rates in water treatment. Nanomaterials used as sorbents for removing heavy metal ions in waste water should satisfy the following criterions; (a) the nano sorbents themselves should be non toxic; (b) the sorbent should have relatively high sorption capacities and selectivity to the low concentration of pollutants; (c) the adsorbed pollutant should be removed from the surface of the nano adsorbent easily; (d) the sorbents should be infinitely recycled.

A variety of nano materials such as carbon nanotubes, carbon based material composites graphenes, nanometal or metal oxides are known to show high adsorption capacities. As one of the inorganic materials, carbon based nanomaterials [28] are widely used for removal of heavy metals due to its non toxic nature and high sorption capacities. Earlier activated carbon was used but it was difficult to remove heavy metals at ppb levels. But in due course of time, with the development of nanotechnology carbon nanotubes, fullerenes and graphenes was synthesized and used as nanosorbents. Carbon nano tubes (CNT's) which were discovered by Lijima are also used widely to remove heavy metals in waste water treatment. They show unique structural, electronic, optoelectronic, semiconductor, mechanical, chemical and physical properties. To enhance the sorption capacities CNT's were modified by oxidation [29, 30] combining it with other metal ions [31] or metal oxides [32] and coupled with organic compounds [33]. Smith et al. [34] showed that carboxyl carbon sites are over 20 times more energetic for zinc sorption than unoxidised carbon sites. Salam et al. [33] modified CNT with 8-hydroxyquinoline, which are used to remove Cu^{2+}, Pb^{2+}, Cd^{2+} and Zn^{2+}. Graphene is another type of carbon material used as nanosorbent which is a kind of one or several atomic layered graphites, possessing special two dimensional structure and good mechanical, thermal properties. Hwang et al. [35] reported magnetic graphene adsorbents with a particle size of ≈10 nm which provide a high binding capacity for As^{3+} and As^{5+} and the results indicate that the high binding capacity is due to the increased adsorption site in the graphenes composite. Nanoparticles formed by metal or metal oxides are another inorganic nanomaterials which are used broadly

ISSN: 2277-9655
(I2OR), Publication Impact Factor: 3.785

to remove heavy metal ions in waste water treatment. Nanosized metal or metal oxides include nano-sized silver nanoparticles [36], ferric oxides [37], manganese oxide [38] and so on and all these provide high surface area and specific affinity. Moreover, metal oxides possess minimal environmental impact and low solubility and no secondary pollution.

Nanosized metal oxides show great removal efficiency of heavy metal in waste water, owing to their higher surface area and much more surface active sites than bulk materials. But, it is very difficult to separate them from the waste water due to their higher surface energy and nano size. So, many researchers have now turned to design polymer based nanosorbents. Most of the current inorganic sorbents rarely have the two main characteristics i.e. functional groups and a large surface area. Because of this polymer based silicate nanocomposites [39] have attracted attention because they exhibit dramatic improvement in properties at very low filer contents. Xu et al. [40] synthesized the hybrid polymers from the ring opening polymerization of pyromellitic acid dianhydride (PMDA) and phenylaminomethyl trimethoxysilane (PAMTMS). This hybrid polymers are used to remove Cu^{2+} and Pb^{2+}. Adsorption for Cu^{2+} and Pb^{2+} followed lagergren second order kinetic model and Langmuir isotherm model, demonstrating that the adsorption process might be Langmuir monolayer adsorption.

Chitosan

Chitosan is another biopolymer which is extracted from crustacean shells or from fungal biomass. The structure of chitosan is presented schematically in the figure 1.

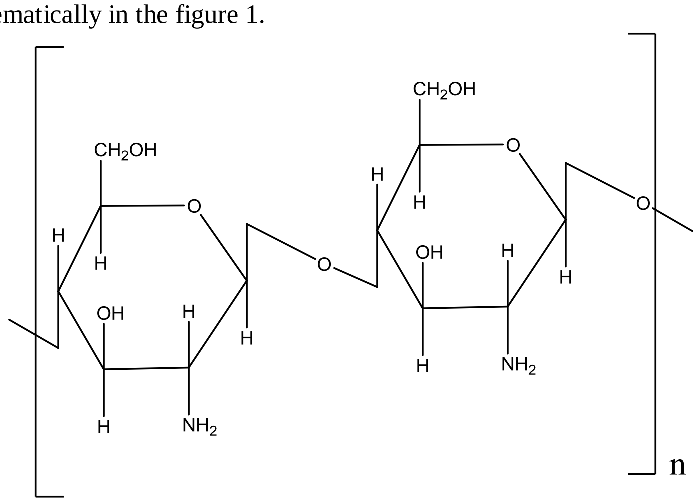

Figure 1 Structure of chitosan

Chitosan has been used for about three decades in water purification processes because high porosity of this natural polymer results in novel binding properties for metal ion such as cadmium, copper, lead, uranyl, mercury and chromium. When chitosan is spread over oil spills it holds the oil mass together making it easier to clean up the spill. Similarly, chitosan is widely being used to remove oil, grease, heavy metals and fine particulate matter that causes turbidity in waste water [41]. Some commercially attractive properties of chitosan are that they are polymeric, including natural decomposition, non-toxic to both environment and humans with no side effects or allergic effects if implanted in the body. They occur naturally in the environment in large quantities and run second in abundance to cellulose. It has an amine functional group which is strongly reactive with metal ions.

CONCLUSIONS

Throughout in this review paper, the need and importance of removing toxic heavy metals from aqueous environment in general have been discussed. Different methods are already being used and many more are under study. The paper throws light on methods like physico-chemical methods, biosorption, complexation-ultrafiltration technique, electrochemical techniques, use of nanomaterials, certain polymers as well as natural biopolymer like chitosan. The current physiochemical processes for heavy metal removal like precipitation, reduction, ion-exchange etc are expensive and inefficient in treating large quantities. In this regard bio-adsorption which is the physical adhesion of chemicals onto the surface of the solid is a good alternative to traditional processes. To sum up, nano-materials including traditional inorganic nanoadsorbents and novel polymer supported composites are used to remove the heavy metal ions in wastewater treatment due to their novel size and shape dependent properties and excellent removal efficiency. Similarly bio-polymers like chitosan which is a renewable polymer have the potential to reduce and solve some environmental pollution problems for creating greener environment. However, we are confronted with the development of cheaper methods, since in most countries wastewater treatment has to be a low-cost plan for its majority approval. More work by scientist and technologist are required in order to accomplish this objective. In this regard exploitation of new and efficient methods than the ones existing will infinitely continue.

Table 2: Summary of different techniques commonly used for removal of heavy metals from water

S. No.	Experiment	Adsorbent	Adsorbate	Conclusion/Result	Reference
1.	Biopolymer adsorption	Chitosan	Cd, Cu, Pb, U, Hg and Cr.	Chitosan is a renewable polymer and has the potential for creating greener environment. It has attractive properties like natural decomposition, non-toxic to both environment and humans with no side-effects or allergic effects if implanted in the body.	1, 41-42
2	Adsorption	Pyrolusite Zeolite Activated carbon Clay Surface Kaolinite and alumina Calcite Coffee Egg shells Rice straw Garlic Cloves	Pb, Zn Pb, Zn Mg Pb Pb^{2+} Mn, Co, Ni, Zn, Pb Pb, Cu, Hg, Cd, Zn, Pb^{2+} Pb^{2+}, Mn^{2+}, Zn^{2+} Cd^{2+}, Hg^{2+}, Pb^{2+}	Adsorption is a good tool for controlling the level of aqueous Pb pollution. The utilization of low cost adsorbents is helpful as it is simple, effective and economical.	43-52
3.	Biosorption	Syzygium cumini L. (jamun) Tridax procumbens (Asteraceae)	Pb^{2+} Pb^{2+}	Natural adsorbents are cheaper and environmentally safe, low cost adsorbents for treatment of polluted water from heavy metals	53-54
4.	Biological adsorption methods by microalgae	M. spicatum P.lucens S.herzegoi E. crassipes	Pb, Zn, Cu Pb, Zn, Cu Pb, Zn, Cu Pb, Zn, Cu	Microalgae are used in bioremediation of metal contaminated sites due to their ability to tolerate heavy metals, their high yield of recovery per unit mass and their high specific outer area coupled with a cell wall loaded with ionisable groups.	55-57

5.	Nanosorption	Carbon nano tube (CNT) Modified CNT with 8-hydroxyl quinoline Graphene oxide nano sheets Magnetite-graphene adsorbents with particle size ~ 10 nm Nanosized silver nano particles Ferric oxide Manganese oxide Titanium oxide Magnesium oxide Copper oxide Cerium oxide $Mg(OH)_2/Al_2O_3$ composite membranes Pyrometallic acid dianhydride (PMDA) and phenylamino-methyl trimethoxy silane (PAMTMS)	Co^{2+}, Cu^{2+}, Cu^{2+}, Pb^{2+},Cd^{2+}, Zn^{2+} Co^{2+}, Cd^{2+} As^{3+}, As^{5+} Heavy metals As^{3+} As^{5+} As^{3+} Toxic pollutants As^{3+}, As^{5+}, heavy metal ions Ni^{2+} Cu^{2+}, Pb^{2+}	Nanomaterials have a number of physiochemical properties due to their unique structure and surface characteristics. They are able to remove heavy metal ions at low concentrations with high selectivity and adsorption capacity. Metal oxides provide high surface and specific affinity and have minimal environmental impact and low solubility and no secondary pollution Nanosized metal oxides show great removal efficiency of heavy metal in waste water owing to their higher surface area and more surface active sites than bulk materials	58 33 3 35-38 59-63 39-40
6.	Complexation-ultrafiltration techniques	Carboxymethyl cellulose (CMC)	Cu(II), Ni(II) and Cr(III)	The use of water soluble metal binding polymers in combination with ultrafiltration is a hybrid approach to concentrate selectively and to recover valuable elements as heavy metals. The advantage of this process is high separation selectivity due to the use of a selective binding and low energy requirements.	24
7.	Electrochemic-al techniques	Titanium as working electrode	Pb(II, Ni(II), Cr(II), Cd(II), Hg(II)	Titanium as a working electrode is stable, energy efficient and involves control and minimization of environmental pollution through remediation of toxic metal ions from aqueous solution.	25

8.	Ion Exchange method	Cation Exchange resins macro-porous AMBEREJET 1200 Na	Ni(II), Pb(II)	Ion exchange is a mass transfer process. There are two main rate-determining steps which are considered in most of the ion exchange reactions. Among the materials used in ion exchange processes, synthetic resins are commonly preferred as they are effective and inexpensive.	64

REFERENCES

1. Palanisamy,K.,Nomanbhay, S.M. 2005. Removal of heavy metal from industrial wastewater using chitosan coated oil palm shell charcoal. Electronic journal of Biotechnology:8.
2. Jjemba PK (2004) "Interaction of metals and metalloids with microorganisms in the environment". In: Jjemba PK (ed) Environmental microbiology- principles and applications. Science Publishers, Enfield, pp 257-270.
3. Zhao G, Li J, Ren X, Chen C, Wang X (2011) Few layered grapheme oxide nanosheets as superior sorbents for heavy metal ion pollution management Environ Sci Technol 45: 10454-10462.
4. Moreno-Castilla C, Alvarez-Merino MA, Lopez-Ramon MV, Rivera-Utrilla J (2004) Cadmium ion adsorption on different carbon adsorbents from aqueous solutions. Effect of surface chemistry, pore texture, ionic strength and dissolved natural organic matter. Langmuir 20: 8142-8148.
5. P.Hepple, Lead in the environment, Institute of Petroleum, London, (1972).
6. Center for Disease Control, Preventing Lead Poisoning in young children. Washington DC : U.S. Dept of Health and Human Services, (1991).
7. World Health Organization (W.H.O), Environmental Health Criteria, No. 200, Lead. –CH-1211 Geneva 27-Switzerland.(1998).
8. Volesky, B., 2001, Detoxification of metal-bearing effluents: biosorption for the next century, Hydrometallurgy. 59:203-216.
9. Fu F, Wang Q (2011) Removal of heavy metal ions from wastewaters: A review. J Environ Manage 92: 407-418.
10. Wang LK, Vaccan DA, Li Y, Shammas NK (2005) Chemical Precipitation Physicochemical treatment Processes. In Wang LK, Hung YT, Shammas NK, Eds. Humana Press 3141-197.
11. Bodalo-Santoyo A, Gomez-Carrasco JL, Gomez-Gomez E, Maximo-Martin F, Hindalgo-Montesinos AM (2003) Application of reverse osmosis to reduce pollutants present in the industrial wastewater, Desalination 155:101-108.
12. Walsh FC, Reade GW (1994) Electrochemical techniques for the treatment of dilute metal-ion solutions. Studies in environmental science 59: 3-44.
13. Xing Y, Chen X, Wang D (2007) Electrically regenerated ion exchange for removal and recovery of Cr (VI) from wastewater. Environ Sci Technol 41: 1439-1443.
14. Ersahin ME, Ozgun H, Dereli RK, Ozturk I, Roest K, et al. (2012) A review on dynamic membrane filtration. Materials, applications and future perspectives. Bioresour Technol (in press).
15. Zhang P, Hahn HH, Hoffmann E (2003) Different behavior of iron (III) and aluminium (III) salts to coagulate silica particle suspension. Acta hydroch hydrob 31: 145-151.
16. Rykowska I, Wasiak W, Byra J (2008) Extraction of copper ions using silica gel with chemically modified surface. Chem Pap 62: 255-259.
17. Batley GE, Farrar YJ (1978) irradiation techniques for the release of bound heavy metals in natural waters and blood. Anal Chim Acta 99: 283-292.
18. Srivastava V, Weng CH, Singh VK, Sharma YC (2011) Adsorption of nickel ions from aqueous solutions by nano alumina; Kinetic, mass transfer, and equilibrium studies. J Chem Eng Data 56: 1414-1422.
19. Fourest E. and Roux C.J. 1992. Heavy metal biosorption by fungal mycilial by-products: mechanisms and influence of pH. Applied Microbiology and Biotechnology, 37(3): 399-403.

20. Kobya M, Demirbas E, Senturk E, Ince M (2005) Adsorption of heavy metal ions from aqueous solutions by activated carbon prepared from apricot stone. Bioresour Technol 96: 1518-1521.
21. Oubagaranadin JUK, Murthy ZVP (2009) Adsorption of divalent lead on a montmorillonite-illite type of clay. Ind Eng Chem Res 48: 10627-10636.
22. Sun S, Wang L, Wang A (2006) Adsorption properties of crosslinked carboxymethyl-chitosan resin with Pb(II) as template ions. J Hazard Mater 136: 930-937.
23. Wang X, Zheng Y, Wang A (2009) Fast removal of copper ions from aqueous solution by chitosan-g-poly(acrylic acid)/attapulgite composites. J Hazard Mater 168: 970-977
24. Rether, A., and Schuster, M., Selective separation and recovery of heavy metal ions using water-soluble N-benzoylthiourea modified PAMAM polymers, Reactive and Functional Polymers 57 (2003) 13-21.
25. APHA Standard Methods for the Examination of Water and Waste Water, 17^{th}. Edition, New York, USA (1985).
26. Lee J, Mahendra S, Alvarez PJJ (2010) Nanomaterials in the construction industry; A review of their applications and environmental health and safety considerations. ACS Nano 4: 3580-3590.
27. Ali I (2012) New generation adsorbents for water treatment. Chem Rev (in press).
28. Mauter MS, Elimelech M (2008) Environmental applications of carbon based nanomaterials. Environ Sci Technol 42: 5843-5859.
29. Rao GP, Lu C, Su F (2007) Sorption of divalent metal ions from aqueous solution by carbon nanotubes: A review. Sep Purif Technol 58: 224-231.
30. Afzali D, Jamshidi R, Ghaseminezhad S, Afzali Z (2011) Preconcentration procedure trace amounts of palladium using modified multiwalled carbon nanotubes sorbent prior to flame atomic absorption spectrometry. Arab J Chem (in press).
31. Gupta VK, Agarwal S, Saleh TA (2011) Synthesis and characterization of alumina-coated carbon nanotubes and their application for lead removal. J Hazard Mater 185: 17-23.
32. Zhao X, Jia Q, Song N, Zhou W, Li Y (2010) Adsorption of Pb(II) from an aqueous solution by titanium dioxide/carbon nanotube nanocomposites: Kinetics, thermodynamics, and isotherms. J Chem Eng Data 55: 4428-4433.
33. Kosa SA, Al-Zhran G., Abdel Salam M (2012) Removal of heavy metals from aqueous solution by multi-walled carbon nanotubes modified with 8-hydroxyquinoline. Chem. Eng. J. 181-182, 159-168.
34. Cho HH, Wepasnick K, Smith BA, Bangash FK, Fairbrother DH, et al (2009) Sorption of aqueous Zn (II) and Cd (II) by multiwall carbon nanotubes: the relative roles of oxygen-containing functional groups and graphinic carbon, Langmuir 26; 965-981.
35. Chandra V, Park J, Chun Y, Lee JW, Hwang IC, et al (2010) Water-dispersible magnetite-reduced grapheme oxide composites for arsenic removal, ACS Nano 4: 3979-3986.
36. Fabrega J. Luoma SN, Tyler CR Galloway TS, Lead JR (2011) Silver nanoparticles: Behaviour and effects in the aquatic environment;, Environ Int. 37: 517-531.
37. Feng L, Cao M, Ma X, Zhu Y, Hu C (2012) Superparamagnetic high- surface- area Fe3O4 nanoparticles as adsorbents for arsenic removal; J Hazard Mater 217-218:439-446
38. Gupta K, Bhattacharya S, Chattopadhyay D, Mukhopadhyay A, Biswas H, et al,(2011) Ceria associated manganese oxide nanoparticles; Synthesis, characterization and arsenic(V) sorption behavior, Chem Eng J 172: 219-229.
39. Pavlidou S, Papaspyrides CD (2008) A review on polymer- layered silicate nanocomposites. Progress Polym Sci 33: 1119-1198.
40. Liu J, Ma Y, Xu T, Shao G (2010) Preparation of zwitter ionic hybrid polymer and its application for the removal of heavy metal ions from water. J Hazard Mater 178:1021-1029.
41. Varma, A.J., Deshpande, S.V., Kennedy, J.F. 2004. Metal complexation by chitosan and its derivatives: a review. Carbohydrate Polymers, 55: 77-93.
42. Niu, H.,Volesky, B.2003.Characteristics of anionic metal species bisorption with waste crab shells. Hydrometallurgy, 71: 209-215.
43. M. Ajmal, A. K. Rifaqt and B. A. Siddiqui, Environ. Monit. And Ass., 38 (1995) 25.
44. G. Yuan, H. Seyama, M. Soma, B.K. Theng and G. Tanaka, A.J. environ. Sci. and Health Part A, 34 (1999) 625.

45. B.S. Girgis and A.N.A. Hendawy, "Capacity of activated carbon from Date pits in the removal of organic pollutants and heavy metals" In: 1st Inter. Conference on chem. Edu. Cairo, Egypt (1997)
46. Z. Lin and R.W. Puls, Environmental Geology, 39 (2000) 725.
47. M.J. Hall, "Kaolinite sorbent for the removal of heavy metals from incinerated lubricating oils. Project", University of Taxas (1998).
48. R.J. Reeder, Geochimica et Cosmochimica Acta, 60 (1996) 1543.
49. Strong, B. "Coffee removes heavy metals from tap water" http://www.beyond2000.com/news/story-427html (2000).
50. G. Suyama, M. Takazo, M. Palavinal and Z.B. Dessouki, Environ. Science and health Part (A), (1995) 28.
51. Nagwa Nawar, Mohamed Ebrahim, Eslam Sami, Academic Journal of Interdisciplinary Studies Vol 2 No. 6, 2013.
52. Elhadi M. I. Elzain, Abdelrahim A. Ali, *J. Basic. Appl. Sci. Res.*, 3(2)77-81, 2013
53. N. Khalid and S. Ahmad, Sep. Sci. Technol., 33 (1998) 15.
54. P. King, N. Rakesh, S. Beenalahari, Y. Prasanna Kumar and V.S.R.K. Prasad, J Hazard Mater., 142 (2007) 40.
55. Keskikan O et al, "Heavy metal adsorption characteristics of a submerged aquatic plant (Myriophyllum spicatum)". Process Biochemistry, 1-5 (2003).
56. Schneider IAH et al, "Sorption of heavy metal ions by the non-living biomass of freshwater macrophytes" Environ Sci Technol, 33:2213-7 (1999).
57. Wang T.C. et al , "Parameters for removal of toxic heavy metals by water milfoil" Bull Environ Comtam Toxicol, 57:779-786 (1996).
58. Pyrzyriska K, Bystrzejewski M. (2010), comparative study of heavy metal ions sorption onto activated carbon, carbon nanotubes and carbon-encapsulated magnetic nanoparticles, Colloids Surf A 362: 102-109.
59. Luo T, Cui J, Hu S, Huang Y, Jing C (2010) Arsenic removal and recovery from copper smelting wastewater using TiO2. Environ Sci Technol 44: 9094-9098.
60. Gao C, Zhang W, Li H, Lang L, Xu Z (2008) Controllable fabrication of mesoporous MgO with various morphologies and their absorption performance for toxic pollutants in water, Cryst. Growth. Des. 8: 3785-3790
61. Goswami A, Raul PK, Purkait MK (2011) Arsenic adsorption using copper (II) oxide nanoparticles. Chem Eng J (in press).
62. Cao CY, Cui ZM, Chen CQ, Song WG, Cai W (2010) Ceria hollow nanospheres produced by a template-free microwave-assisted hydrothermal method for heavy metal ion removal and catalysis. J Phys chem. 114: 9865-9870.
63. Zhang S, Cheng F, Tao Z, Gao F, Chen J (2006) Removal of nickel ions from wastewater by $Mg(OH)_2$/ MgO nanostructures embedded in Al_2O_3 membranes. J Alloys Compd 426: 281-285.
64. **Yousef NS, Darwish S, Zewail TM and El-Tawail YA** J Chem Eng Process Technol 2013, 4:6