Journal of Scientific Research
Banaras Hindu University, Varanasi

Vol. 60, 2016 : 65-72
ISSN : 0447-9483

ANIMAL WASTES : AN ALTERNATIVE ADSORBENT FOR REMOVAL OF TOXIC HEAVY METALS FROM INDUSTRIAL WASTEWATER

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Abstract

Animal wastes, such as, bones, crab shell, arca shell, egg shell etc. are currently being investigated as potential adsorbents for removal of heavy metals from wastewater. The utilization of low cost adsorbents obtained from animal waste as a replacement for costly conventional methods of removing heavy metal ions from wastewater has been reviewed. The mechanisms of adsorption, influencing factors, competitive ions effect and favourable conditions etc. on the heavy metal adsorption process have also been discussed in present article. From the review, it is evident that certain animal waste materials have shown high metal adsorption capacities from wastewater. However, the capacity of metal adsorption varies depending on the adsorbents characteristics, operating conditions, and the extent of chemical modification of adsorbents. The present review concludes that there are also few issues and drawbacks on the utilization of animal waste as low cost adsorbents that should have to be addressed. Thus to find out the practical utilization of animal waste based adsorbent on the commercial scale, more research should be conducted in this direction.

Key words: Animal waste, wastewater, adsorption, heavy metal, commercial scale.

Introduction

Water pollution by toxic heavy metals through the discharge of wastewater from industrial, agricultural and domestic sectors is a worldwide problem and a major cause of concern for environmental researchers. Rapid industrialization and increased population have seriously contributed to the release of arsenic, cadmium, chromium, lead, copper, nickel, zinc, mercury etc. as toxic heavy metals to the waterstreams. These metals can be distinguished from other toxic pollutants, since they are non-biodegradable and bioaccumulative, therefore becoming concentrated throughout the food chain. Various industries are responsible for the release of heavy metals into the environment in the form of industrial effluents (Braukmann 1990). Battery manufacturing, electroplating, metal processing, mining, paint and pigment manufacturing, petroleum refining, pesticides, printing and photographic industries, tanneries, textiles, etc. (Srivastava et al., 2015) are the main source of heavy metal contamination in the environment. These heavy metals are documented as hazardous causing various diseases and disorders; hence, they must be removed prior to discharge.

The toxicity of these heavy metals can result in reduce or damage mental and central nervous function, damage to lungs, kidneys, liver, blood circulatory systems and other vital organs. The body energy level gets down because of metal toxicity. Also the presence of heavy metals in waterstreams and marine environment causes a significant threat to the health of aquatic community prominently the damage of gill of the fish (Tunali et al., 2006; Corbitt 1999). Table 1 shows various heavy metals and their adverse health effects at higher concentration. Keeping in mind the adverse health effects of these heavy metals, various regulatory bodies have set the maximum prescribed limits as listed in Table 2 for the discharge of toxic metals into the waterbody. However, the metal ions are being added to the water stream at a much higher concentration than the prescribed limits. Metal ions removal from the polluted waterbody in an effective manner has become an important issue today.

Table 1: Heavy metals and their hazardous health effects.

Metals	**Adverse health effects**
Arsenic	Carcinogenic, producing liver tumors, and gastrointestinal effects
Cadmium	Carcinogenic, cause lung fibrosis, dyspnoea
Chromium	Suspected human carcinogen, producing lung tumors
Copper	Long term exposure causes stomach ache, irritation of nose, mouth, eyes, headache
Iron	Excess amounts cause rapid pulse rates, congestion of blood vessels, hypertension
Lead	Suspected carcinogen, anemia, muscle and joint pains, kidney problem and high blood pressure
Manganese	Excess amounts toxic, and causes growth retardation, fever, sexual impotence, muscles fatigue, eye blindness.
Mercury	Excess dose may cause headache, abdominal pain, and diarrhea, paralysis, and gum inflammation, loosening of teeth, loss of appetite, etc.
Nickel	Causes chronic bronchitis, reduced lung function, cancer of lungs
Vanadium	Very toxic, and may cause paralysis
Zinc	Causes short-term illness called “metal fume fever” and restlessness

Table 2: Permissible limits of various toxic heavy metals for potable water.

Metal	Permissible limits for potable water (mg/L)			
	BIS	WHO	USEPA	European Commission
Arsenic (As)	0.05	0.01	0.01	0.01
Cadmium (Cd)	0.01	0.003	0.005	0.005
Chromium (Cr)	0.05	0.05	0.1	0.05

Copper (Cu)	0.05	2.0	1.3	2.0
Iron (Fe)	0.3	0.3	0.3	0.2
Lead (Pb)	0.05	0.01	0.015	0.01
Manganese (Mn)	0.10	0.4	0.05	0.05
Mercury (Hg)	0.001	0.006	0.002	0.001
Molybdenum (Mo)	-	0.07	-	-
Nickel (Ni)	-	0.07	0.1	0.02
Selenium (Se)	0.01	0.01	-	0.01
Silver (Ag)	-	0.1	-	-
Uranium (U)	-	0.015	-	-
Zinc (Zn)	5.0	3.0	5.0	-

The main techniques used to reduce heavy metals from contaminated waterbody include, coagulation, chemical precipitation, solvent extraction, ultra filtration, biological systems, electrolytic processes, reverse osmosis, oxidation with hydrogen peroxide/ozone, membrane filtration, ion exchange and photo catalytic degradation (Ahmaruzzaman, 2011). These conventional treatment methods have been found to be restricted use, due to high capital and operational costs, and may be coupled with the production of secondary waste which further raised treatment problems, such as the large quantity of chemical sludge generation during precipitation processes. Alternatively reverse osmosis, ion exchange and adsorption are more striking processes because the metal values can be recovered along with their removal from the effluents. Reverse osmosis and ion exchange do not seem to be economically feasible because of their relatively high investment and operational cost. On the other hand, adsorption have advantages over the other methods because of simple design with a sludge free environment and can involve low investment in terms of both initial cost and land required, ease of operation, flexibility, simplicity, insensitivity to toxic pollutants and also proper design of the adsorption process will produce a high quality treated effluent (Bradl 2004). These processes provides an attractive alternative for the treatment of contaminated water, especially if the adsorbents are inexpensive and does not required any pre-treatment step before its application. Adsorbents of biological origin have been identified as highly effective materials for the removal of heavy metal-ions from the concentrated and dilute metal contaminated waterstreams (Babel and Kurniawan, 2003; Pollard et al., 1992; Mohan and Singh, 2005).

An overview of some animal wastes as low cost adsorbents is presented in present review and their removal performance is compared. The main goal of this review is to provide a summary of information concerning the use of animal wastes as adsorbents for the removal of various heavy metals from wastewater. A comparison of the adsorption capacity of various animal wastes on the removal of the toxic heavy metals is also presented in this article.

Adsorption by animal waste products

In developing countries, dumping of animal waste products as solid waste in the environment without any processing or composting, or just washing in to the water canals, leads to hazardous health effects on human beings and other living organisms. If these animal wastes are dumped without any planning, the possibility of using these wastes for some beneficial purpose is lost. Some researchers have paid their attention on utilization of these animal waste products as low cost, easily available potential adsorbent for removal of heavy metals from wastewater. Studies have been conducted on animal wastes as potential adsorbent for adsorption of heavy metals. Some of them are animal bones, pretreated fish bones, crab shell, pretreated arca shell, pretreated crab and arca shell, egg shell, *Musca domestica,*etc. Summary of the adsorption study conducted on animal byproducts have been represented in Table 3.

Kizilkaya et al. (2010) utilized pretreated fish bones obtained from bogue (*Boop boops*), gilthead seabream (*Sparus aurata*), bluefish (*Pomatomus saltotrix*), European canchovy (*Engraulis encrasicolus*, *Sordine pilchardus*) as natural, cost effective adsorbent for the adsorption and removal of Cu^{2+} from aqueous solution. Parameters studied were fish species, cleaning process, adsorbent dose, pH, contact time, temperature and initial metal ion concentration. At optimum operating conditions, the maximum adsorption capacity was found to be 150.7 mg/g. Cu^{2+} adsorption data was best fitted to the Langmuir isotherm and followed pseudo-second-order model with endothermic adsorption mechanism. Dried animal bones were investigated to adsorb Zn^{2+} from aqueous solution by Banat et al. (2000). Addition of salt (NaCl) on the adsorption process along with other parameters (particle size, pH, temperature, contact time, initial concentration of the adsorbate) was studied. An increase in the pH, temperature and metal ion concentration results in increased metal ion uptake per unit mass of adsorbent but reverse trend was found with particle size. At 4000 mg/L initial metal ion concentration and 96 h of adsorption time, the uptake of Zn^{2+} ions by bones was 0.1764 mmol/g. Langmuir and Freundlich isotherm models were found to be applicable for the experimental data of Zn^{2+}adsorption on animal bones. Al-Asheh et al. (1999) studied adsorption of Cu^{2+} and Ni^{2+} by spent animal bones. Increased concentration of bones in the suspension results in an increased metal removal from the solution. Adsorption of Cu^{2+} and Ni^{2+} ions increased with increase in metal ion concentration and initial pH of the solution. The experimental data indicates that after 96 h of contact time, and 100 mg/L initial metal concentration the maximum adsorption capacity was 0.325 and 0.123 mmol/g for Cu^{2+} and Ni^{2+}, respectively. Freundlich isotherm model fits the Cu^{2+} and Ni^{2+} experimental data reasonably.

Biosorption potential of crab shell was explored by Vijayaraghavan et al. (2006) for treatment of wastewater contaminated with Cu^{2+} and Co^{2+}. Maximum adsorption capacity of 243.9 and 322.6 mg/g was obtained for Cu^{2+} and Co^{2+}, respectively at optimum particle size of 0.767 mm, initial pH 6, and biosorbent dosage of 5 g/L. Pseudo second order model fitted the data well with very high correlation coefficients (more than 0.998). At different initial metal ion concentration, the kinetic data indicated that biosorption rate was fast and most of the removal was completed within 2 h, followed by slow attainment of equilibrium. Pre-treated arca shell biomass was used by Dahiya et al. (2008 a) for adsorption of heavy metals and radionuclide. In batch experiment, effect of common ions (sodium, potassium, calcium and magnesium), initial metal ion concentration, pH, contact time and biosorbent dosage were studied. At equilibrium, the maximum adsorption of metals by arca shell biomass was 18.33, 17.64, 9.86, 3.93 and 7.82 mg/g for Pb^{2+}, Cu^{2+}, Ni^{2+}, Cs^{2+} and Co^{2+}, respectively. Dahiya et al. (2008 b) also utilized pretreated crab and arca shell biomass for biosorption of Pb^{2+} and Cu^{2+} from aqueous solutions. Crab shell biomass could remove a maximum of 19.83 and 38.62 mg/g Pb^{2+} and Cu^{2+}, respectively at equilibrium, while by arca shell biomass the maximum uptake capacity was 18.33 and 17.64 mg/g for Pb^{2+} and Cu^{2+} ions, respectively. Crab shell biomass has higher uptake capacity for Cu^{2+} than Pb^{2+}. Analysis of biosorption data of Pb^{2+} and Cu^{2+} were best suited to Langmuir adsorption model with high R^2 value (0.985 and 0.979 for Pb^{2+} and Cu^{2+}, respectively) than Freundlich model for both biomasses indicating that the monolayer biosorption was dominant process. Vijayaraghavan et al. (2005) explored crab shell based biosorbent in a packed and up flow column experiment for the treatment of nickel bearing electroplating industrial effluents. Authors have used two types of nickel bearing effluents characterized as effluent -1 (considerable amount of light metals along with trace amount of Pb^{2+} and Cu^{2+}) and effluent- 2 (relatively low conductivity, total dissolved solids and total hardness compared to effluent-1). For effluent-1, maximum uptake was 15.08 mg/g and for effluent-2, it was found to be 20.04 mg/g.

Fly larva shell (*Musca domestica*) has been used by Gyliene et al. (2008) as adsorbent for removal of heavy metal ions. Metal ions and ligands adsorption capacity was dependent on pH, concentration of complexes metal ions and the ligand species in the solution. Complex metal ions adsorption capacity of fly larva shell was up to 0.2-0.4 mmol/g. Experimental results revealed that EDTA (ethylenediamine tetracetic acid) enhances the Cu^{2+} ion adsorption and glycine has the retarding effect on the adsorption of Ni^{2+} and Cu^{2+} ions. Langmuir isotherm model was obeyed by glycine and Ni^{2+}adsorption.

For treatment of wastewater contaminated with Pb^{2+}, Cd^{2+} and Cr^{3+}, Kim (2003) have utilized crab shell biomass as adsorbent. These three ions were used in single, binary and ternary systems. In single metal ion system, equilibrium was about 3 h for Cr^{3+} and Pb^{2+} and 10 hh for Cd^{2+}. Adsorption capacity of 0.49, 0.47 and 0.48 mmol/g was achieved for Cr^{3+}, Pb^{2+} and Cd^{2+}, respectively. Before 10 h, the removal of Cr^{3+} and Pb^{2+} were much higher than Cd^{2+}. While at equilibrium time of 10 h, the removal of Cr^{3+}, Pb^{2+} and Cd^{2+} were in all similar. In binary and ternary systems, one heavy metal has been shown prominent effect on the removal efficiency over other metal ions.

Table 3: Summary of performance of various animal cells used for heavy metal removal.

Adsorbent	Metal ions	Optimum temperature (° C)	pH	Adsorbent dose (g/L)	Initial metal ion concentration (mg/L)	Contact time (h)	Adsorption capacity (mg/g)	Reference
Chicken feathers	Zn^{2+} Cu^{2+}	25	5	5	100	8	0.0978 0.1860	Banat et al. (2002)
Animal horn	Zn^{2+} Cu^{2+}	25	5	5	100	8	0.7843 5.1585	Banat et al. (2002)
Human hair	Zn^{2+} Cu^{2+}	25	5	5	100	8	0.1313 0.0873	Banat et al. (2002)
Engraulis encrasicolus, Sardine pilchardu, Boops boops, Pomatomus saltatrix and *Sparus aurata*	Cu^{2+}	20	4.5	4.9	500	30	150.7	Kizilkaya et al. (2010)
Animal bones	Zn^{2+}	20	5	4	148.23	96	11.53	Banat et al. (2000)
Crab shell	Cu^{2+} Co^{2+}	-	6	5	500	2	243.9 322.6	Vijayaraghavan et al. (2006)
Crab shell	Pb^{2+} Cu^{2+}	25	5.5 3	2.5 5	100	4 2	19.83 38.62	Dahiya et al. (2008)
Arca shell	Pb^{2+} Cu^{2+}	25	5.5 3	5	100	4 2	18.33 17.64	Dahiya et al. (2008)
Crab shell	Ni^{2+}	-	7.91	-	109	-	25.62	Vijayaraghavan et al. (2005)
Fly larva shell	Many metals	-	4	10	10	10-20 min	0.6-0.8 mmol/g	Gyliene et al. (2002)
Animal bone	Cu^{2+} Ni^{2+}	-	5	4	100	96	20.65 7.22	Al-Asheh et al. (1999)

Animal bones	Cu^{2+} Zn^{2+} Ni^{2+}	23	4.5-5	4	-	-	123.92 122.52 10.39	Banat et al. (2002)
Chinocetes-opilio shell	Pb^{2+} Cd^{2+} Cr^{3+}	30	5	1	100	3	99.46 33.72 25.48	Kim (2003)

Conclusion

The role of animal wastesin the removal of heavy metals ions from wastewater of industrial origin has been reviewed. Among various animal wates, animal bones, crab shell, chicken feathers, animal horn and human hair etc. have been identified as a promising raw material for development of adsorbent of biological origin to remove heavy metal ions from wastewater.

The adsorption of heavy metal ions on the adsorbent studied by various researchers could be influenced by a number of operating conditions, such as, initial metal ion concentration, solution pH, contact time, adsorbent dose, temperature and on the ionic strength of the aqueous solution. Generally, removal of metal ions increased with increased adsorbent dose and contact time. However, favourable adsorption conditions may be different for different adsorbents and metal ions. If it is possible to develop such biosorbents from animal wastes, then these adsorbents may offer significant advantages over currently available commercially expensive activated carbons, and in addition contribute to an overall waste minimization strategy. Further more studies are required to apply the design and simulation model to larger scale pilot plant and not on small scale laboratory applications.

Acknowledgement

Authors gratefully acknowledge all necessary facilities provided by the Department of Botany, Banaras Hindu University and Department of Chemical Engineering, Indian Institute of Technology (Banaras Hindu University), India to undertake the work.

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