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Overview of heavy metal ions removal from wastewater by agricultural wastes

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Abstract
Presence of heavy metals in water poses a very serious environmental concern since these metal ions are toxic to human beings. It has been significantly observed that the low-cost agro-based waste material exhibits great potentiality to be used as adsorbents for the removal of toxic metal ions from waste water. This paper presents a review of the available literature using agro-based waste material for the removal of heavy metals, Chromium and Mercury in particular.

Keywords: Wastewater, adsorbents, chromium, mercury

Introduction
Water is a precious resource for mankind. Almost all industrial and commercial activities generate effluent containing one or more heavy metals. Some of these in trace quantities serve as micronutrients for the life processes of living organisms. But most of these beyond their permissible limits are the most dangerous pollutants because of their toxicity and being non-biodegradable [1]. Heavy metals that have an atomic density greater than 5 g cm^{-3} and atomic weights range from 63.5 to 200.6 such as arsenic (As), cadmium (Cd), chromium (Cr), lead (Pb), mercury (Hg) and nickel (Ni), are considered the major pollutants for fresh water reserves because of a direct effect on living creatures [2]. At the same time, they are non-biodegradable unlike organic contaminants and are persistent in the environment. The main sources of heavy metals are the wastewater from modern industrial sources including chemical industries such as mining, metal plating facilities, surface coating, battery manufacturing, electrolysis, tannery, metallurgical, fossil fuel, paper and production of different plastics. Even at a trace level, exposure to heavy metals can cause risk for human beings [3]. Because heavy metals tend to accumulate in living organisms and most of them are carcinogenic and teratogenic.

Chromium metal and its compounds have wide applications in making alloys, chrome plating, leather tanning, batteries, refractories, dyes, paints, welding, catalysis and wood preservatives [4]. However, its removal from industrial wastewater is essential before discharging it into the hydrosphere. The tanning process is one of the major sources of chromium pollution on a global scale. In the chromium tanning process, the leather takes up only 60-80% of the applied chromium, and the rest is usually discharged into the wastewater causing serious environmental impact. Chromium ion in liquid tanning wastes occurs mainly in trivalent form, which gets further oxidized to hexavalent form. Overexposure to a high concentration of chromium can result in epigastric pain, nausea, vomiting, severe diarrhea and haemorrhage [5]. The maximum contaminant level of chromium for the drinking water is 0.05 mg/L

Mercury is one of the most toxic metals found in the environment. The major anthropogenic sources of mercury pollution in aquatic systems include industrial and urban discharges, atmospheric deposition, agricultural materials, mining and combustion [6]. The major industrial culprits of mercury are chlor-alkali plants and thermal power plants. The toxic potency of mercury varies depending on the chemical nature and the route of entry into the human body. Mercuric (divalent) salts are usually more toxic than mercurous(monovalent)salts [7]. Mercury is also known to induce hypersensitivity reactions such as contact dermatitis and acrodynia [8]. Due to its toxic effects, the standard limit of mercury in drinking water is 0.001 mg/g and in industrial wastewater mixed with surface water is 0.01 mg/g [9].

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Consequently, the removal of heavy metal ions from water is of utmost importance. Treatment methods such as chemical precipitation, coagulation, reverse osmosis, ion exchange, and membrane separation have been applied for reducing concentrations from various aqueous solutions. However, most of these methods require either high-energy or large quantities of chemicals. Conventional methods for the removal of heavy metals from wastewater, however, are often cost prohibitive having inadequate efficiencies at low metal concentrations, particularly in the range of 1 – 100 mg/L. Adsorption, on the other hand, is an effective technique for metal ions removal from water. Activated carbons as carbonaceous porous adsorbents are found to be very effective and among the most extensively used methods for the removal of toxic metal ions. For this reason, low-cost adsorbents have been evaluated for the removal of heavy metals from aqueous solutions. Biosorption is a promising technique for the removal of heavy metals from aqueous environments especially when adsorbents are derived from lignocelluloses materials [10]. The search for new technologies to remove toxic metals from wastewater has directed attention to biosorption, which is based on metal binding to various biological materials. Have shown that Lignocelluloses have ion-exchange capacity and general sorptive characteristics, which are derived from their constituent polymers and structure. The polymers include extractives, cellulose, hemicelluloses, pectin, lignin and protein [11]. Agricultural by-products vary greatly in their ability to remove metals from the solution. The ability of biological materials to adsorb metal ions has received considerable attention for the development of an efficient, clean and cheap technology for wastewater treatment at metal concentrations as low as 1 mg/L [12]. In recent years, special attention has been focused on the use of natural sorbents as an alternative to replace conventional adsorbents, based on both environmental and economical points of view [13]. Natural materials that are available in large quantities, or certain waste products from agricultural wastes and operations, may have the potential as inexpensive sorbents. Due to their low cost, when these materials the end of their lifetime, they can be disposed of without expensive regeneration. The abundance and availability of agricultural by-products make them good sources of raw materials for natural sorbents. This paper presents an overview of the adsorbents used for the removal of chromium and mercury from water.

Literature review

Farai Mutongo *et al* 2014 analysed Potato peels for the removal of hexavalent chromium from aqueous effluents. Batch experiments were carried out with an artificial effluent comprising potassium dichromate in deionised water. The effects of the initial hexavalent chromium concentration, dose of biosorbent, and removal kinetics were explored. An adsorbent dosage of 4 g/L was effective in the complete removal of the metal ion, at pH 2.5, in 48 minutes. The kinetic process of Cr(VI) adsorption onto potato peel powder was tested by applying pseudo-first-order and pseudo-second-order models as well as the Elovich kinetic equation to correlate the experimental data and to determine the kinetic parameters. The adsorption data were correlated by the Langmuir and Freundlich isotherms. A maximum monolayer adsorption capacity of 3.28 mg/g was calculated using the Langmuir adsorption isotherm, suggesting a functional group-limited adsorption process [14].

Deepa *et al* 2014 involved the batch biosorption process for the removal of chromium in the aqueous solution using the dried pods of Prosopis spicigera. Factors influencing the biosorption are pH, contact time, adsorbent dose and initial metal ion concentration. The maximum biosorption occurred at pH 3, contact time 120 min, Biosorbent dose 2 g/l and initial metal ion concentration of 200 mg L-1. Kinetic models were also described and fit well in Pseudo second order. The equilibrium data were also analyzed using Langmuir and Freundlich isotherms [15].

Erhan Demirbas *et al* 2004 removed of Cr(VI) from an aqueous solution using low-cost adsorbents such as cornelian cherry, apricot stone and almond shell under different experimental conditions. Adsorption of Cr(VI) is highly pH-dependent and the results indicated that the optimum pH for the removal was found to be 1 for all types of carbon. A comparison of kinetic models applied to the adsorption of Cr(VI) ions on the adsorbents was evaluated for the pseudo-first-order, the pseudo-second-order, Elovich and intraparticle diffusion kinetic models, respectively. Results show that the pseudo-second-order kinetic model was found to correlate with the experimental data well [16].

Dula *et al* 2014 reported on the adsorption of Hexavalent Chromium from aqueous solutions using activated carbon prepared from bamboo (*Oxytenanthera abyssinica*) waste by KOH activation heating in an electrical furnace at 1073 K for 3 hrs. Batch adsorption experiments were also carried out as a function of pH, contact time, initial concentration of the adsorbate, adsorbent dosage, and temperature of the solution. Kinetic studies of the data showed that the adsorption follows the pseudo-second-order kinetic model. Thermodynamic parameters showed that adsorption on the surface of BWAC was feasible, spontaneous in nature, and exothermic between temperatures of 298 and 318 K. Adsorption efficiency and capacity of Hexavalent Chromium were found to be 98.28% at pH 2 and 59.23 mg/g at 300 K [17].

Monika Jain *et al* 2009 investigated the Cr(VI) removal efficiency of sunflower waste from the aqueous system under different process conditions. Two adsorbents were prepared by pre-treating the sunflower stem waste. One adsorbent was prepared by boiling it and the second adsorbent was prepared by treating it with formaldehyde. Batch mode experiments were carried out as a function of solution pH, adsorbent dosage, Cr(VI) concentration and contact time. FT-IR spectra and SEMs of the adsorbents were recorded to explore the number and position of functional groups available for the binding of Cr(VI) ions and the morphology of the studied adsorbents. The removal of chromium was dependent on the physicochemical characteristics of the adsorbent, adsorbate concentration and other studied process parameters. Maximum metal removal was observed at pH 2.0. The efficiencies of boiled sunflower stem absorbent and formaldehyde-treated sunflower stems absorbent for the removal of Cr(VI) were 81.7 and 76.5%, respectively for dilute solutions at 4.0 g/L adsorbent dose. The applicability of Langmuir, Freundlich and Dubinin–Radushkevich isotherms was also tested [18].

Shanmugavalli *et al* 2007 prepared activated carbon from silk cotton hull and investigated the removal of mercury (II) from an aqueous solution by adsorption technique. Batch mode adsorption studies were carried out under varying conditions of agitation time, metal ion concentration, adsorbent dose and pH. Adsorption equilibrium was obtained in 150 min for 10, 20, 30 mg/L of Hg (II) concentration. Adsorption followed Langmuir isotherm. The percent removal increased with an

increase in pH from 2 to 5 and remains static from pH 5 to 10. Desorption studies were performed with a dilute hydrochloric acid solution [19].

Hai *et al* 2013 investigated the activated carbon derived from coconut shells and impregnated with copper chloride solution and the removal of Hg(II) from the aqueous solution was effectively demonstrated. Adsorption of Hg(II) from aqueous solutions was carried out under different experimental conditions by varying solution pH, agitation time, Hg(II) concentration and carbon dosage. It was shown that Hg(II) uptake decreases with increasing pH of the solution and the optimum pH value is 6 and equilibrium time was attained at 60, and 90 min for activated carbon, and copper chloride solution-impregnated activated carbon, respectively. The monolayer adsorption capacity of these particular adsorbents was obtained as 90.9 and 167 mg/g for activated carbon and copper chloride-impregnated activated carbon, respectively. It was determined that Hg(II) adsorption follows both Langmuir and Freundlich isotherms as well as pseudo-first-order kinetics [20].

Madhava Rao *et al* 2009 analysed the removal of mercury from aqueous solutions using activated carbon prepared from Ceiba pentandra hulls, Phaseolus aureus hulls and Cicer arietinum waste was investigated. The influence of various parameters such as the effect of pH, contact time, initial metal ion concentration and adsorbent dose for the removal of mercury was studied using a batch process. The experiments demonstrated that the adsorption process corresponds to the pseudo-second-order-kinetic models and the equilibrium adsorption data fit the Freundlich isotherm model well. The prepared had removal capacities of 25.88 mg/g, 23.66 mg/g and 22.88 mg/g, respectively, at an initial Hg(II) concentration of 40 mg/L [21].

Khoramzadeh *et al* 2013 studied the biosorption of mercury ions from aqueous solutions using Sugarcane Bagasse (SCB). The pre-treatment of the biosorbent was determined by NaOH and HCl. The parameters affecting the biosorption such as solution pH, contact time and temperature were investigated. The pseudo-first-order and pseudo-second-order kinetic models were used to describe the kinetic data. The adsorption equilibrium data were analyzed by Freundlich and Langmuir's isotherm models. According to the results, both models were suitable for describing the biosorption equilibrium. The maximum adsorption capacity was found to be 35.71 mg/g. The kinetic was found to be the best-fit pseudo-second-order equation. The maximum mercury removal of 97.584% at a pH of 4.0 was observed [22].

Shaban W. Al Rmalli *et al* 2008 prepared a new biosorbent produced from castor leaves powder [*Ricinus communis* L.] to remove mercury(II) from aqueous solutions. The initial mercury concentrations, contact time and initial pH were evaluated. The ability of castor leaves to remove mercury at various pH (2-8) was studied. The maximum capacity (Q_{max}) of biomass was found to be 37.2 mg Hg(II)/g at pH 5.5. Biosorption equilibrium was established in approximately 1 h. The equilibrium data were described well by Langmuir and Freundlich's models. The adsorbed mercury on biomass was desorbed using 10 ml of 4 M HCl solution. The biomass could be reused for other biosorption assays. The ability of biomass to adsorb mercury(II) in a column was investigated [23].

Conclusion
Most studies for heavy metal removal focused on the development of cheap and effective adsorbents. Researchers have looked into the availability of waste products especially biomass waste from agriculture to be used as adsorbents. Application on a large industrial scale has to be focussed.

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