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Rice husk as a potential adsorbent for removal of metal ions – A review

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ABSTRACT

In the ever increasing blind race of industrialization and urbanization environmental contamination by toxic heavy metals is becoming a serious issue for both scientists and masses. These heavy metal contaminants directly or indirectly affect the health of animals in general and human beings in particular by their incremental accumulation in the soil, plants and water bodies. Effluents of many industries like chemical manufacturing, paper, textile, refinery, petrochemicals, metal manufacturing, electroplating, printing, dye, paint, leather goods manufacturing, fertilizer and pesticides and many more are loaded with various heavy metals and their ions. These heavy metal ions enter the various food chains and food webs through air, water and soil causing various diseases and disorders. These metal ions are highly toxic even in their relatively low concentrations, are non biodegradable in nature and have tendency of bioaccumulation. In view of their toxicity, removal of these heavy metal ions from industrial effluents has stressed the development and testing of new materials. Most extensively investigated and used such materials include low cost, eco-friendly and abundant waste biomaterials including chitin, chitosans and cellulosics in various forms. Rice is most widely eaten food that fulfils the food needs of half the world's population. Various varieties of rice are cultivated in more than 75 countries in the world. The annual rice husk output on the planet is about 500 million metric tonnes. Many research groups have evaluated unmodified rice husk for removal of toxic heavy metal ions. In order to enhance sorption abilities of rice husk for metal ions, many other groups have used various modifications of rice husk. This review will summarise some latest developments using rice husk and its derivatives for removal of heavy metal ions.

Keywords: Rice husk, Metal ion, Adsorption, Sorption

INTRODUCTION

Contamination of air, water and soil with heavy metal ions is hazardous to plants, animals and microorganism and mankind [1,2]. These toxic metal ions are added to air, soil and water bodies from industrial effluents and mining processes. These toxic metal ions have become a serious health hazard because of their toxicities in relatively low concentration and tendency to bioaccumulation [3,4]. These metal ions are not only non biodegradable, but also they tend to accumulate in living organisms, resulting in deterioration of public health and causing various diseases and disorders [5-9]. The compounds formed by these heavy metals can be toxic, carcinogenic or mutagenic even in low quantities [10]. Even, their traces can bio-accumulate and enter the food chains and food webs. This not only interferes with normal cellular metabolism but also damages nervous system, causes mental retardation and reduces haemoglobin production. Cases of gastric pain, nausea, diarrhoea, vomiting, haemorrhage and even cancer in the digestive tract and lungs have also been reported [11, 12].

In view of toxicities associated with these heavy metal ions, their removal from industrial effluents has become one of the thrust areas in modern research [13]. Many separation methods like chemical precipitation, reverse osmosis, carbon adsorption, sedimentation, lime precipitation, floatation, filtration, electrochemical, biological and membrane processes have been reported to remove metal ions from wastewater. These traditional methods have many disadvantages such as some of them are very slow, generate toxic sludge [14], have poor efficiency, requires continuous input of chemicals and involve high cost [15].

In order to overcome the above mentioned limitations of conventional methods and materials, adsorption, ion exchange and chelation by chelating biopolymers have widely been investigated for removal of heavy metal ions. Major advantages associated with the biopolymers include their low cost, easy availability, reusability, easy separation, higher adsorption capacities, selectivity, ease of operation, and high removal efficiency [3,8, 16-19] Biopolymers form complexes with metal ions using their ligands or functional groups. Many research groups have reported the use of biosorbents from numerous lignocellulosic agro wastes for removal of heavy metals [20-30]. In recent past, the use of biomaterials for removal of toxic heavy metal ions has increased to great extent. Rice husk is the biopolymer that has been recently investigated for removal of toxic metal ions. Rice husk is the by-product of the rice milling industry which is produced in large quantities as a waste. Rice husk mainly consists of 35% cellulose, 25% hemicelluloses, 20% lignin, 17% ash (including silica) and 3% crude protein. This composition is associated with many chelating ligands and functional groups those make it suitable for metallic cations fixation. Rice husk is also used as a fuel in a number of industries to produce steam. The ash produced by burning of rice husk, called rice husk ash (RHA) is collected from the dust collection device attached upstream to the stacks of rice husk-fired boilers and furnaces. Just like rice husk, RHA has also good adsorptive properties and has been reported for the removal of metal ions [31–35] and dye [36]. In this review an attempt has been made to enlist some latest developments in the removal of toxic heavy metal ions by using rice husk and their derivatives.

USE OF RICE HUSK FOR REMOVAL OF HEAVY METAL IONS

Akhtar *et al.* [37] used activated rice husk (RHA) for the removal of Pb(II), Cd(II), Zn(II) and Cu(II) divalent metal ions from aqueous solutions over pH range (1–10) via batch adsorption technique. Rice husk was activated by chemical and thermal activation with 0.1M HNO_3 and 1M K_2CO_3 at 473K. The surface area analysis of RHA by Brunauer, Emmett and Teller (BET) nitrogen adsorption method provided pore area and average pore diameter. Surface morphology of RHA was analysed by SEM and functional groups involved in metal binding mechanism were detected by FTIR studies. The adsorption equilibrium was well described by Freundlich, Langmuir and Dubinin–Radushkevish (D–R) isotherm models at equilibrium time of 20 min at pH 6 and using 0.2 g of sorbent. The kinetics of mass transfer and intra-particle diffusion for metal ions sorption onto RHA were studied with Lagergren and Morris–Weber kinetic models. The numerical values of thermodynamic parameters indicated the exothermic nature, spontaneity and feasibility of the sorption process. The desorption study of metal components from RHA surface was carried out with 0.1MHCl. The sorption mechanism developed illustrates the strong interactions of sorbates with the active sites of the sorbent coupled with efficient and environmentally clean exploitation of rice waste product.

Srivastava *et al.* [38] has reported the competitive adsorptive removal of Cd(II)) and Zn(II)) ions from binary systems using rice husk ash (RHA). The adsorption capacity was studied as a function of pH and optimum pH for the removal of Cd(II) and Zn(II) ions was found to be 6.0. Different adsorption isotherms were studied for equilibrium adsorption. The single ion equilibrium adsorption from the binary solution is better represented by the non-competitive Redlich–Peterson (R–P) and the Freundlich models than by Langmuir model in the initial metal concentration range of 10–100 mg/l. It was observed from the adsorption studies that Zn(II) ions are adsorbed more than Cd(II) ions. These results are in agreement with the single-component adsorption data. It was also observed that the equilibrium metal removal decreases gradually with increase in concentration of the other metal ion and the combined effect of Cd(II) and Zn(II) ions on RHA is generally found to be antagonistic. Non-modified Langmuir, modified Langmuir, extended-Langmuir, extended-Freundlich, Sheindorf–Rebuhn–Sheintuch (SRS), non-modified R–P and modified R–P adsorption models were tested to find the most appropriate competitive adsorption isotherm for the binary adsorption of Cd(II) and Zn(II) ions onto RHA by minimizing the Marquardt's percent standard deviation (MPSD) error function. The extended-Freundlich model satisfactorily represents the adsorption equilibrium data of Cd(II) and Zn(II) ions onto RHA.

A biomatrix prepared from rice husk has been used for biosorption of nine heavy metal ions as a function of pH and metal concentrations in single and mixed solutions by Krishnani *et al*. Raw rice husk was subjected to 1.5% alkali treatment and then autoclaved at 121◦C for 30 min in order to remove the low molecular weight lignin compounds. After filtration, this material was washed with deionized water until the pH reached a constant value close to neutrality. This fraction was then filtered off and dried in oven at 50◦C. The characterized of biomatrix was done by scanning electron microscope and Fourier transform infrared spectroscopy. Different experimental approaches were applied to show mechanistic aspects, especially the role of calcium and magnesium present in the biomatrix in ion exchange mechanism. The increasing order of adsorption capacity obtained from the Langmuir isotherm in mmol/g was: Ni(II) (0.094), Zn(II) (0.124), Cd(II) (0.149), Mn(II) (0.151), Co(II) (0.162), Cu(II) (0.172), Hg(II) (0.18)(II), Pb(II) (0.28) and Cr(III) (1.0) mmol/g. Speciation of chromium, cadmium and mercury loaded on the biomatrix was determined by X-ray photoelectron spectroscopy. The biomatrix has adsorption capacity comparable or greater to other reported sorbents [39].

Removal of Zn(II) and Hg(II) from aqueous solution on a carbonaceous sorbent chemically prepared from rice husk has been reported. Rice husk sorbent was prepared by mixing 20 g of clean air-dried rice husk, 100 ml of 13M sulfuric acid and the mixture was heated to 175–180 °C for 20min with occasional stirring. The resulting black mixture was allowed to cool, and then filtered using a Buchner funnel under vacuum. The sorbent was ground and the size range between two sieves of 16 and 60 mesh were selected for the sorption experiments [40]. Rice husk has been used for the elimination of heavy metals ions Fe(II), Pb(II), Ni(II), Cd(II) and Cu(II) from wastewater of electroplating industries as an actual case study. Results show that this low cost adsorbent can be successfully used for the removal of heavy metal ions with a concentration range of 20–60 mg/l. Extent of removal of heavy metal ions was dependent on the dose of low cost adsorbent and adsorbat concentration [41]. Rice husk was used to adsorb Zn(II) and Pb(II) ions to remove the metals ions in dairy wastewater by batch method. Amount of adsorbent, contact time and pH value of wastewater were the factors influencing Zn(II) and Pb(II) ions sorption. The percent adsorption of Zn(II) and Pb(II) ions increased with an increase in contact time and dosage of rice husk. The binding process was strongly affected by pH and the optimum pH for Zn(II) and Pb(II) ions were 7.0 and 9.0, respectively. The experimental data were analyzed by Langmuir isotherm. The maximum adsorption capacity of the adsorbent for Zn(II) and Pb(II) ions were found to be 19.617 and 0.6216 mg/g, respectively and the maximum percent adsorption of Zn(II) and Pb(II) ions was found to be 70% and 96.8%, respectively [42]. Sikarwar *et al.* [43] has reported the removal of heavy metal ions i.e.Cu(II), Pb(II) and Zn(II) using low cost hybrid precursor prepared from rice husk. Synthesis of hybrid precursor containing silicon and carbon was carried out by refluxing 100 gm of rice husk with 1000 ml solution of sodium hydroxide of different concentrations i.e. 3, 6, 9 and 12 M separately in the presence of 250ml ethylene glycol at 200^0C. Removal capacity of the adsorbent was found to be approximately 90 percent.

Iraqi Rice Husk (IRH) was used for the removal of nine heavy metal ions i.e. Al, As, Cd, Cr, Cu, Fe, Ni, Pb and Zn from industrial wastewater using different design parameters by the adsorption process. Samples of the IRH were taken after being used for the removal of the nine metal ions above from aqueous solutions using different methods. One of these methods was the preparation of a promoted type Y-zeolite catalyst which was compared with normal type Y-zeolite catalyst prepared from IRH alone and tested in the process of n-heptane isomerization under different temperatures. Another method involved the study of IRH as a rodenticide directly without any pre-treatment. It was found that the promoted type Y-zeolite catalysed by Cd^{+2}, Cr^{+6}, Cu^{+2}, Fe^{+3}, Ni^{+2} and Zn^{+2} ions gives a higher conversion and better selectivity of n-heptane isomerization than the normal type Y-zeolite catalyst and the IRH which had previously adsorbed Al^{+3}, As^{+5}, $Zn^{+2}$and Pb^{+2} from an aqueous solution and also showed good behaviour as rodenticidal properties [44]. Singh *el al.* [45] has reported used rice husk carbon activated by H_3PO_4 (40%) for the removal of Cr(VI) by batch mode experiments. Extent of adsorption was studied as a function of adsorbent dose, pH and contact time. The maximum adsorption of chromium (VI) was found to be (93-94%) at low values of pH (around 2) for the carbon dosage of 1000mg/L and nearly 100% for carbon dosage of 1200mg/L.

CONCLUSION

The rice husk has high potential for removal of heavy metals like Cu, Zn, Pb, Cd, Cr, Ni, Mn, Co, Fe, Hg and many more in terms of experimental conditions, high adsorption capacity, binding mechanisms and pretreatment methods. The use of rice husk as potential bioadsorbent for metal remediation and environment management technologies has increased in recent past due to its easy availability, low cost, reusability, high efficiency, easy processing, application and recovery without any adverse impact on the environment. Some more advantages associated with rice husk are its high adsorption even with low metal concentrations no additional nutrients requirements, easy operation, its strong affinity and high selectivity towards heavy metals which is because of the presence of binding groups on its surface. A number of research groups have reported that adsorption capacity of rice husk is equal or even greater as compared to other conventional bioadsorbents. Apart from this its use is eco friendly and innovative and is hence a perfect example of sustainable waste management. Due to these advantages associated with rice husk, it is expected to replace the traditional adsorbents used for decontaminating heavy metals from industrial effluents and waste water in near future. The adsorption of heavy metals from industrial effluents and waste water is influenced by various physical and chemical parameters like pH, temperature, initial heavy metal concentration, amount of adsorbent and adsorbate, particle size of adsorbent etc. These parameters determine the overall adsorption by affecting the selectivity and amount of heavy metals removed.

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