A Review on removal of heavy metal from industrial wastewater by using chemically modified natural adsorbents

Rice husk and Sugarcane bagasse

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Abstract—The study works on the removal of heavy metal by chemically modified natural adsorbents such as rice husk and sugarcane bagasse which gives better results than untreated adsorbents. Numerous chemicals used for modifications which include mineral and organic acids, bases, oxidizing agent, organic compound etc. The purpose of this study is to investigate the effectiveness of adsorbent for removal of heavy metal. Treated rice husk and sugarcane bagasse shows good adsorption capacities for Cu, Pb, Cd, Fe, Co, Ni& Al.

Keywords— Rice Husk, Sugarcane bagasse, Heavy metal, Wastewater treatment

I. INTRODUCTION

The presence of heavy metals in wastewater has become one of the major environmental worries. Heavy metals and metalloids have adverse impacts on human health. Heavy metals are elements having atomic weights between 63.5 and 200.6, and a specific gravity greater than 5.0 (Fu and Wang, 2011). Heavy metals generally refers to the elements such as Cd (cadmium), Cr (chromium), Cu (copper), Hg (mercury), Ni (nickel), Pb (lead), Fe (ferum) and Zn (zinc) which are commonly associated with pollution and toxicity problems. For removal of heavy metals and metalloids many conventional techniques such as chemical precipitation, membrane filtration, ion exchange, carbon adsorption and co-precipitation have been used. But they are not suitable for high concentration of metals and also not cost effective. For increasing the adsorption efficiency of bio adsorbents, treatment of adsorbents is done by using various kinds of treating agents like tartaric acid, NaOH or sodium carbonate and ethylene diamine. The bio adsorbents have Affinity for heavy metal ions to form metal complexes or chelates due to having functional groups including carboxyl, hydroxyl, imidazole, sulphydryl, amino, phosphate, sulfate, thioether, phenol, carbonyl and amide etc. and chemical treatment increases the number of these functional groups. Rice husk (RH) and a sugarcane bagasse is a low cost (agricultural by-product) bioadsorbent which has been studied intensively for the removal of various heavy metals. For decontamination of heavy metals from wastewater treated adsorbent (rice husk or sugarcane bagasse) is comparatively better than untreated one, because untreated adsorbent can further generate the problems such as low adsorption capacity, high chemical oxygen demand, biological oxygen demand, total organic carbon due to release of soluble organic compounds in plant Shrikant Bhosale Assistant professor, Department of technology Shivaji University Kolhapur, India

material. The increase of the COD, BOD and TOC can cause depletion of oxygen content in water and can threaten the aquatic life. Therefore, plant wastes need to be modified or treated before being applied for the decontamination of heavy metals.

- A. Physicochemical characteristics of rice husk
 - Surface area 438.05m2/g
 - Bulk density 0.3086 g/cm3
 - Porosity 0.38 by fraction.
 - Cellulose by weight- 32.24%
 - Hemicellulose by weight -21.34%
 - Lignin by weight -21.44%
 - Mineral ash by weight -15.05%
 - Rice husk is insoluble in water
 - Having good chemical stability
 - Structural strength due to high silica content

B. Physicochemical characteristics of Sugarcane bagasse

- Cellulose -50%
- Polyoses 27% and
- Lignin 23%.

The presence of these three biological polymers causes sugarcane bagasse rich in hydroxyl and phenolic groups and these groups can be modified chemically to produce adsorbent materials with new properties.

C. Chemical treatment on rice husk

To increase the specific surface of rice husk, the rice husk was ground using a disintegrator and after sieving the particle size ≤ 1 mm was retained for further experiment. This rice husk was mixed with acid or base solution (1 M of H₃PO₄ /NaOH/ Tartaric acid) at room temperature for 24 h in 500 mL with a stirring speed of 150 rpm so that the reagents were fully adsorbed onto the raw material. After this treatment, the modified rice husk was filtered and washed with distilled water

for several times until the pH reached a constant value. Later on, this adsorbent was oven-dried at 110°C for 4 h. Then the treated rice husk was obtained.

D. Chemical treatment on Sugarcane bagasse

Sugarcane bagasse was dried at 100 C in an oven for approximately 24 h and next fiber size was reduced to powder by milling with tungsten ring. The resulting material was sieved with a 4-sieve system (10, 30, 45, and 60 mesh). Then, the material was washed with distilled water under stirring at 65° C for 1 h and dried at 100 °C. Finally, it was washed a new in a sohxlet system with n-hexane/ ethanol (1:1) as solvent for 4 h.

II. MODIFICATION OF RICE HUSKS ADSORBENT

Rice husk can be used to treat Cd in the form of either untreated or modified using different methods. Hydrochloric acid, sodium hydroxide (NAOH), sodium carbonate (Na₂CO₃), epichlorohydrin (C3H5ClO), and tartaric acid are commonly used in the chemical treatment of rice husk. Pretreatment of rice husks can remove lignin, hemicelluloses, reduce cellulose crystalline and increase the porosity or surface area. In general, chemically modified or treated rice husk exhibited higher Cd adsorption capacities than unmodified rice husk. For example, Kumar and Bandyopadhyay (2006) reported that rice husk treated with sodium hydroxide, sodium carbonate and epichlorohydrin enhanced the adsorption capacity of cadmium. Most of the acids used for treatment of agricultural wastes were in dilute form such as sulfuric acid, hydrochloric acid and nitric acid. When rice husk is treated with hydrochloric acid, adsorption sites on the surface of rice husk will be protonated, leaving the heavy metal ions in the aqueous phase rather than being adsorbed on the adsorbent surface.

Ying Zhang et al. reported that Rice husk, a surplus agricultural byproduct, was applied to the sorption of copper from aqueous solutions. Chemical modifications by treating rice husk with H_3PO_4 increased the sorption ability of rice husk for Cu (II). This work investigated the sorption characteristics for Cu (II) and examined the optimum conditions of the sorption processes.

Tarley et al. (2004) found that adsorption of Cd increase by almost double when rice husk was treated with NaOH. The reported adsorption capacities of Cd were 7 and 4 mg g_1 for NaOH treated and unmodified rice husk, respectively.

Wong et al. (2003a) carried out an adsorption study of copper and lead on modified rice Husk by various kinds of carboxylic acids (citric acid, salicylic acid, tartaric acid, oxalic acid, mandelic acid, malic and nitrilotriacetic acid) and it was reported that the highest adsorption capacity was achieved by tartaric acid modified rice husk. Esterified tartaric acid modified rice husk however significantly reduced the uptake of Cu and Pb.

III. MODIFICATION OF SUGARCANE BAGASSE

Adsorbent Junior et al., (2006) reported the use of succinic anhydride modified sugarcane bagasse for treatment of Cd from aqueous solutions It was found that sugarcane bagasse treated with ethylene diamine and triethylene tetramine shows a remarkable increase in nitrogen content compared to untreated sample, and triethylene tetramine modified sugarcane bagasse has a higher increasing extent.

The performance of hydrogen peroxide treated bagasse fly ash, a solid waste of sugar industry for removal of lead and chromium was explored by Gupta and Ali (2004). Hydrogen peroxide is a good oxidizing agent and used to remove the adhering organic matter on the adsorbent. It was found that hydrogen peroxide treated bagasse fly ash was able to remove chromium in a shorter period of time (60 min) compared to lead (80 min).

Handojo Djati Utomo1et al. reported that Methylene Blue (MB) has been found to be one of the most common dyes used in the industries. Adsorption process using Activated Carbon (AC) has been proven to be able to remove MB effectively but the treatment cost using the adsorbent is considered expensive due to its high energy cost. Sugarcane Bagasse (SGB) is an agricultural by-product and abundantly available material in many developing countries. FTIR and XRD were used to confirm the existence of ligno-cellulose content of SGB after experiencing various chemical treatments.SGB showed a much better performance in adsorbing MB in alkaline environment than in acidic environment.

Sr. No.	Adsorbents	Modifying agents	Heavy Metal	Qmax (mg/g)	Source
2	-	Epichlorohydrin	Cd, Cr	11.12	(2006)
3	-	Sodium carbonate	Pb, Zn	16.18	
4		Sodium hydroxide	Cd	20.24	
5		Tartaric acid	Cu	31.85	
6			Pb	120.48	
7	Sugarcane bagasse	Sodium bicarbonate	Cd	189	Junior et al.(2006)
8			Pb	196	
9			Cu	114	
10	1	Ethylendiamine	Cd	189	

 TABLE I.
 THE AGRICULTURAL WASTE AND THEIR MAXIMUM ADSORPTION CAPACITIES

11		Cu	164	
12		Рb	139	
13	Triethylene tetramine	Cd	313	
14		Pb	313	
15		Cu	133	

CONCLUSION

Pollution control board has very strict rules for the effluents which are leaving in the industries, some of the constituents of these effluents are the harmful. They cause effect on human beings and leaving organisms. Also effluent causes poisoning of agro lands and natural water sources like river, ponds etc. This project serves better for heavy metal removal, because Rice husk and sugarcane bagasse are easily available & they can reduce the expensive uses chemical, machineries for removal of heavy metal from industrial waste. Sugarcane bagasse may be used where % zinc removal is less. Modified sugarcane bagasse presented a good adsorption capacity for copper, cadmium & lead. Modified rice husk shows better results for Cd, Cr, Zn, & Pb.

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