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Removal of heavy metals from wastewater using modified agricultural adsorbents

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Abstract

Agricultural waste has been investigated as an efficient adsorbent for heavy metal removal because of their low cost. The functional groups present in agricultural wastes such as carbonyl, phenolic, acetamido, alcoholic, amido, amino and sulphydryl group etc. have an affinity for heavy metal ions to form metal complexes or chelates. The removal of heavy metal ions from wastewater using agricultural waste is based upon metal biosorption. The mechanism of biosorption includes chemisorption, complexation, adsorption on the surface, diffusion through pores and ion exchange etc. These heavy metal ions cause life-threatening problems for the humans and aquatic ecosystem. Certain modifications in these adsorbents enhance the adsorption capacity of these adsorbents. Some chemicals such as mineral and organic acids, bases, oxidising agent are used for modification of adsorbents. The purpose of this article is to compare removal efficiency of different adsorbents.

Keywords: Adsorbent; Agricultural waste; Heavy metals; Modified adsorbents

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1. Introduction

The source of heavy metals in wastewater are metal plating industry, mining operations, fertilizer industries, tanneries, batteries, paper industry, petroleum refining, electroplating, metallurgy, textiles, manufacturing of dye and pesticide, etc. Because of the development of these industries heavy metals are directly or indirectly discharged into the environment especially in developing countries. The heavy metals which mainly discharge from industries are chromium (Cr), cadmium (Cd), iron (Fe), nickel (Ni), selenium (Se), vanadium (V), copper (Cu), cobalt (Co), mercury (Hg), lead (Pb), zinc (Zn) and arsenic (As). Conventional treatment technologies for removal of heavy metals are chemical precipitation, ion exchange, oxidation, reduction, reverse osmosis, electrodialysis and ultrafiltration. However, they have their inherent limitations such as they generate a large amount of sludge, less efficiency, sensitive operating conditions and costly disposal. Thus, adsorption method is the relatively new process that is emerging as a potential alternative for the removal of heavy metals. Chromium is one of the toxic heavy metal in wastewater and it exists in two stable oxidation states such as Cr (III) and Cr (VI). The presence of cadmium even at lower concentration is very harmful. Cadmium can cause renal degradation, muscular cramps, testicular atrophy and skeletal deformity. The world health organisation has set a maximum limit of .003 mg/l in wastewater for cadmium [5]. Cadmium comes from natural sources, anthropogenic sources, mining, industrial processes and domestic residues. Iron is one of the most abundant metals in the Earth's crust. It occurs naturally in water in soluble form. Iron enters in water by many industries such as mining, iron and steel industry, metals corrosion, etc. Iron in drinking water supplies causes problems such as giving reddish color and odor [2]. Its main issues involve taste, visual effects, and clogging. Nickel and its compounds are odourless and have no taste. Nickel can cause cancer and insomnia that is lost of ability to smell [1]. As nickel exceeds in its critical level, it might bring serious lung and kidney problems aside from pulmonary fibrosis and skin dermatitis [3].Selenium (Se) is an interesting element due to its necessity for human health and high toxicity at high concentrations. However selenium is present in Earth's crust at low levels, and it is introduced into the environment by natural and anthropogenic sources [6,8]. Excessive selenium can cause irritation of skin and eyes, neurological damage and monstrous deformities, liver cirrhosis, pulmonary edema and death [7]. Also, it is classified as mutagenic and teratogenic due to the toxicity [8]. Similarly other heavy metals vanadium, copper, cobalt, mercury and lead cause hazardous health problems.

2. Experimental study

2.1. Materials and methods

In the present work, the stock solution containing 1000 mg/l of Cr (VI) was prepared by dissolving 2.835 g of $K_2Cr_2O_7$ in 1000 mL of deionized, double distilled water and different adsorbents were used such as activated carbon, egg shell, calcined egg shell, alumina balls, wheat bran, modified wheat bran and their removal efficiency for chromium were compared. The absorbance was measured by using UV-Spectrophotometer by the formation of complex with 1, 5 diphenylcarbazide, acetone and 5,7 dibromo-8-hydroxyquinoline at a maximum wavelength of 540 nm that forms a red-violet colored complex (Gilcreas et al., 1965). The absorbance of the colored complex was measured using UV–VIS spectrophotometer.

2.2 Preparation of adsorbents

Egg shell powder, calcined egg shell: The egg shells were collected from the bakery shop. Then these egg shells were thoroughly washed with tap water and rinsed several times in DI water and membranes were removed. Washed egg shells were dried in an oven for 12 hrs at 70°C. Finally egg shells were crushed into fine powder. Further, Calcined egg shells were prepared by calcinating egg shell at 700°C in muffle furnace.

Wheat bran and modified wheat bran: Wheat bran was collected from flour mills. Then it was washed several times with tap water and with DI water. Then it is dried at 70°C for 1 hr and crushed with a grinder. Further modified wheat bran was prepared by treating it with hydrochloric acid to improve its adsorption capacity for heavy metal removal.

3. Results and Discussion

3.1 Characterisation of Adsorbents

X-Ray diffraction analysis

The X-Ray diffraction pattern of prepared adsorbents has shown in fig 1. In XRD pattern of natural and calcined egg shell the main peak appeared at 2θ = 29.6. In addition, this spectrum shows several peaks at 2θ = 23.26, 39.61, 47.29 and 47.73. In XRD pattern of wheat bran there are lesser no. of sharp peak and smaller peak height which indicates an amorphous structure of wheat bran and XRD pattern of hydrochloric acid treated wheat bran shows that it become more amorphous after treating with hydrochloric acid.

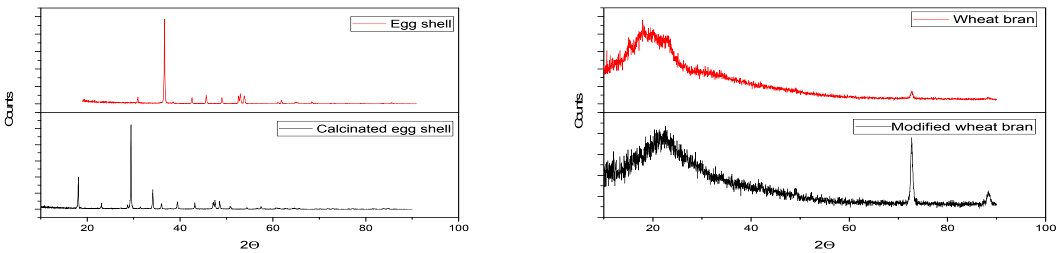

Fig.1. XRD pattern of (a) Natural egg shell/ Calcinated egg shell (b) Wheat bran/ Modified wheat bran

FTIR analysis

Fig.2. Shows FTIR spectra of natural egg shell, calcined egg shell, wheat bran and chemically modified wheat bran. In natural egg shell, Broad transmission band at around 2863 cm^{-1} can be attributed to OH stretching vibration of the waste of residual and the weak band at 2920 cm^{-1} is attributed to C=O bonds from carbonate. Infrared bands at 1426 cm^{-1} and 875 cm^{-1} show the C – O stretching and bending of $CaCO_3$, meanwhile the sharp band at 712 cm^{-1} represents a Ca – O bond. While after calcinations, calcined eggshell shows the

existence of OH in Ca $(OH)_2$ in the peak of around 3643 cm^{-1} and 2513 cm^{-1}. It was formed during adsorption of water by CaO. Another band existence at 430 cm^{-1} is due to Ca – O band. The functional group of 1796 cm^{-1} , 1425 cm^{-1} , 1083 cm^{-1}, 712 cm^{-1}, 675 and 545 cm^{-1} represent the stretching vibration of the CO_3^{2-} group present in the eggshell. Here Infrared results show that $CaCO_3$ had completely converted to CaO because of Ca – O bond in the calcined eggshell. Fig 2(b) shows FTIR spectra of raw wheat bran and chemically modified wheat bran. The FTIR spectra show some functional groups such as carboxyl, hydroxyl etc. O-H, C-H, COOH, C=O, C=C, CH_2 and C-O-C are various functional groups present in the raw and chemically modified wheat bran.

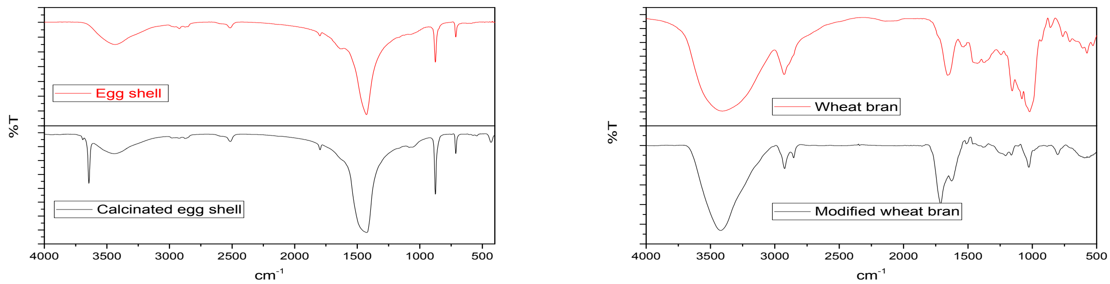

Fig.2. FTIR pattern of (a) Natural egg shell/ Calcinated egg shell (b) Wheat bran/ Modified wheat bran

3.2 Batch Adsorption of Chromium using various adsorbents

Batch adsorption study was carried out using synthesized adsorbents at constant operating conditions and results obtained were reported in Table-1. The table 1 shows that wheat bran after modification gives maximum removal efficiency compared to other adsorbents.

Table-1 Percent removal of chromium using different adsorbents

Chromium Removal efficiency of various adsorbents, operating conditions: Initial metal concentration 10 mg/l; rpm-180; Temperature-35°C.					
	Contact time				
Adsorbent	**1 hr**	**2 hr**	**3 hr**	**4 hr**	**5 hr**
Activated Carbon	97.80%	97.93%	98.27%	98.64%	98.75%
Activated alumina balls	58.60%	58.86%	59.03%	59.33%	60.60%
Egg shell	59.46%	60%	60.43%	61.2%	64%
Calcined egg shell	60.83%	62.95%	65.80%	66.74%	70.19%
Wheat bran	65.20%	66.66%	74.64%	75.61%	75.89%
Modified wheat bran	90.46%	92.98%	94.19%	96.37%	96.96%

Conclusions

Different type of adsorbents has been used for removal of heavy metal from wastewater. In this respect, agricultural wastes are economical for removal of heavy metal because of their low cost, easy availability, renewability and high affinity for heavy metals. Different types of adsorbents have been tried for chromium removal in the laboratory.

Thus in our work, it was observed that percent removal capacity is higher for activated carbon and chemically modified wheat bran. After modification removal capacity of wheat bran reaches nearly up to activated carbon. The heavy metal removal by using agricultural wastes requires further investigation in the direction of modelling, adsorbent regeneration and metal ion recovery.

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