Asian Journal of Chemistry; Vol. 31, No. 5 (2019), 1009-1012

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2019.21783

Adsorption of Heavy Metals Using Mixture of Waste Products

SHALINI and PRATIBHA NAITHANI*

Department of Environmental Sciences, Graphic Era University (Deemed to be University), Dehradun-248002, India

*Corresponding author: E-mail: pnaith1@gmail.com

Received: 29 October 2018; *Accepted*: 29 November 2018; *Published online*: 28 March 2019; AJC-19321

A new adsorbent for removing lead, nickel, chromium and arsenic ions from industrial wastewaters has been investigated. This new adsorbent consists of four waste products tea waste, rice husk, sugarcane bagasse and peanut shell. The adsorbent was prepared without any physical and chemical treatment. Batch experiments were conducted to assess the removal of selected metal ions from wastewaters. The results have shown that the mixture of four waste products presented an excellent adsorption of heavy metal ions. The equilibrium time was dependent on type of adsorbent and sample. The highest percentage of metal ion removal was 100 %. The results showed pseudo second order kinetics. The surface chemical nature of prepared adsorbent was studied by Fourier transform infrared spectroscopy. The functional group present in adsorbent has affinity towards heavy metal ions to form metal complexes. The surface morphology of prepared adsorbent was confirmed by scanning electron microscopy and chemical composition was analyzed by energy dispersive X-ray spectroscopy.

Keywords: Heavy metals removal, Batch method, Adsorption mechanism, SEM, EDX, FTIR.

INTRODUCTION

Toxic heavy metals get introduced to the aquatic streams by means of various industrial activities *viz.* mining, refining ores, fertilizer industries, tanneries, batteries, paper industries, pesticides, *etc.* and possess a serious threat to the environment and human health [1-4]. The major toxic heavy metal ions dangerous to humans as well as other forms of life are Cr, Fe, Se, V, Cu, Co, Ni, Cd, Hg, As, Pb and Zn, *etc*. Disasters due to the contamination of heavy metals in aquatic streams were resulted in Minamata tragedy in Japan due to methyl mercury (CH_3Hg) contamination and ''Itai-Itai'' was a consequence of contamination of Cd in Jintsuriver of Japan [5]. When metal ions are being added to the water stream by various activities at much higher concentration than the prescribed limits, it badly effect health of living organisms and also cause environmental degradation.

Recently attention is being paid towards utilization of biomaterials which are byproducts or the wastes from largescale industrial operations and agricultural waste materials such as rice husk, bagasse fly ash, coconut shell fibers, neem leaf powder, raw rice bran, rice polish, wheat bran, bagasse, tea waste, mustard oil cake and powder of green coconut shell *etc.* The major advantages of biosorption treatment method include: low cost, high efficiency, minimization of chemical, minimization of sludge and no need for additional nutrient. Agricultural waste materials, particularly those containing cellulose show potential heavy metal adsorption capacity and the basic components of the agricultural waste materials include hemicellulose, lignin, extractives, lipids, proteins, simple sugars, water hydrocarbons, starch containing variety of functional groups that facilitate metal complexation which helps in adsorption of heavy metals [6-8].

This study is based on peanut shell, sugarcane bagasse, rice husk and tea waste. The average length of the peanut shell fibers was found to be 0.25 to 38 mm diameter, the average tenacity of peanut shell fiber is of 1.06 g/den, average strain of the fibers was 7.45 % and average modulus 25.3 g/den. Peanut shell contains cellulose, lignin, hemicelluloses and luteolin. soda, potassium oxide, magnesium oxide, calcium oxide and phosphorous oxide [9]. Rice husk is the byproduct of rice, a major food material of most of the developing countries. This agricultural waste material is available in plenty in rice producing countries. India, Pakistan, Bangladesh, Sri Lanka, Australia, Thailand, Indonesia and USA are some rice producing countries. Sugarcane is largely grown in Brazil, Cuba, Australia, South Africa, Peru, Mexico and India, it is a tall grass with big stems [10]. Bagasse from sugarcane consists of cellulose, hemicelluloses, lignin, ash and some other components. A large quantity of tea waste is discarded into the environment. Tea waste is gaining much attention by researchers because it is an excellent adsorbent in removing heavy metals like As, Cr, Pb and Ni [11].

In this article the efficiency of four mixed adsorbent peanut shell, sugarcane bagasse, rice husk and tea waste has been reported for the removal of toxic heavy metals As, Pb, Cr and Ni present in industrial wastewater.

EXPERIMENTAL

Adsorbent preparation, analysis of sample and adsorbent: The industrial wastewater samples were collected from SIDCUL, Haridwar. All adsorbent (peanut shell, tea waste, rice husk and sugarcane bagasse) were washed with water and then rinsed with distilled water. They were oven dried at 100 °C, powdered to 600 μm particle size and then stored in polythene bags. All adsorbents were weighed equally to form the adsorbent mixture used in this study.

All samples were prepared and analyzed according to the guidelines of American Public Health Association (1995). The heavy metals Pb, Cr, As and Ni were analyzed by inductively coupled plasma mass spectrometry (Perkin-Elmer SCIEX-ELAN DRC-e). The surface morphology of mixture of adsorbent was analyzed by SEM (Make Zeiss EVO 40 EP), chemical composition was determined by EDX (Bruker LN2 Free effect of X- Flash 4010 SD detector) and FTIR (Perkin Elmer model) was used for the study of functional groups present in the mixture.

Batch adsorption experiments: Batch experiments were carried out to assess the heavy metal removal ability of the waste products. Experiments were conducted for 5, 15, 25, 35, 45, 60, 180 and 240 min. In batch adsorption experiments, 1.5 g of each product (peanut shell, sugarcane bagasse, rice husk and tea waste) was transferred into 250 mL plastic bottles and then 100 mL of industrial wastewater was added. Samples were filtered and the final concentration of lead, nickel, chromium and arsenic in the filtrate was determined by ICPMS.

RESULTS AND DISCUSSION

From the batch extraction of wastewater samples A and B, the trend of removal of Pb, Ni, Cr and As with time was analyzed (Figs. 1 and 2). Hundred percent of lead removal was observed in sample B within 5 min of batch extraction whereas highest lead removal for sample A was obtained after 60 min of treatment. Similar trend was observed for nickel removal, it was 100 % for sample B in 5 min and 90 % removal in 45 min for sample A. Concentration of chromium was very high in samples A and B and maximum adsorption (90 %) occurred after 5 min of treatment for both samples. Arsenic was completely removed within 5 min of extraction for sample A but only 86 % has been removed for sample B after 15 min of treatment.

Kinetics study was conducted as it provides information about the mechanism of adsorption. The results have shown that the adsorption system followed a pseudo second-order kinetic model which can be expressed as:

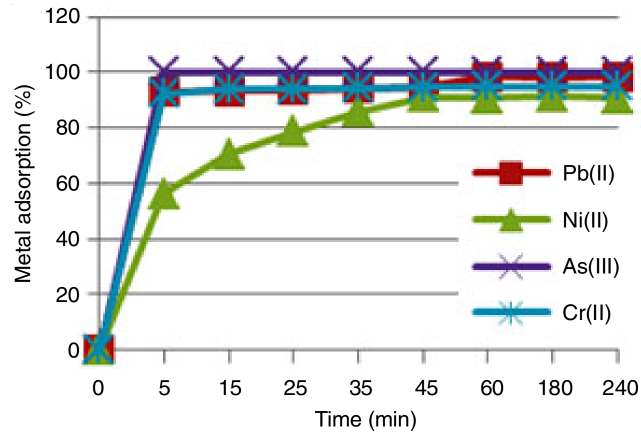

Fig. 1. Removal of Pb, Ni, Cr and As in sample A

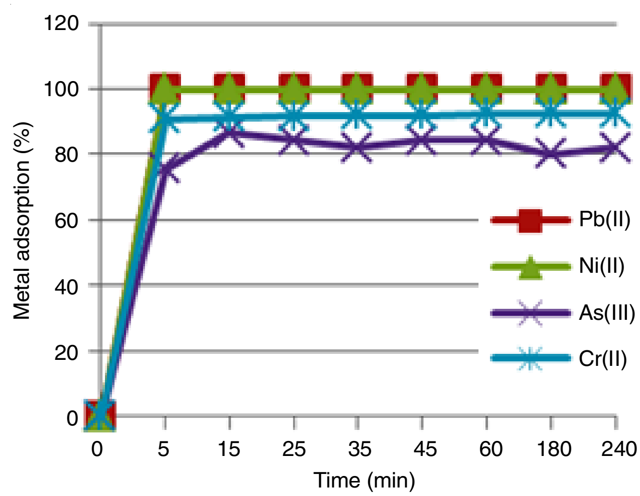

Fig. 2. Removal of Pb, Ni, Cr and As in sample B

$$\frac{t}{q_t} = \frac{1}{k_{ps}q_e^2} + \frac{t}{q_e}$$

where k_{ps} is the adsorption rate constant. The correlation coefficients for the second-order kinetics model (R^2) are greater than 0.99 (Fig. 3), indicating the applicability of this kinetics equation and the second order nature of adsorption process of metals onto mixture used as adsorbent.

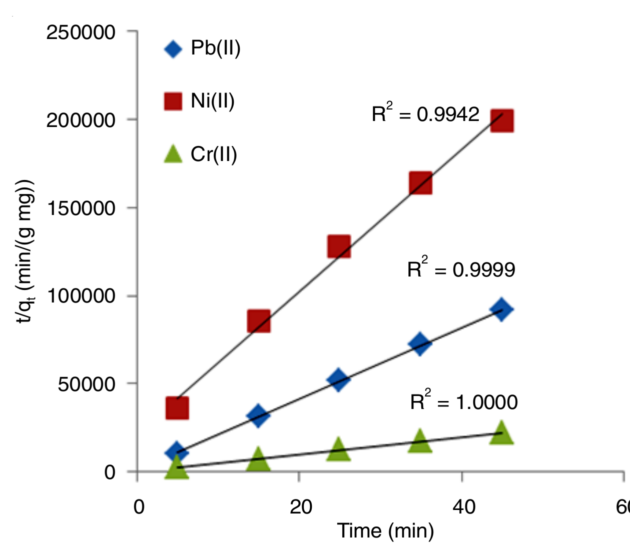

Fig. 3. Pseudo second order adsorption kinetics

The adsorption process involves interaction between the solid and liquid which contains the dissolved species to be adsorbed. Agricultural by-products or waste material generally are composed of lignin and cellulose as key constituents. They may also include other polar functional groups such as aldehydes, alcohols, carboxylic, ketones, phenolic and ether groups. These groups have the capacity to bind heavy metals by the donation of an electron pair from these groups to form complexes with the heavy metal ions in solution [12]. The chemical composition of rice husk, peanut shell, sugarcane bagasse and tea waste are shown in Table-1.

The FTIR spectra of adsorbent before treatment indicated that the adsorbent contains alcohol, alkene and ether groups. Peak observed at 1644.8 cm^{-1} is the stretching C=O bond due to non-ionic carboxyl groups (–COOH, $–COOCH_3$) and has shifted to 1632.5 after adsorption for sample A and 1625 cm^{-1} for sample B. This showed that carboxyl group might be uptaking Pb, Ni, As and Cr from the solution. Before the adsorption a main peak was obtained at 1058.6 cm^{-1} and after the adsorption it was shifted to 1034.6 cm^{-1} and 1036.8 for samples A and B, respectively. This was indicative of C-O-C stretching of the ether functional group.

SEM images of a mixture of adsorbent indicated the presence of grains in the structure (Fig. 4) whereas after adsorption presence of grains and irregular surface were very less in the structure of adsorbent (Fig. 5). The morphology of this mixture of adsorbent has favoured adsorption of heavy metals due to the irregular surface structure. From the SEM image it can be concluded that this adsorbent material presents a capable structural profile to adsorb heavy metals. The irregular cavities were present on the surface of mixture of adsorbent, which show the possibility of binding sites and after the treatment irregular cavites were very less. Less grains and fewer irregular surface proves that adsorption of heavy metals is taking place on the surface of adsorbent.

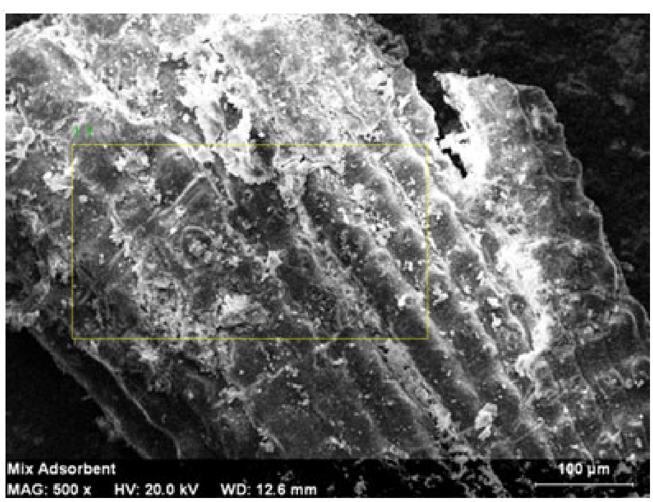

Fig. 4. SEM image of adsorbent before treatment

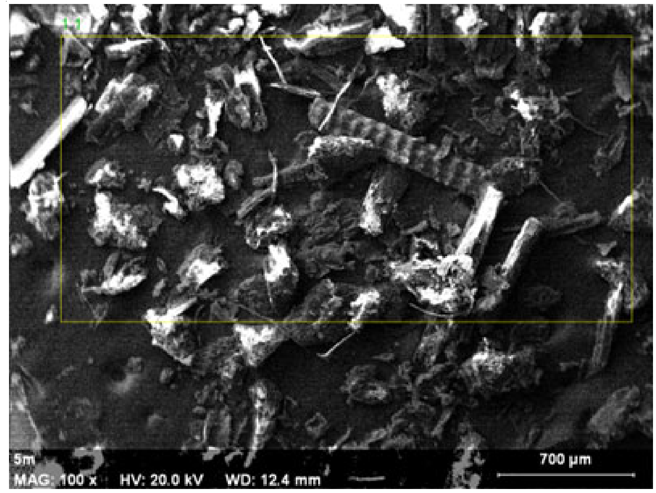

Fig. 5. SEM image of adsorbent after treatment

The qualitative EDX spectra for dried mixture of adsorbent (Fig. 6) indicated that oxygen, carbon and silicon are the main elements. These have been known as the main constituents of rice husk, peanut shell, bagasse and tea waste (mixture of adsorbent). After the adsorption (Fig. 7) EDX spectra indicate oxygen, carbon, silicon and calcium are the major elements of adsorbent as well as heavy metals were also seen in the

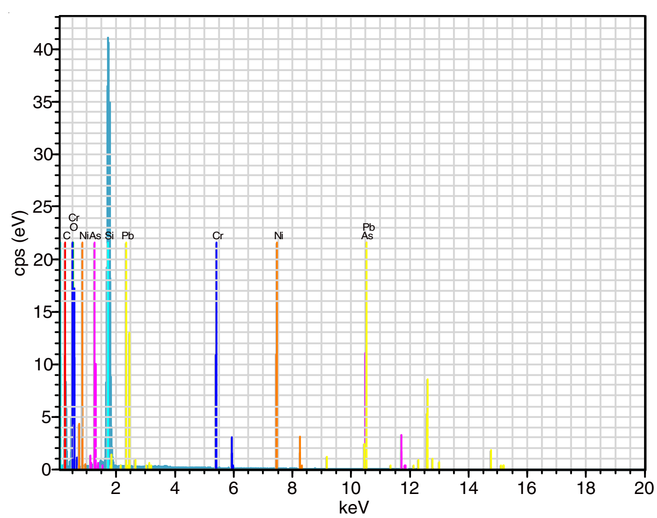

Fig. 6. EDX spectra before adsorption

TABLE-1
CHEMICAL COMPOSITION OF RICE HUSK, PEANUT SHELL, SUGARCANE BAGASSE AND TEA WASTE

Mass (%)	Peanut shell [Ref. 13]	Rice husk [Ref. 14]	Sugarcane bagasse [Ref. 15]	Tea waste [Ref. 16]
Cellulose	46.5	28.6	45.4 ± 0.8	29.42 ± 0.57
Alpha cellulose	–	–	–	26.53 ± 0.58
Holocellulose	9.7	28.6	–	60.81 ± 1.14
Hemicellulose	–	–	28.7 ± 0.7	
Lignin	41.3	24.4	23.4 ± 0.2	36.94 ± 0.34
Ashes	–	–	2.7 ± 0.1	4.53 ± 0.10
Extractive matter	–	18.4	–	–

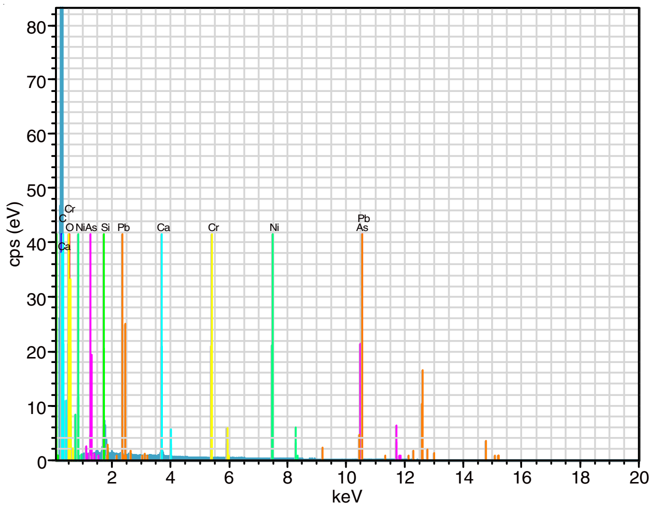

Fig. 7. EDX spectra after adsorption of heavy metals from sample A

spectra. EDX spectra suggest that the Pb, As, Cr and Ni were adsorbed on the surface of the adsorbent.

Conclusion

The results have shown that the mixture of adsorbent can be used as an adsorbent for the effective removal of heavy metal ions from industrial wastewater samples. Nearly complete removal of Ni and Pb was observed for sample B whereas 90 % of Cr was removed from both the samples. Arsenic removal was 100 and 86 % for samples A and B, respectively. Pseudo second order kinetics was obtained for both the samples with R^2 value greater than 0.99. The mixture of adsorbent was characterized by determining different parameters such as SEM-EDX and FTIR. FTIR studies have also shown carboxyl, hydroxyl and alkene groups are present in the adsorbent that helps in adsorption of heavy metals. SEM image and EDX spectra has confirmed that the mixture is adsorbing Pb, As, Cr and Ni from the industrial wastewater. It can be concluded that adsorbent made by mixing tea waste, rice husk, bagasse and peanut shell has helped in removing Pb, As, Cr and Ni from the industrial wastewater.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. A. Celik and A. Demirbas, *Energy Sources*, **27**, 1167 (2005); https://doi.org/10.1080/00908310490479583.
2. M.S. Masri and M. Friedman, *Environ. Sci. Technol.*, **6**, 745 (1972); https://doi.org/10.1021/es60067a010.
3. T. Kjellstrom, Doctoral Thesis, Department of Environmental Hygiene, Karolinska Institute, Stockholm: Sweden (1977).
4. K. Pastircakova, *Energy Education Sci. Technol.*, **13**, 97 (2004).
5. L. Friberg, C.G.T. Elinder, T. Kjellstrom and G.F. Nordberg, Cadmium and Health: A Toxicological and Epidemiological Appraisal: Effects and Response, vol. 2, CRC Press: Cleveland (1986).
6. A. Hashem, E.S. Abdel-Halim, K.F. El-Tahlawy and A. Hebeish, *Adsorpt. Sci. Technol.*, **23**, 367 (2005a); https://doi.org/10.1260/026361705774355478.
7. A. Hashem, H.H. Sokker, E.S.A. Halim and A. Gamal, *Adsorpt. Sci. Technol.*, **23**, 455 (2005b); https://doi.org/10.1260/026361705774859901.
8. A. Hashem, E.S. Abdel-Halim and H.H. Sokker, *Polym. Plast. Technol. Eng.*, **46**, 71 (2007); https://doi.org/10.1080/03602550600950364.
9. E.D. Zanotto, ed. E.D. Guire, Crystals in Glass: A Hidden Beauty, Wiley (2013).
10. T.C.C. Rípoli, F.M. Walter Jr. and M.L.C. Rípoli, *Sci. Agric.*, **57**, 677 (2000); https://doi.org/10.1590/S0103-90162000000400013.
11. G. Dhania M. Nandal and R. Hooda, *Int. J. Curr. Eng. Technol.*, **4**, 243 (2014).
12. F. Pagnanelli, S. Mainelli, F. Veglio and L. Toro, *Chem. Eng. Sci.*, **58**, 4709 (2003); https://doi.org/10.1016/j.ces.2003.08.001.
13. Z.F. Fang, K.L. Liu, F.S. Chen, L.F. Zhang and Z. Guo, *BioResources*, **9**, 1290 (2014).
14. C. Di Blasi, G. Signorelli, C. Di Russo and G. Rea, *Ind. Eng. Chem. Res.*, **38**, 2216 (1999); https://doi.org/10.1021/ie980711u.
15. H.F.P. Paulo, C.J.V. Herman and H.C. Mariaodila, *BioResources*, **6**, 2471 (2011).
16. A. Tutus, Y. Kazaskeroglu and M. Çiçekler, *BioResources*, **10**, 5407 (2015); https://doi.org/10.15376/biores.10.3.5407-5416.