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Adsorption of zinc from aqueous solution using chemically treated newspaper pulp

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Abstract

Adsorption of zinc was studied using chemically modified newspaper pulp as an adsorbent in the aqueous medium. Quantitative chemical analysis showed the presence of trace quantities of some inorganic elements along with phosphorous in TNP. The experimental adsorption data fitted reasonably well to both Freundlich and Langmuir isotherm. pHzpc of TNP was 5.1, which indicated that the adsorbent was more potential for cationic adsorption. The adsorption kinetic data followed a pseudo-second order model for zinc. Optimum Zn^{2+} loading was 9.20 mg/g for 10.31 mg/l initial zinc concentration at pH 5.80. Zn^{2+} loading on TNP was dependent on initial zinc concentration. TNP was a potential adsorbent for the removal of Zn from the effluent of electroplating industry.

Keywords: Adsorption; Newspaper pulp; Zinc; TNP

1. Introduction

Cellulose is the most abundant naturally occurring biopolymer. It is made of glucose units, linked by β-1,4-glycosidic bonds. Adsorptive properties of cellulose, especially with regard to reactive dyes have been well known since long and these have been extensively exploited in the textile industry. Affinity of cellulose toward metals and minerals has also been observed and exploited though to a much lesser extent.

A wide variety of natural products comprising mostly cellulosic matrix, were tried by different workers for the removal of various heavy metals from aqueous and non-aqueous solution. These included pine bark (Al-Asheh et al., 2000), peanut shell (Wilson et al., 2006), saw dust (Argun et al., 2007; Sciban et al., 2007), cotton (Ozsoy and Kumbur, 2006), shea butter seed husk (Eromosele and Abare, 1998), sunflower stalk (Sun and Shi, 1998), CACM2, an adsorbent extracted from a cactus (Carrillo-Morales et al., 2001), etc. A comprehensive list of naturally occurring adsorbents for the removal of heavy metals may be obtained from Bailey et al. (1999). Low cost cellulosic materials such as bamboo pulp and saw dust dyed with monochlorotriazine type reactive dyes have been found to remove Cu^{2+}, Pb^{2+}, Hg^{2+}, Fe^{2+}, Fe^{3+}, Zn^{2+} and Ni^{2+} from their aqueous solutions (Shukla and Sakhardande, 1991). Recently, an extensive review has been carried out on the possible exploitation of wood industry by products such as barks, sawdust in the field of heavy metal removal from contaminated effluents. Different sawdust species such as red fir, mango, lime, pine, cedar, teak, barks of pine, oak and spruce have been examined with regard to their adsorption of different heavy metals, namely, Cd, Cr, Cu, Hg, Ni, Pb and Zn. The issues discussed relate to preparation methods (washing, drying and screening) and chemical treatments such as acid base treatment, formaldehyde

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treatment, phosphation, carboxylation, sulfoethylation, carboxymethylation etc. (Fiset et al., 2000). Functionality of cellulose by impregnating with inorganic substances has been reviewed by Kurokawa and Hanaya (1995).

Old newspaper is an unavoidable form of domestic waste that keeps on accumulating steadily. An attempt was made to examine the reuse of treated newspaper as an adsorbent for the inorganic contaminants with an objective to assess the potential of treated newspaper as an adsorbent for the purpose of wastewater treatment.

2. Methods

2.1. Preparation of treated newspaper pulp (TNP)

Old newspaper was treated with concentrated sodium bicarbonate solution for removing foreign materials like grease, black ink and bleaching material (chlorine dioxide). The newspaper pulp was washed several times with distilled water till the pH of the supernatant water layer of the pulp was around 6.5–7.0. A definite amount of air-dried newspaper pulp was then refluxed with 5.0% Na_2HPO_4 using water condenser for 4 h to impregnate the phosphate into the cellulosic matrix. All the parameters such as the amount of NP, concentration of disodium hydrogen phosphate and time were optimised for the maximum impregnation. After phosphorylation, the pulp was again washed with distilled water till the solution was free from phosphate. The solution was cooled and gravity filtered through Whatman 40 filter paper. The treated newspaper pulp was air-dried and finely ground with the help of mixer grinder to make it fluffy.

The solution of metal ion was obtained by dissolving analytical grade salt of zinc sulphate, disodium hydrogen orthophosphate. The stock solutions of zinc were diluted as required. All other chemicals used for experiments were of analytical grades.

2.2. Instrumental

Quantitative elemental analysis for Si, Al and P was carried out with Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES), Varian, Vista MPX. Other elements, viz Ca, Mg, Fe, were carried out with GBC Avanta Atomic Absorption Spectrometer (AAS). Cellulosic phases were identified by X-ray diffractogram, XRD, PTS 3003, Seifert Germany. Characterisation of functional groups in NP and TNP were carried out using Fourier Transfer Infrared Spectrophotometer, Thermo Nicolet 870.

2.3. Batch adsorption experiments

All adsorption experiments were carried out in batches for TNP after the preliminary study of Zn adsorption on NP and TNP. Synthetic zinc solution (50 ml) of predetermined concentration was taken separately in 100 ml Stoppard conical flasks. A measured quantity of adsorbent was added to this solution and shaken in a mechanical shaker for a definite period of time. Adsorption parameters namely, adsorbent dose, shaking time were optimised by the method of continuous variation. For optimisation, adsorbent dose was varied between 0 and 0.25 g for 10.31 mg/l of Zn, shaking time varied between 0 and 30 min. After shaking, the solution was allowed to settle for 30 min, filtered and analysed for zinc by AAS. The difference in the adsorbate (Zinc) content before and after adsorption represented the amount of adsorbate adsorbed by TNP. Optimum adsorbent dose and shaking time were found to be 0.05 g and 30 min for 10.31 mg/l of Zn to reach the equilibrium.

Adsorption of zinc was studied in the pH range of 2.0–6.0. For adsorption of Zn, a similar method as mentioned in batch adsorption experiment was followed with 0.05 g of adsorbent and 50 ml of 18.77 mg/l aqueous zinc solution at desired pH. pH of the solution was adjusted using dilute HCl and dilute NaOH. The entire solution was shaken further for half an hour in a mechanical wrist shaker and allowed to settle for one hour before it was filtered and analysed for adsorbate concentration. For adsorption kinetics, 50 ml of three different concentrations of zinc solutions were adsorbed on 0.05 g of TNP over a time period of 0–180 min following the procedure outlined above.

3. Results and discussion

3.1. Characterisation of adsorbent

X-ray diffraction of newspaper pulp (NP) and treated newspaper pulp (TNP) was carried out to ascertain the cellulose matrix present in the NP and TNP. It was observed that there were phases in both biosorbents which were very close to native cellulose phases. In addition to these, three identified peaks ($d = 3.906$, 5.674, and 2.538), some low intensity peaks were present due to foreign materials in the XRD of NP. It was apparent from the study that after chemical treatment, TNP was more close to native cellulose in a pure form.

Quantitative chemical analysis of NP and TNP showed that there were some inorganic elements present as impurities (iron – 0.11%, silica – 1.07%, calcium – 1.07%, magnesium – 0.56%, and aluminium – 0.32%) in untreated newspaper pulp (NP), which were almost negligible in TNP. Similar observation was further corroborated in X-ray diffraction pattern of NP and TNP. Moreover, the presence of phosphorous was also estimated in TNP (Phosphorous – 0.61%) by chemical analysis confirming impregnation of phosphorous during the chemical treatment. The moisture content in NP and TNP was 8.18% and 7.23%.

The FTIR spectra of NP and TNP were in the range of 4000–350 cm^{-1} (not shown). The FTIR spectra showed characteristic cellulose peak in the finger print region of 1000–1200 cm^{-1} (Zhbankov et al., 2000). The band near 1162 cm^{-1} and 1111 cm^{-1} corresponded to C–O–C groups from β-(1-4)-glycosidic bonds in cellulose (Suflet et al.,