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EFFICACY OF LIGNOCELLULOSICS MATERIALS, ZEOLITE AND PERLITE FOR REMOVAL OF CATION AND ANIONS FROM SEA AND WASTE WATER

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ABSTRACT

The adsorption of Ca, Zn, Na, Cd (II), Cr (III) and NO_3^- ions from sea water, industrial and urban wastewater and aqueous solutions by poplar (*Populus nigra* L.) sawdust, cotton linter, zeolite and expanded perlite were examined on the basis of a batch adsorption technique. The results revealed that application of sawdust, cotton linter, perlite and zeolite are effective in improving elimination of Ca, Zn, Na ions from sea water, industrial and urban wastewater and Cd (II), Cr (III) and NO_3^- from aqueous solutions. Generally, Ca, Zn, Na removal efficiency of mixture of W+α+P+Z was reported to be higher than other adsorbents. The removal efficiency of heavy metals with W and mixture of W+α were reported to be higher than other adsorbents. Also the results indicated that adsorbents were effective on total dissolved solids (TDS) removal from petrochemical and rural wastewater as well as on sea water.

KEYWORDS: Adsorption, caution, onions, sawdust, expanded perlite, zeolite and cotton linter.

INTRODUCTION

Excessive pollution of the environment due to industrialization and urbanization has posed a great problem worldwide. Due to this fact, providing safe and sufficient drinking water and proper sewerage system is challenging tasks for many developing countries especially in urban areas (Gupta et al. 2001). In the face of growing water scarcity, use of urban waste water in agriculture has become inevitable in developing areas. Waste water includes both industrial and municipal waste water. The industrial waste water is often discharged into municipal sewers where it requires extensive pretreatment to remove the incompatible substances (suspended solids, biodegradable organics, pathogens etc.) prior to discharge into municipal systems or re-use (Mohd 2013).

The use alternative low-cost material as potential sorbents has been investigated as a replacement for costly current methods. Certain industries with natural materials or waste products with a high capacity for heavy metals can be obtained, employed, and disposed of with little cost (Mohan and Singh 2002). Some of the reported low-cost adsorbents include bark, tannin-rich materials, lignin, chitin, chitosan, peat moss, moss, modified wool and cotton (Rao et al. 2000). The adsorption of heavy metals by these materials might be attributed to their proteins, carbohydrates, and phenolic compounds which have carboxyl, hydroxyl, sulfate, phosphate, and amino groups that can bind metal ions.

Sawdust is another possible material because it is produced in large quantities at sawmills as a solid waste. Sawdust contains primarily lignin and cellulose. Interest in the use of sawdust as an adsorbent has increased due to the promising results obtained from current studies (Shukla et al. 2002). Wood shavings have been proposed as a mechanism for preventing environmental damage to marsh grasses and for absorbing oil from the deep water drilling operations (Borazjani et al. 2012). Woodwastes are the best source of polysaccharides. Among the polysaccharides, the structure of cellulose is unique and simple. However, this influences its chemical reactions significantly. Cellulose being rigid, highly crystalline, and insoluble in common organic solvents is an ideal structural engineering material (Mathur and Mathur 2001). Various cellulose derivatives have been used as ion exchange or chelator in resin because they are hydrophobic and advantageous for such applications (Aoki et al. 1999). Cellulose is a natural polymer, easily available, which has widely been used as substrate for reactants immobilization with many applicants (Acemoglu 1998). Chemical functionalization of cellulose aims to adjust the properties of macromolecule for different purposes, particularly, as a chemical feedstock for production of cellulose derivatives for a variety of applications. The conventional sources of cellulose include cotton linters and wood pulp which now-a-days are discouraged on account of the cost of the former and environment conservative regulations associated with the latter (Varshney and Naithani 2011).

Perlite is very cheap and also a viable candidate as an economical adsorbent for removing heavy metals (Silber 2012). Expanded perlite provides larger volumes with low bulk density compared to other adsorbents; Expanded perlite as a filter aid is a finely graded material which, when added to theliquid to be filtered, collects on the particles (Torab-Mostaedi et al. 2010). Zeolites have huge potential as a cost-effective, environmental-friendly solution that can improve the efficiency of wastewater treatment. The low price and the additional ecological benefit (reduced raw materials mining and solid wastes disposal) of the production of zeolites from wastes increase their popularity. Zeolites are hydrated aluminosilicates with a precise geometry of crystal structure and pores of uniform size, which form channels of molecular dimensions with high capacity of exchange cations from their structure (Wang 2007). Zeolites have a satisfactory capacity adsorption to remove certain metal ions presents in solutions, and has therefore potential to be used as an adsorbent in the treatment of produced water (Abreu et al. 2012).

The objective of the present study is to investigate the adsorption potential of poplar sawdust, cotton linter, zeolite and expanded perlite in the removal of Cd (II), Cr (III) and NO_3^- from aqueous solutions and Ca, Zn, Na ions from sea water, industrial and urban wastewater and their effects on the amounts of TDS of water samples.

MATERIAL AND METHODS

Adsorbents

The absorbent materials chosen for the present work were sawdust of poplar (*Populus nigra* L.) (w), cotton linter (α cellulise) (α), zeolite (Z) and perlite (P). The sawdust of poplar was obtained from a Corporation sawmill in Iran's Bojnourd city. It was washed with distilled water to remove surface impurities and dried at 100°C for 24 h and sieved in the size range of 70 mesh ASTM. The cotton linter (α cellulose, 99.3 %; crystallinity 82 %; degree of polymerization, 885) was obtained from the Linter Pak Company in Iran. Expanded perlite samples were obtained from Omid Co. (Semnan, Iran). A zeolite was used for removal of dissolved cation and anions in solutions and obtained from Pars Zeolite Co. The expanded perlite was used without any chemical treatment for the sorption reported here. The particle size ranged between 10 and 40 µm and its porosity was 82 %. The chemical composition of the expanded perlite is given in Tab. 1.

Tab. 1: Chemical composition of expanded perlite.

Constituent	SiO_2	Al_2O_3	Na_2O	K_2O	Fe_2O_3	MgO	CaO	P_2O_5	TiO_2
Percentage (wt. %)	75.22	13.08	3	4.95	1.83	0.1	1.43	0.02	0.13

Water sampling for analysis

Industrial wastewater was acquired from the Petrochemical Company of North Khorasan, Iran. Urban wastewater was obtained from "Municipal Sewage Treatment", Bojnourd, Iran and sea water from Caspian Sea. Since amount of Cr, Cd and NO_3^- were minor in water samples; solutions of heavy metal and nitrate ions were prepared by Chromium chloride ($Cr\ Cl_3$), Cadmium chloride ($Cd\ Cl_2$) with 20 ppm concentration and Sodium nitrate ($NaNO_3$) with 60 ppm concentration.

Batch adsorption experiments

In this experiment, a batch adsorption technique was used to attain data. Adsorption experiments were carried out by mixing of the test solution of 1000 ml with 25 g of sawdust, 10 gof cotton linter, 25 g, zeolite and 25 g of perlite samples was stirred in a thermostated shaker bath at 220 $r.min^{-1}$ and 30°C continuously for 30 min. The solutions were then subjected to a magnetic stirrer for proper adsorption. Then the adsorbents were separated from the sample by using filter paper. Atomic absorption spectrometer (AAS) (Model 929, Unicam) was used to analyze the concentrations of heavy metal and other elements. Amount of TDS was measured by using TDS meter No. I-1100. Taking a requisite amount of sample wastewater in a beaker, the probe of the TDS meter was then immersed, making sure that the sensor was fully covered until the reading was stabilized (Gilbert et al. 1992). In order to obtain the adsorption capacity of adsorbents, the removal efficiency was evaluated using the following expression:

Removal efficiency = $(C_0-C)/ C_0 \times 100$ (%)

where: C_0 and C - the concentrations of the heavy metal and other elements in initial and final solutions, respectively.

Each experiment was replicated three times, and mean values were used in our analyses.

RESULTS AND DISCUSSION

Effect of adsorbents on Ca removal efficiency

Effect of sawdust of poplar (w), cotton linter (α), zeolite (Z) and perlite (P) on Ca removal efficiency insea water, petrochemical and rural wastewater is presented in Fig. 1. The concentration of Ca in seawater was 300 mg/li. Results of Ca removal efficiency measurement showed that the highest value was found in the mixture of wood, alpha-cellulose, perlite and zeolite (W+α +P+Z) (52.33 %); the lowest value was observed in mixture of wood, alpha-cellulose and perlite (W+α+P) (6.66 %).

The concentrations of Ca in petrochemical and rural wastewater samples were 10 and 70 mg/li respectively. Generally, removal values of calcium with adsorbent of the mixture of wood, alpha-cellulose, perlite and zeolite (W+α+P+Z) were reported to be higher than other adsorbents; the reason was reported to be the zeolites are hydrated aluminosilicates with a precise geometry of crystal structure and pores of uniform size, which form channels of molecular dimensions from their structure. Experimental data obtained with synthetic solutions and produced water of oil industry on the zeolite showed that value Calcium ions are removed almost 80-90 %, while for other ions (Mg^{2+}, Na^+, K^+) the removal was around 60 % (Abreu et al. 2012).

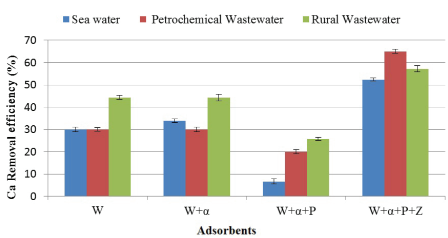

Fig.1: Effect of adsorbents on Ca removal efficiency from sea water, petrochemical and rural wastewater.

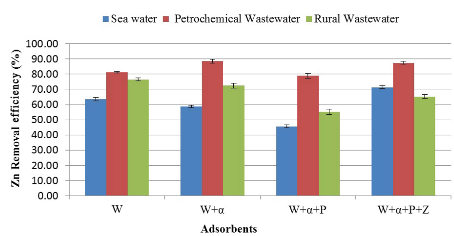

Fig. 2: Effect of adsorbents on Zn removal efficiency from sea water, petrochemical and rural wastewater.

Effect of adsorbents on Zn removal

Fig. 2 illustrates the effect of adsorbents on Zn removal efficiency in sea water, petrochemical and rural wastewater. The concentrations of Zn in seawater, petrochemical and rural wastewater were 0.63, 1.44 and 0.98 mg/li respectively. Results showed that the adsorbents had more effective on elimination of Zn on water samples; the highest Zn removal efficiency was found in W+α+P +Z (87.5 %) and W+α (88.56 %) for petrochemical wastewater; the lowest value was observed in W+α +P (45.68 %) on sea water.

Effect of adsorbents on Na removal

The relation between the percentage of elimination of Na from sea water, petrochemical and rural wastewater and adsorbents is shown in Fig. 3. The concentrations of Na in seawater, petrochemical and rural wastewater were 2530, 64.8 and 225 mg/li respectively. The results showed that the highest Na removal efficiency was found in W (82.95) and W+α (81.33) for petrochemical wastewater; the lowest value was observed in W+α +P+Z (13.04 %) on sea water. The efficiency of a synthetic zeolite on the removal of Na^+ and K^+ were lower than Ca^{2+} due to presence of several matrix effects (Loiola et al. 2012).

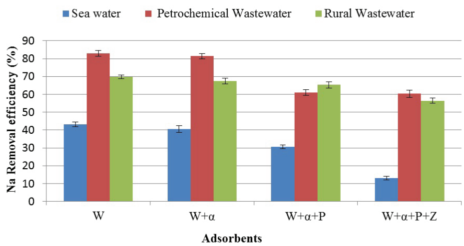

Fig. 3: Effect of adsorbents on Na removal efficiency from sea water, petrochemical and rural wastewater.

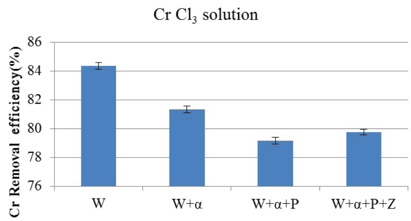

Fig. 4: Effect of adsorbents on Cr removal efficiency from aqueous solution.

Effect of adsorbents on Cr removal

Fig. 4 illustrates the effect of adsorbents on Cr removal efficiency from $Cr\ Cl_3$ aqueous solution. The concentration of Cr in aqueous solution was 24 mg/li. Results showed that the adsorbents had greater effect on the elimination of Cr from this solution. This increasing effect is outstanding in W (84.33), as well as W+α (81.33 %); concentration of Cr in aqueous solution after exposed to these adsorbents reached 3.76 and 4.48 mg/li respectively; the lowest value of Cr removal efficiency was observed in W+α+P (79.17) with 4.99 mg/li and W+α+P+Z (79.75 %) with 4.86 mg/li concentration of Cr. The metal adsorption capacity of a lignocellulosic material is due to lignin surfaces that contain two main types of acid sites, attributed to carboxylic- and phenolic-type surface groups. Such groups have a high affinity for metal ions (Guo et al. 2008)

Effect of adsorbents on Cd removal

The effect of adsorbents on Cd removal efficiency in $Cd\ Cl_2$ aqueous solution is presented in Fig. 5. The concentration of Cd in aqueous solution was 22 mg/li. The results showed that there was a significant difference between the concentration of Cd in aqueous solutions after exposed to adsorbents and the control solution. This increasing effect is outstanding in W (96.00), as well as W+α (93.18), W+α+P (75.36) and W+α+P +Z (72.86 %); concentration of Cd in aqueous solution after exposed to these adsorbents reached 0.88, 1.5, 5.42 and 5.97 mg/li respectively.

Effect of adsorbents on NO_3^- removal

Fig. 6 illustrates the effect of adsorbents on NO_3^- removal efficiency from $NaNO_3$ aqueous solution. The concentration of NO_3^- in aqueous solution was 60.94 mg/li. The results showed that the highest NO_3^- removal efficiency was found in W (16.69) with concentration of 50.77 mg/li; the lowest value was observed in W+α +P (5.15 %) with 57.8 mg/li concentration of NO_3^-.

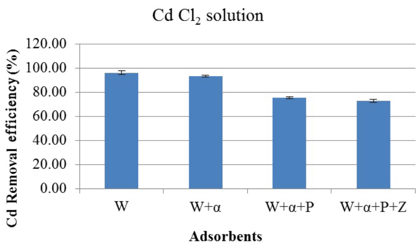

Fig. 5: Effect of adsorbents on Cd removal efficiency from aqueous solution.

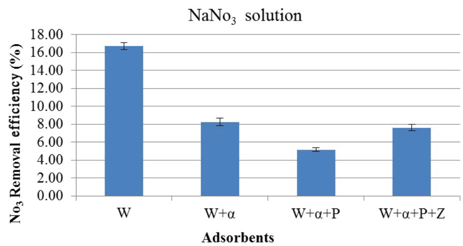

Fig. 6: Effect of adsorbents on NO_3^- removal efficiency from aqueous solution.

Effect of adsorbents on TDS (Total dissolved solids)

Fig. 7 illustrates the effect of adsorbents on TDS in sea water, petrochemical and rural wastewater. Total dissolved solids (TDS) are comprised of inorganic salts and small amounts of organic matter that are dissolved in water.

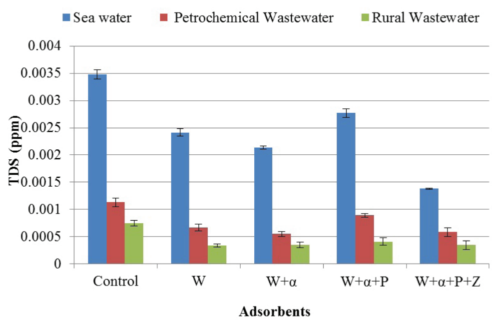

Fig. 7: Effect of adsorbents on TDS in sea water, petrochemical and rural wastewater.

The principal constituents are usually the cations calcium, magnesium, sodium and potassium and the anions carbonate, bicarbonate, chloride, sulphate and particularly in groundwater, nitrate (from agricultural use). Results showed that the adsorbents had more effective on TDS from petrochemical and rural wastewater specially sea water. Results showed that the lowest TDS was found in W+α +P adsorbent as compared to the control samples.

CONCLUSIONS

In recent years, the need for safe and economical methods for the elimination of heavy metals from contaminated waters has necessitated research interest towards the production of low cost alternatives to commercially available activated carbon. Application of sawdust, cotton linter, perlite and zeolite are effective in improving elimination of Ca, Zn, Na ions from sea water, industrial and urban wastewater and Cd (II), Cr (III) and NO_3^- from aqueous solutions. Generally, Ca, Zn, Na removal efficiency of the mixture of W+α+P+Z were reported to be higher than other adsorbents due to zeolite having a satisfactory adsorption capacity to remove certain metal ions presents in solutions as well as the sawdust containing primarily lignin, cellulose and hemicellulosic. The hydroxyl group of cellulose in cotton linter and its ability for metal ions exchanges depends on the amorphous and crystalline percent. Expanded perlite provides larger volumes with low bulk density as compared to other adsorbents.

The removal efficiency of heavy metals with W and the mixture of W+α were reported to be higher than other adsorbents due to the adsorption of heavy metals by these materials. This adsorption is attributed to their proteins, carbohydrates, and phenolic compounds which have carboxyl, hydroxyl, sulfate, phosphate, and amino groups that can bind metal ions.

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