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ADSORPTION OF Zn(II), Cu(II), Pb(II), Fe(II) AND Cr(III) FROM AQUEOUS SOLUTION USING ACTIVATED CARBON PREPARED FROM MUNG POD SHELLS

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Abstract: The performance of Mung Pod Shell activated carbon (MPSAC) for the adsorption of Zn^{2+},Cu^{2+} ,Pb^{2+} Fe^{2+}, and Cr^{3+} ions was studied through batch technique. MPSAC were prepared by carbonization followed by activation. Mung Pod Shells were activated with 2N H_2SO_4 and 10% KOH solution at 100°C. The optimum adsorption conditions were specified as a function of contact time, initial metal ion concentration and pH. Langmuir and Freundlich isotherms were observed to fit the equilibrium data and the model parameters were calculated using linearized equations. The adsorption capacities were 13.32 mg/g (Zn^{2+}), 18.80 mg/g (Cu^{2+}), 19.68 mg/g (Pb^{2+}), 37.29 mg/g (Fe^{2+}) and 20.72mg/g (Cr^{3+}). The results showed that MPSAC is an economically feasible and environment friendly material for removal of Zn^{2+},Cu^{2+} , Pb^{2+}, Fe^{2+} and Cr^{3+} from industrial effluents.

Keywords: Adsorption Cu(II), Zn(II), Pb(II), Fe(II), Cr(III), Chemical activation of Mung Pod Shells

Introduction:

Increasing Environmental pollution by heavy metals like Cu, Fe, Pb, As, Co, Ni, Cr, Hg, Cd, Sn Cd, etc. is a serious matter of ever-growing concern because of their toxic nature. Heavy metals are those having specific gravity 5 times more than specific gravity of water and are toxic or poisonous even at low concentrations. Some well-known toxic metallic elements are arsenic, (sp. gravity 5.7), iron (7.9), chromium (7.19), cadmium (8.65), lead (11.34), mercury (13.54), Cu (8.93) and Zn (7.2). They are proven to be hazardous even at relatively low concentrations due to their long term health effects on humans[1]. Heavy metal ions are discharged into water system from various industrial activities such as electroplating industries, electronic equipment manufacturing and chemical processing plants. Due to rapid development of industrial activities, the levels of heavy metals in water systems have substantially increased. Heavy metals can easily enter the food chain because of their high solubility in water. Trace amounts of copper, zinc, and iron are essential for humans, microorganisms, and animals. Prolonged intake of zinc in large quantity can cause dizziness, fatigue and neutropenia[2]. Zinc could be toxic to some aquatic organisms such as fish. For proper functioning of all living organisms the maintenance of "glucose tolerance factor", Cr (III) is considered as an essential trace element as it is an insulin action cofactor and performs a major role in the activity of this hormone. Chromium is toxic, corrosive and irritant. Lead is serious cumulative body poisons. Excess lead causes neurological and behavioral effects of the central and peripheral nervous system. It may cause kidney damage, reduction in IQ, hearing loss and hypertension. As a trace element copper is essential for various life processes, but increase in copper concentration beyond its threshold limit causes various diseases and disorders like damage of liver, Wilson disease and insomnia[3]. Presence of iron in ground water above certain limit can cause metallic taste, turbidity, odour, staining of cloths and plumbing fixtures. The formation of iron oxides in reservoirs increases growth of micro-organisms in water.

Several treatment methods like reverse osmosis, precipitation, electrodialysis ion exchange, coagulation and flocculation, filtration adsorption have been employed to remove hazardous heavy metals from aqueous solutions[4]. However, most of these methods have some limitations like high operating costs, their inability to remove toxic elements from a wide range of wastewaters and their ineffectiveness in lower concentrations[5]. Adsorption has emerged as promising technique for heavy metal removal due to ease in operation, low cost, environment friendliness and easy availability.

Activated carbons are most widely used as adsorbent material due to their microporous structure, large surface area and high adsorption efficiency for metal ions[6]. At present, the use of commercially produced activated carbons is still limited due to their high cost. Searching for low-cost and easily available adsorbents to remove heavy metal ions have become a main research focus. Heavy metal removal by using low cost adsorbent is found to be more encouraging in extended terms due to the presence of several materials existing locally and profusely such as agricultural wastes, which can be utilized as low-cost adsorbents[7].The objective of present study is to prepare a more effective, economical, and environment friendly activated carbon. Mung Pod Shells (green gram) are used as a raw material for the production of activated carbon because it is abundant, easily available and inexpensive.

Materials and methods:

Chemicals, Materials and Equipments

To perform the adsorption experiments, 1000mg/L of copper, zinc ,lead, iron and chromium standard solutions were prepared from $CuCl_2.2H_2O$, $ZnSO_4.7H_2O$, $Pb(NO_3)_2.6H_2O$, $FeCl_3.6H_2O$ and $K_2Cr_2O_7$ using distilled water. All chemicals used were of analytical grade purity. To stock solution 3-6 drops of concentrated HNO_3 were added to prevent hydroxide formation. The required concentrations of solutions for experiments were made from the synthetic stock solution with required amount of distilled water. 0.1N Hydrochloric acid and 0.1N Sodium hydroxide were used to adjust the solution pH. Distilled water was used throughout the experimental studies.

Mung Pod Shells were used as an adsorbent for removal of Zn (II), Pb (II), Cr (III), Fe (II) and Cu (II) ions from wastewater. The agro waste from local fields was washed many times with distilled water to remove dust. It was sundried for two weeks. The dried agro waste was carbonized in Muffle Furnace (Bio Techniques, India BTI 36) at 450°c for 1 hr.

Activation of Mung Pod Shell Carbon

The carbonized Mung Pod Shells (MPS) were finely groinded to powder and then soaked in 2N H2SO4 for 24 hrs. pat room temp. The sample was placed in an oven and heated to 100°c for 2 hrs. After cooling sample was washed with distilled water and then soaked in 10% KOH solution for 30 min. and then washed several times with distilled water to remove any remaining acid until a neutral pH was achieved. The sample was then dried in an oven at 100°c for 1 hr. This activated agro waste carbon was used for further studies in removal of heavy metal ions in aqueous solutions.

Result and Discussion:

Adsorption Batch Experiments

Batch adsorption experiments of Zn(II), Pb(II), Cr(III), Fe(II) and Cu(II) were carried out to determine the adsorption capacity of Mung Pod Shell Activated Carbon (MPSAC) for three different parameters i.e., pH, Initial metal ion concentration and contact time in a series of five 100 ml flasks and agitated at 25°C and 200 rpm. The initial and final concentrations of the solutions were measured by AAS (Elico SL 168) at the maximum adsorption wavelength and the adsorption capacities of the adsorbent were calculated. After equilibrium was attained, the metal uptake capacity for sample was calculated according to a mass balance on the metal ion using equation,

$$q_e = \frac{(C_0 - C_e)V}{m}$$

Where m is the mass of adsorbent (g), V is the volume of the solution (L), c_o is the initial concentration of metal (mg/ L), c_e is the equilibrium metal concentration (mg/L) and q_e is the metal quantity adsorbed at equilibrium (mg/g).

The percent removal of metals from the solution was calculated by the following equation.

$$\% \text{ Removal} = \frac{(C_0 - C_e)}{C_0} \times 100$$

Effect of pH

pH affects adsorption reactions through H^+ and OH^- that are emitted into the solution. A more acidic pH releases more H^+ ions that may react with the adsorbent or adsorbate, hence affecting results. Likewise, an alkaline pH solution releases OH^- which may also react with the adsorbent or adsorbate[8]. Hence, it is crucial while performing batch tests to evaluate the process at different pH levels.

The effect of solution pH on the sorption of heavy metals was investigated by using 1 g of MPSAC and 5 mg/L of metal ion concentration at initial pH values ranging from 2 to 10 for a 5 hrs shaking time at 25°C. At a pH from 2 to 6, the sorption of metals onto the activated carbon was found to be low. This could be due to increasing the competition between the studied cations with H^+ ions on active sites at a lower pH. Metal uptake increased gradually with increasing pH from 6 to 10 for Zn^{2+}, Pb^{2+} and Fe^{2+} ions, from 6 to 8 for Cu^{2+} and Cr^{3+} ions. This may be attributed to an increase in pH.

Effect of Contact time

To investigate the effect of contact time on the adsorption of the investigated cations from synthetic wastewater solutions, the experiments were conducted with a constant concentration of salt solution (5 mg/L). The sorption equilibrium of the all studied cations was reached at 5 hrs of contact time. All the studied cations were fast removed in the first 3 hrs; this may be attributed to the pores of MPSAC that were nearly completely blocked by the ions in the first 3 hrs. Therefore, five hours were designated for the subsequent studies to ensure complete equilibrium.

Effect of initial metal ion concentration

The effect of the initial concentration of heavy metal ions was studied at a pH 10 for Zn^{2+} and Fe^{2+}, at pH 8 for Cu^{2+}, Pb2+ and Cr^{3+} ions and a shaking time of 5 hours. It was noticed that the percentage removal efficiency values increases as metal ion concentration increases i.e. maximum percentage removal occurs at 8 mg/L metal ion concentration for Pb^{2+}, 9 mg/L for Zn^{2+}, Fe^{2+} and Cr^{3+} and 10 mg/L for Cu^{2+} ions by keeping all other parameters constant.

Determination of Langmuir constants

Langmuir constants are calculated and are tabulated as follows:

Metal ion	Constants	MPSAC
Zn(II)	Q_0(mg/g)	13.32
	R_2	0.8614
	RL	0.0576
	b(L/mg)	3.271
Cu(II)	Q_0(mg/g)	18.80
	R_2	0.9712
	RL	0.0943
	b(L/mg)	1.918
Pb(II)	Q_0(mg/g)	19.68
	R_2	0.9922
	RL	0.0906
	b(L/mg)	2.007
Fe(II)	Q_0(mg/g)	37.29
	R_2	0.9527
	RL	0.2513
	b(L/mg)	0.594
Cr(III)	Q_o(mg/g)	20.72
	R_2	0.8228
	RL	0.0148
	b(L/mg)	13.294

Table-1.Determination of Langmuir constants

3.6 Determination of Freundlich Constants

The calculated Freundlich constants are:

Metal ion	Constants	MPSAC
Zn(II)	K_f	1.8513
	n	8.8809
	R_2	0.9783
Cu(II)	K_f	1.0988
	n	7.7519
	R_2	0.9534
Pb(II)	K_f	1.0948
	n	3.8197
	R_2	0.9962
Fe(II)	K_f	1.2857
	n	4.4543
	R_2	0.9521
Cr(III)	K_f	1.0149
	n	4.3630
	R_2	0.9756

Table-2.Determination of Freundlich Constants

Conclusions:

In the present study, the removal of Zn^{2+} ,Cu^{2+}, Pb^{2+},Fe^{2+} and Cr^{3+} ions from aqueous solution by adsorption on Mung Pod Shell Activated Carbon (MPSAC) via batch technique was investigated. The results showed that the removal of the five cations was favorable at a higher pH. It was observed that during adsorption of the five cations, an increase in the solution pH was noticed with contact time. The rate of adsorption for the five elements was very fast in the first 3 hrs, reaching equilibrium at 5 hrs. The equilibrium adsorption data was described by both Langmuir and Freundlich models and the adsorption capacity of MPSAC decreased in the following sequence: 37.29 mg/g (Fe^{2+})>20.72 mg/g (Cr^{3+})>19.68 mg/g (Pb^{2+})>18.80 mg/g (Cu^{2+})>13.32 mg/g (Zn^{2+}). The obtained results indicated that MPSAC has the potential to be used as a low-cost material for the sorption of Zn^{2+}, Cu^{2+}, Pb^{2+}, Fe^{2+} and Cr^{3+} ions from aqueous medium.

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