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Adsorption of toxic metal ions from laboratory effluents by agricultural waste

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ABSTRACT

The chemistry laboratory effluents usually contains highly toxic organic and inorganic pollutants including metal ions .These hazardous chemical wastes pose serious health problems to living beings. The persistency of toxic metals in environment and their ill health effects are well known. Out of the possible methods to check toxic metal ion pollution, the bio-remediation is of great importance as conventional methods used to remove these toxic metal ions are quite expensive and have certain limitations in terms of efficiency and disposal of secondary waste produced in the process. Adsorption of these metal ions by agricultural waste materials has advantage because of the low cost and high efficiency. Moreover these are environment friendly and there is a possibility of metal ion recovery also. These cellulosic agricultural wastes contain various functional groups like carbonyl, alcohol, acetamido, sulfhydryl etc. which can form chelateswith metal ions and help sequestering of these toxic metals. In the present study rice husk and orange peel have been used for the removal of metal ions from laboratory effluents. Our studies have indicated that the adsorption of metal ions by these bio-sorbents is efficient for the bio-remediation of the laboratory wastewater. Some of these are highly efficient and remove nearly 85% of toxic metal ions. Kinetics of adsorption of metal ions on these materials is also studied. Both Langmuir and Freundlich isotherm models have been studied for mono component adsorption of metal ion by these bio-sorbents. Free energy change for sorption is also calculated. Various physical parameters of laboratory effluent water were compared before and after the adsorption.

Keywords:Laboratory Effluents, Toxic Metal ions, Adsorption, Agricultural Waste, Chemical kinetics

INTRODUCTION

Laboratory effluents contain considerable amount of heavy toxic metal ions, which could endanger environment and public health when discharged without treatment. Various regulatory bodies have set the maximum limits of toxic metals in the aquatic system. But even if these are present below these set limits, these have potential for contamination due to their bio-accumulating and persisting nature.[1] Japan experienced 'Itai – itai' disaster in past due to contamination of cadmium in aquatic stream. These toxic metals when accumulated above tolerance level in human beings and aquatic animals are carcinogenic and affect central nervous system and brain (Table I) . The important toxic metal ion are Cr^{3+}, Zn^{2+}, Pb^{2+}, As^{3+}, Cd^{2+}, Cu^{2+}, Co^{2+}

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and Hg^{2+}.[2-4] In this paper we will concentrate on the removal of Co^{2+} and Cr^{3+} ions from the laboratory effluents by adsorption on rice husk and orange peel.

Table 1: Toxicological effects of $Cr^{3+}$and Co^{2+} metal ions.

Metal ion[2,3]	Toxic effect
Cr^{3+}	Kidney Problems, Carcinogenic in nature, Arthritis, Weight Loss
Co^{2+}	Liver and Heart Diseases, Systemic toxicity

Advanced or tertiary treatment methods such as chemical precipitation, electrodialysis by cation selective membranes, ion exchange and reverse osmosis are required to remove non biodegradable heavy metal ions as secondary methods of water treatment can not remove these metals. The high cost and certain limitations associated with these conventional treatments such as sensitive operating conditions, less efficiency, disposal of secondary sludge are a major problem. Large amount of agricultural waste produced around the world can be explored as potential adsorbents for various metal ions[5] and chemicals because of their edge over conventional methods as they can be used with minimum processing, have good adsorption capacity, inexpensive and produce minimum sludge.[6] These can be regenerated and there is possibility of recovery of metal ions during regeneration.[7,8]

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Physical Parameters	Co²⁺ (Aq)		Cr³⁺ (Aq)		Laboratory Effluents	
	Before treatment	After treatment	Before treatment	After treatment	Before treatment	After treatment
pH	5.19	6.28	4.46	5.30	6.01	9.32
C (µS)	658.2	110.0	710.1	82.36	676.6	102.1
TDS (ppm)	358.3	63.97	112.8	13.68	376	53.81

Table2: Physical parameters, pH, total dissolved solids (TDS), and conductivity (C) of the metal ion solutions and laboratory effluents before and after adsorption

The agricultural waste are lignocellulose materials composed of high molecular weight structural components; lignin, cellulose and hemicellulose. The other component are lipids, proteins, simple sugar and starch containing various functional groups like alcohols, aldehydes, ketones, carboxylic, phenolic and ether group. These functional groups help in sequestering heavy metals ions by complexation.[8-12]

The cellulose is located in the secondary cell wall.[13] Lignin,a polymeric aromatic compound with infinite molecular weight[14] can be cleaved to smaller fragments and is insoluble in water. High surface area[13] and inertness to chemical reactions make lignin a potential adsorption material to remove heavy metals from water.

Cellulose is an organic polymer composed of anhydroglucose units held together in a straight chain.[15] These chains tend to be arranged parallel by forming intramolecular and intermolecular hydrogen bonds to form a micro fibril in the cell wall structure.[16] Hemi cellulose act as cement material to hold the cellulose micelle and fibre together and it consists of different monosaccharide units that are partially soluble or swellable in water because of their amorphous nature.[17] The agricultural natural adsorbents showed high efficiency and selectivity for complexation with metal ions due to the following reasons:

1. The polymer chain provide suitable configurations
2. Large numbers of hydroxyl and amino groups
3. Primary amino groups provide high reactivity

EXPERIMENTAL METHODS

The Orange Peel and Rice Husk were washed with distilled water to remove impurities then these were cut into small pieces and washed again. After washing these agricultural wastes were dried in oven at 110⁰ C for 24hrs and grounded to fine powderand sieved through 2mm stainless steel. All the reagents used were of AR grade. Stock solutions of metal ions were prepared by dissolving their respective salts in distilled water. All absorption measurements were made with UV-Visible spectrometer (Systronics PC Based DoubleBeam Spectrometer 2202). Absorbance values were recorded at the wavelength for maximum absorbance (λ_{Max}) corresponding to each metal ions solutions. These solutions were initially calibrated for concentration in terms of absorbance units.

The physical parameters pH, total dissolved solids (TDS), and conductivity (C) of these solutions and laboratory effluents were recorded before and after treatment using elico made water quality analyzer. The data of these physical parameters are given in Table 2.

BATCH MODE ADSORPTION STUDIES

All experiments in this study were carried out in 100mL round bottom flask containing 0.500g of the agricultural waste and 50mL of known concentrations solutions.

The contents were stirred on magnetic stirrer without heating. After fixed interval of time, the samples were separated from solutions centrifuged and filtered by using whattman filter paper and residual concentration of metal ions was determined spectrophotometrically.

The equilibrium adsorption amount(q_e) is calculated using the equation:

$$q_e=(C_0-C_e/m)V$$

where C_0 is the initial metal concentration (mgL^{-1}), C_e is the metal ion concentration at equilibrium time in solution (mgL^{-1}), q_e is the amount of metal ion adsorbed, V is the volume of metal ion solutions and m is the mass of the agricultural waste.

Equilibrium sorption study

Adsorption Isotherm is a representation of adsorbateconcentration and quantity of material adsorbed at constant temperature i.e. graph of amount adsorbed against equilibrium concentration at specific temperature.[18]

Langmuir Isotherm Model

Langmuir Adsorption isotherm has found application in monolayer adsorption. It is based on the assumption that adsorption takes place at specific homogeneous sites within the adsorbent and intermolecular forces decreases rapidly with distance. It also takes into account that all the adsorption sites of homogeneous adsorbent are identical and equivalent energetically and no adsorption can takes place after saturation. The Langmuir Isotherm model can be presented by well known equation:

$$C_e/q_e=C_e/q_m+1/q_mk$$

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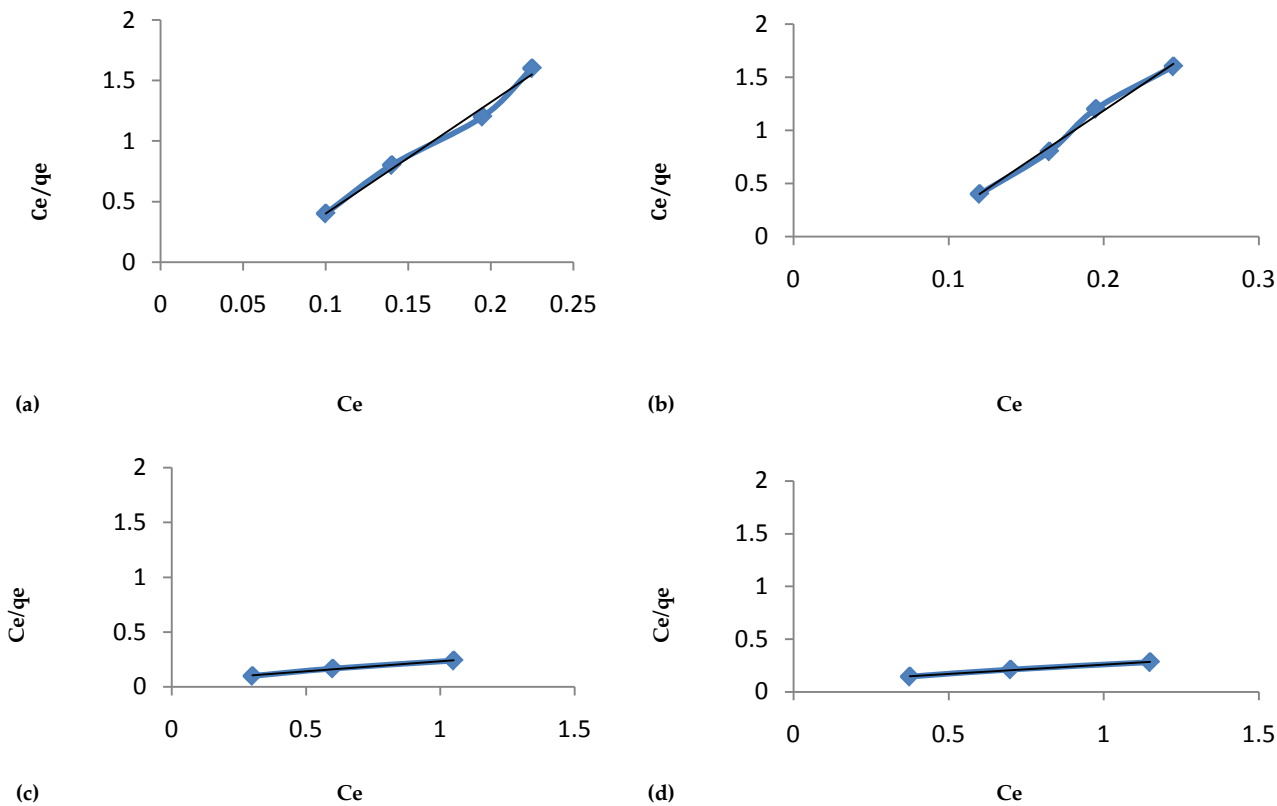J. Integr. Sci. Technol., 2016, 4(2), 70-75   71

Figure 1. Langmuir Adsorption Isotherms for adsorption of Co^{2+} ions on (a) rice husk & (b) orange peel and adsorption of Cr^{3+} ions on (c) rice husk & (d) orange peel

Figure 2. FreundlichAdsorption Isotherms for adsorption of Co^{2+} ions on (a) rice husk & (b) orange peel and adsorption of Cr^{3+} ions on (c) rice husk & (d) orange peel
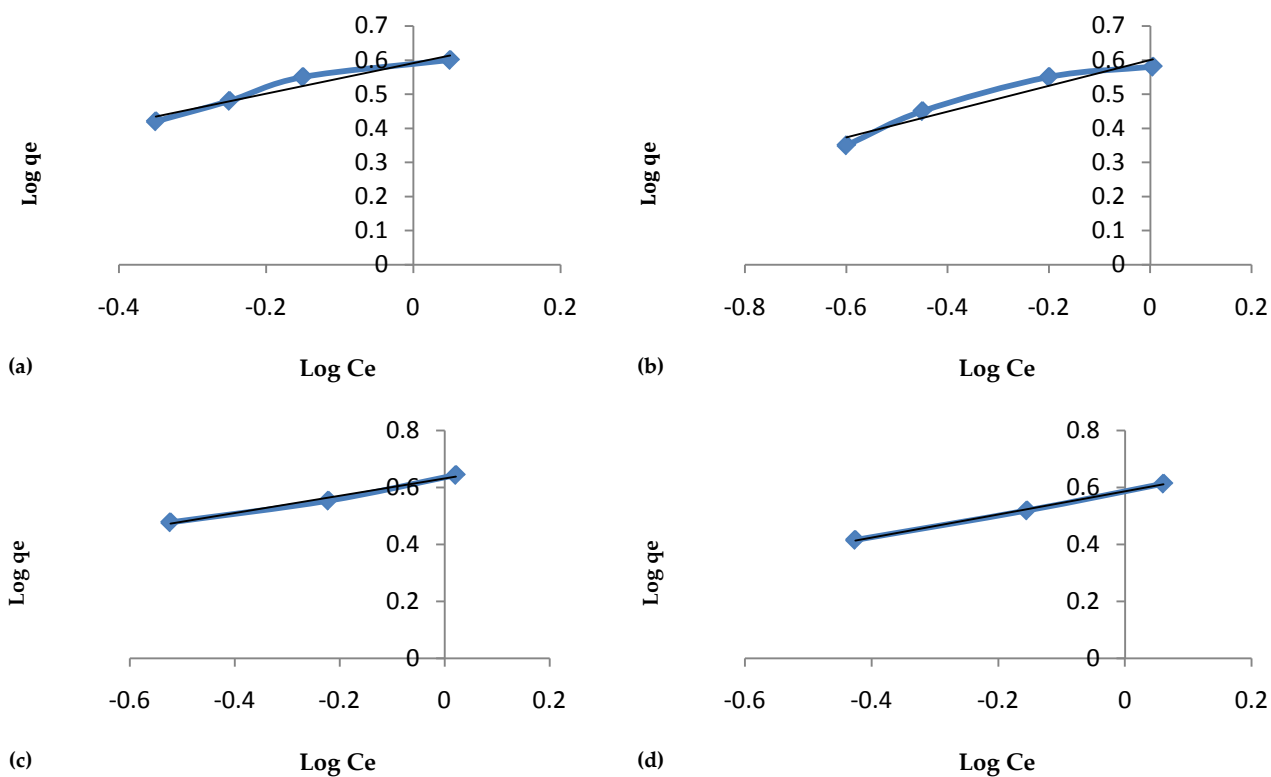
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Table 3: Calculated maximum adsorption capacity (q_m) and the Langmuir isotherm constant (K_L) regression data for adsorption of Co^{2+} and Cr^{3+} ions on rice husk & orange peel.

Adsorbent	Heavy Metals	q_m	K_L	R^2
Rice Husk	Cr^{3+}	5.326	2.100	0.9995
Rice Husk	Co^{2+}	4.302	2.535	0.9887
Orange Peel	Co^{2+}	4.756	2.381	0.9796
Orange Peel	Cr^{3+}	5.826	2.101	0.9918

Where C_e is the metal ions concentration at equilibrium (mgL^{-1}), q_e is the amount of the metal ions adsorbed at equilibrium (mgL^{-1}), q_m is maximum adsorption capacity (mgL^{-1}) and k_l is the Langmuir isotherm constant related to free energy of adsorption (Lmg^{-1}). C_e/q_e Vs C_e was plotted (Fig. 1) Table 3; which give intercept of $(1/q_m).k_l$ and a slope of $1/q_m$.

Freundlich Isotherm Model:

The Freundlich linear form is given by the equation:

$$log q_e = log k_f + (1/n) log C_e$$

where K_f is Freundlich constant and $1/n$ is an empirical parameter (which varies with the heterogeneity of the material). Value of $1/n$ & K_f was calculated from slope and intercept of the plot between $log q_e$ and $log C_e$ respectively (Fig. 2) Table 4. The value of $1/n$ was between 0 and 1. Under the mentioned conditions the sorption of metal ions into studied adsorbents was favourable. The Freundlich type behaviour indicates the surface heterogeneity of the adsorbents. On activation of adsorption site, the probability of adsorption increases through surface exchange mechanism.

Table 4: Calculated Freundlich constant (K_f), empirical parameter ($1/n$) and the regression data for adsorption of Co^{2+} and Cr^{3+} ions on rice husk & orange peel.

Adsorbent	Metal ions	K_f	$1/n$	R^2
Rice Husk	Cr^{3+}	4.005	0.4012	0.9769
Rice Husk	Co^{2+}	2.365	0.2229	0.9427
Orange Peel	Cr^{3+}	1.820	0.2651	0.9364
Orange Peel	Co^{2+}	3.265	0.3099	0.9685

Adsorption Kinetic Study

The adsorption of metal ions was studied by using two kinetic models which are, pseudo first order kinetic model and pseudo second order kinetic model.[19] On the basis of correlation coefficient (R^2) from linear regression, the best

Adsorbent	Conc of metal ions	Pseudo First Order		Pseudo Second Order	
		K_1 (min^{-1})	R^2	K_2 (mgL^{-1})^2 min^{-1}	R^2
Rice Husk	Cr^{3+}	0.019	0.9794	2.6×10^{-8}	0.9821
Rice Husk	Co^{2+}	0.008	0.9541	1.2×10^{-8}	0.9932
Orange Peel	Cr^{3+}	0.012	0.9773	5.5×10^{-8}	0.9962
Orange Peel	Co^{2+}	0.018	0.9312	2.8×10^{-8}	0.9862

Table 5: Chemical Kinetics data on adsorption of Co^{2+} and Cr^{3+} ions on rice husk & orange peel.

fit model was selected, which reveals how much the predicted value from a forecast model match with the experimental data given in Table 5.

Pseudo First Order Kinetic Model:

The pseudo-first order equation[20] in linear form was expressed in equation:

$$log (q_e - q_t) = log q_e - k_1 t / 2.303$$

Where k_1 is first order constant (min^{-1}). The plot of $log (q_e - q_t)$ Vs t gave the intercept of $log q_e$ & slope k_1.

Pseudo Second-Order Kinetic Model:

Equation of Pseudo-second order[21] is:

$$1/q_t = (1/t) k_2 q_e^2 + 1/q_e.$$

Where k_2 is the rate constant of second order. Pseudo second order gave better R^2 values confirming chemisorptions of Co^{2+} ions and Cr^{3+} ions on agricultural wastes. (figure 3)

CALCULATION OF ΔG^0

The adsorption process is exothermic in nature. The increases in the temperature of the system affects the solubility and particularly the chemical potential of the adsorbate metal ions which is known to be a controlling factor in the process of adsorption. Hence the percentage adsorption of these metal ions on the adsorbent decreases on increasing the temperature of the solution. The equilibrium constant was calculated with the help of equation:

$$K = C_{Ae}/C_e$$

Where C_{Ae} is solid phase concentration (mg/L) and C_e is the equilibrium concentration of the metal ions in the solution. The calculated free energy change (ΔG^0) was calculated by using equation:

$$\Delta G^0 = -RT \ln K$$

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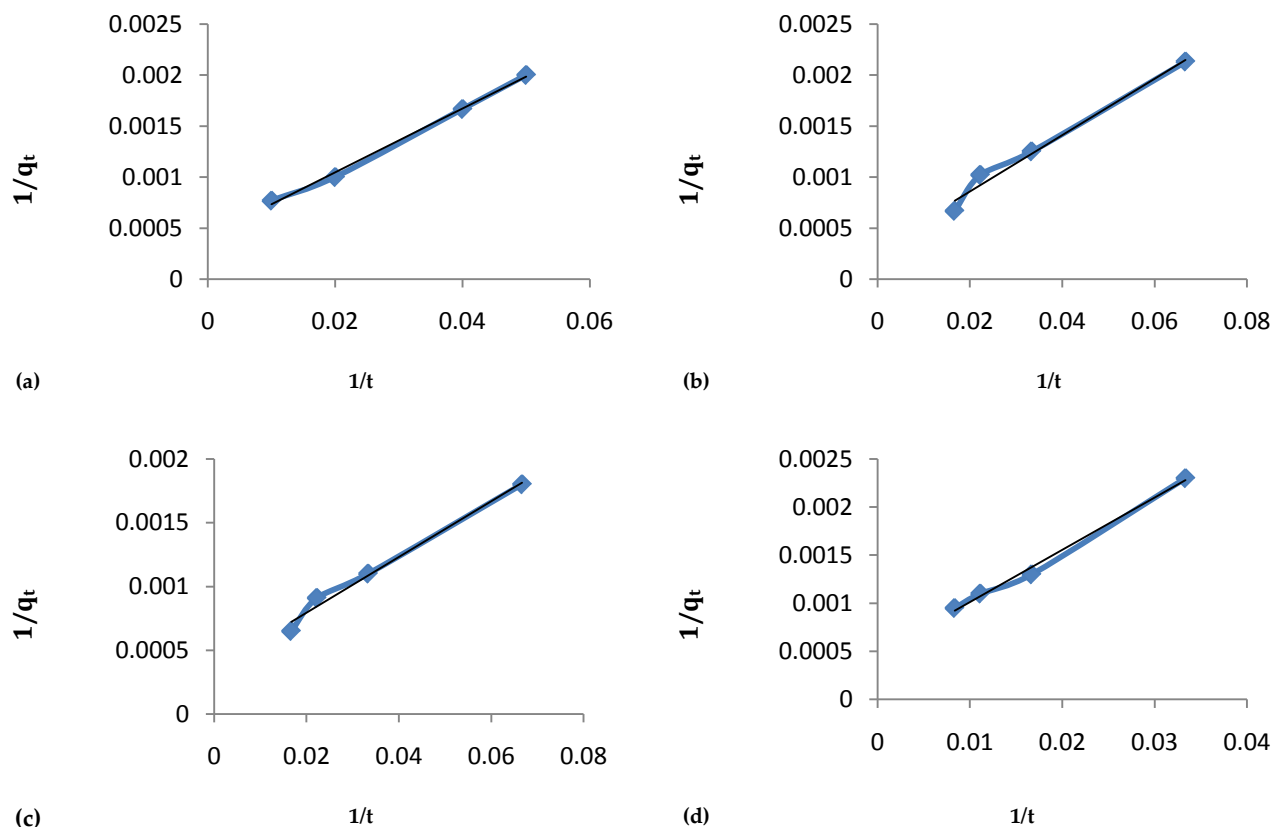J. Integr. Sci. Technol., 2016, 4(2), 70-75   73

Figure 3. Pesudo second order kinetic plots for adsorption of Cr^{3+} ions on (a) rice husk & (b) orange peel and adsorption of Co^{2+} ions on (c) orange peel & (d) rice husk.

Where R is the gas constant and K is the equilibrium constant and T is absolute temperature (303K). The negative values of ΔG^0 indicates that the adsorption of metal ions on rice husk and orange peel is a spontaneous process. (Table 6)

Table 6: Thermodynamic data for adsorption of Co^{2+} and Cr^{3+} ions on rice husk & orange peel.

Adsorbent	Metal ions	K	ΔG (kJ/moL^{-1})
Rice Husk	Cr^{3+}	3.935	-3.394
Rice Husk	Co^{2+}	2.05	-1.999
Orange Peel	Cr^{3+}	8.43	-5.371
Orange Peel	Co^{2+}	5.285	-4.637

CONCLUSION

Rice Husk and Orange Peel agricultural wastes could be used as potential adsorbents for the removal of Chromium and Cobalt ions from aqueous solutions. The amount of cation adsorbed increases with increase in metal ion concentration, Kinetic, equilibrium and thermodynamic results indicate that metal ion removal from aqueous solutions by adsorption proceeded through chemisorption and physisorption mechanisms and upto 85% of metal ions

(Co^{2+} & Cr^{3+}) can be removed from laboratory effluents by using Rice husk and Orange Peel. It is interesting to note that the adsorption ability of orange peel is higher for adsorption of both Co^{2+} and Cr^{3+} ions and therefore is a better option to remove laboratory effluents.

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