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Investigation of Langmuir and Freundlich Adsorption Isotherm of Co^{2+} Ion by Micro Powder of Cedar Leaf

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ABSTRACT

In this paper, the micro powder was the product of cedar leaf (MPCL) is used as a low-cost and natural adsorbent for the removal of $Co2^{+}$ from aqueous solutions. Factors such as the pH effect initial metal ion concentration, contact time, MPCL dosage and temperature on the adsorption performance of MPCL for $Co2^{+}$ ions were experimented by batch method. Results indicate that removal of $Co2^{+}$ ions at pH values of 7, the Langmuir isotherm model is the most suitable one for the adsorption process using MPCL(R2=0.9775), thus indicating the applicability of monolayer coverage of Co(II) ion on MPCL surface.The Relationship between Thermodynamic parameters was used to predict the absorption process. According to Thermodynamic analysis, the process exothermic and natural.

Keywords: Co^{2+}; adsorption; micro powder; cedar leaf; Thermodynamic; MPCL.

INTRODUCTION

Toxic heavy metals pollution is one of the influential environmental problems, because they are Nondegradable and harmful for public health, even at very low concentrations. Cobalt is one of several commonly occurring toxic metals. It is an animal carcinogen producing cancer at various sites. Exposure to cobalt is extremely irritating to the skin both on contact and by provoking an allergic reaction which sensitizes the skin to further contact. It is also irritating to the eyes and mucous membrane, causing severe discomfort in the nose, often leading to perforation of the nasal septum. The threshold limit value for cobalt fume and dust exposures is 0.1 mg/m3 in the U.S. The use of activated carbons to remove cobalt from water was proposed because of their high surface areas and active functional groups leading to a search for low-cost adsorbents in recent years[1-5].

Indeed agricultural waste for example, has two advantages. First, waste material is converted to useful, value-added adsorbents. Disposal of agricultural by-products has become a major costly waste disposal problem. Second, produced activated carbons are used for removing organic chemicals and metals from wastewater [6-9]. Corn cob, flamboyant pods, apricot stone, almond shell, nut shell, peach stone, oat hulls, coconut husk, coconut shell, hazelnut shell, grape seed, olive stone and Rosa cantina sp. Seeds[10,11]. The fruit has a sweet edible pulp, the leaves are applied locally to sores, and the roots are used to cure and prevent skin diseases[12]. In the present study, MPCL prepared used as an adsorbent to remove cobalt from aqueous solutions. The adsorption of cobalt ions onto MPCL was studied in batch equilibrium conditions.

EXPERIMENTAL

Apparatus and Materials

An AA 680 model atomic absorption spectrometer (Shimadzu Co.) was used for measuring the concentration of Co^{2+} ion in studied solutions, a 820A model pH meter (Metrohm Co.) was used to measure pH of solutions and a thermostatic orbit incubator shaker neo lab model (India) was used to measure contact time in solution. All chemical materials used in this study were of analytical grade. MPCL prepared by chemical activation with KOH was characterized. Cobalt nitrate, was purchased from Merck Company.

Batch Adsorption Experiments

Batch adsorption experiments were carried out to determine the Co^{2+} ions adsorption isotherm onto MPCL and its thermodynamic properties. Co^{2+} ions stock solution (100 mg.L^{-1}) was prepared by dissolving the appropriate quantity of Co(NO3)2 salt in deionized water. Adsorption isotherms were obtained by using initial Co^{2+} ion concentration, Co, and its equilibrium concentration, Xe, at 298K. The effect of pH on the Co^{2+} ions adsorption onto MPCL was conducted in a pH range of 3-10.The pH of solutions was adjusted by 0.1 M HCl or 0.1M NaOH solutions. For every experiment, 100ml of the solution with Co^{2+} concentration of 30 mg.L^{-1} was mixed with 50 mg of MPCL in a 250 ml glass conical flask. The flask was shaken in a thermostatic orbit shaker at 220rpm for 60min. The mixed was filtered through a 0.45 µm membrane filter. The filtrate was measured by atomic absorption then, the adsorption percentage (%A) was determined as:

$$\%A_e = \frac{A_0 - A_e}{A_0} \times 100 \quad ...(1)$$

The amount qe(mg g^{-1}) of Co^{2+} adsorbed at equilibrium was calculated using the following equation:

$$q_e = \frac{(X_0 - X_e)V}{M} \quad ...(2)$$

Where M is the mass of MPCL(g) , V is the volume of the solution (L), Xo and Xe are the initial and final concentration of Co2+ ion in solution (mg L^{-1})respectively. To evaluate the thermodynamic properties of the adsorption process, 40 mg of MPCL was added into the 100 ml solution with pH of 7.0 and initial Co^{2+} concentration ranging from 30 mg.L^{-1} in every experiment. Each solution was shaken continuously for 60 min at 298K13.

Then Langmuir and Freundlich models were fitted on experimental data. The Freundlich isotherm is appropriate to both monolayer and multilayer adsorption and is based on the assumption that the adsorbates are adsorbed onto the heterogeneous surface of an adsorbent [14]. The Langmuir isotherm assumes monolayer adsorption on a uniform surface with a finite number of adsorption sites [15].

The essential characteristic separation constant factor, RL, for the Langmuir adsorption is defined as follows:

Table 1: Equation model used in this article

Simple equation	Model Isotherm
$\log q_e = \log K_F + \frac{1}{n}\log X_e$	Freundlich isotherm
$\frac{1}{q_e} = \frac{1}{K_L q_m}(\frac{1}{X_e}) + \frac{1}{q_m}$	Langmuir isotherm

Table 2: Model parameters used in this article

Parameter	explanation
K_F	Freundlich isotherm constant (dimensionless)
n	Freundlich isotherm exponent (dimensionless)
K_L	Langmuir constant (L mg^{-1})
q_m	maximum adsorption capacity (mg g^{-1})

$$R_L = \frac{1}{1 + K_L X_0} \quad ...(3)$$

The value of R_L illustrate the shape of the isotherm to be either unfavorable (R_L>1), linear (R_L=1), favorable (0<R_L<1) or irreversible (R_L=0).

The equations and parameters of isotherms of this research have been presented in Tables 1 and 2, respectively.

RESULTS AND DISCUSSION

Adsorption Study

The Effect of pH

Solution pH is one of the most important parameters to determine the adsorption property of an adsorbent that it controlled the kind and amount surface charge of the adsorbent 16, 17. Table 3 illustrate the effect of the pH of the solution on the adsorption percentage of Co^{2+} ion adsorbed onto MPCL. The adsorption percentage was increased with pH and optimum pH was 7.0.

The Effect of Dosage

The effect of MPCL dosage on the adsorption percentage of Co^{2+} ion are shown in table 3. We concluded that the dosage of 40 mg of MPCL was the most suitable. After optimum dosage, all active sites are entirely exposed and the adsorption on the surface is saturated.

The Effect of Temperature

Table 3 show that the adsorption percentage decrease with increasing temperature. Therefore, it may be concluded that the interaction between Co^{2+} ions and MPCL is exothermic in nature. Adsorption decrease may be due to increase the electrostatic repulsion between of the Co^{2+} ions.

The Effect of Contact Time

The effect of contact time, tc , on the adsorption percentage of Co^{2+} ion onto MPCL are shown in table 3. It becomes slower as the adsorbed amount of Co^{2+} ion reaches its equilibrium value. It can be seen that the adsorption process is rapid due to the availability of very active sites on the adsorbent surface at initial stage. This may be due to the special

Table 3: Efficacy of pH (3-7), MPCL Dosage (10-70 mg), temperature (298-348 K) and Contact Time (10-80 min) on Co^{2+} adsorbed by MPCL.

pH	3	4	5	6	7	8	9	10
Co^{2+} Removal %	71.2	73.2	75	76	77.6	76	75.8	75.5
MPCL Dosage(mg)	10	20	30	40	50	60	70	-
Co^{2+} Removal%	56.2	63.6	78.1	78.3	78.3	78.3	78.3	-
Temperature(K)	298	308	318	328	338	348	-	-
Co^{2+} Removal %	89.6	82	78.1	76.2	70.5	66.4	-	-
Time(min)	10	20	30	40	50	60	70	80
Co^{2+} Removal %	42	53	57.2	67.4	76	76	76	76

Table 4: Adsorption datum for Co2+ ions adsorption onto MPCL (pH = 7, tc=50 min, T=298 K, MMPCL =40 mg)

Parameter	Value					
X0 /mg L^{-1}	10	20	30	40	50	60
%A	54	64	74.6	80	83.34	85.73
Xe / mg L^{-1}	4.6	7.2	7.62	8	8.33	8.562
qe / mg g^{-1}	13.5	32	55.95	80	104.17	128.595
log Xe	0.663	0.86	0.882	0.903	0.921	0.933
log qe	1.13	1.51	1.75	1.9	2.02	2.11
1/Xe /L mg^{-1}	0.22	0.139	0.131	0.125	0.12	0.117
1/qe /g mg^{-1}	0.0714	0.03125	0.0179	0.0125	0.0096	0.00778

one atom layered structure of MPCL18. The optimum contact time was obtained as 50 min.

Adsorption Isotherm

An adsorption isotherm is characterized by certain constant values, which express the

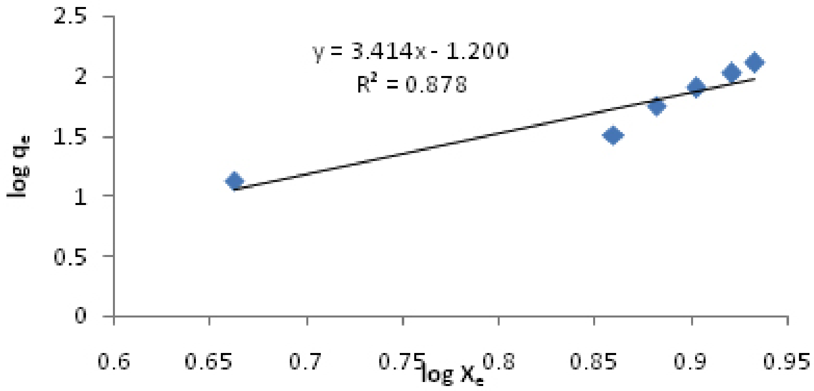

Fig. 1: Freundlich isotherm for cobalt ion adsorption onto MPCL(pH = 7, tc=50 min, T=298 K, MMPCL =40 mg).

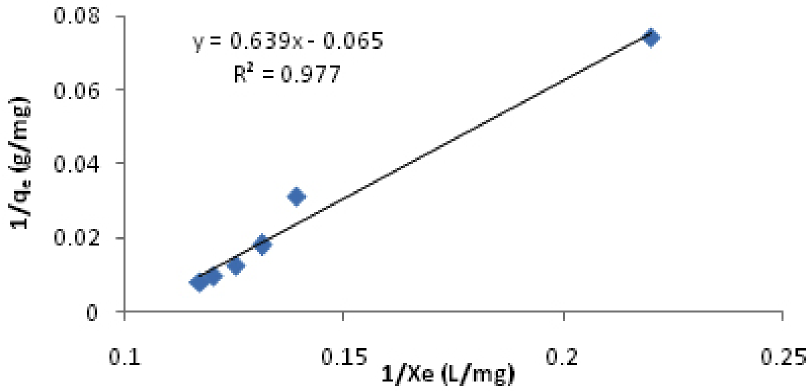

Fig. 2: Langmuir isotherm for cobalt ion adsorption onto MPCL(pH = 7, tc=50 min, T=298 K, MMPCL =40 mg).

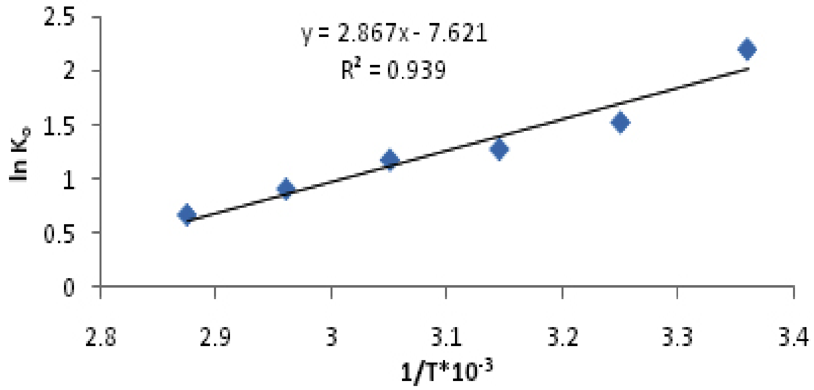

Fig. 3: The effect of temperature on equilibrium constant values (Xo=30 mg.L-1, pH=7, MMPCL =40 mg, tc=50 min).

surface properties of the adsorbent and so on the percentages adsorption of Co^{2+} ion MPCL as a function of initial concentration of Co^{2+} ions are given in table 4.

The plots of two-mentioned Langmuir and Freundlich models are shown in Figs1and 2.

The isotherm parameters calculated from the Langmuir and Freundlich models are listed in Table 5.

The calculated RL values versus initial Co^{2+} concentration are given in table 6, indicating that the Langmuir adsorption of Co2+onto MPCL is favorable19,20.

Thermodynamic Parameters

The thermodynamic parameters of adsorption process can be determined from the variation of thermodynamic equilibrium constant, K_o[22-27]. Where K_o and adsorption standard free energy change (ΔG^0) is calculated according to:

$$K_0 = \frac{a_S}{a_e} = \frac{q_e}{X_e} = \frac{X_0 - X_e}{X_e} \quad ...(4)$$

$$\Delta G^0 = -RTlnK_0 \quad ...(5)$$

Where α_s and α_e are the activity of adsorbed Co^{2+} and the activity of Co^{2+} in solution at equilibrium, respectively.

The average standard enthalpy change (ΔH^o) and the average standard entropy change (ΔS^o) are obtained from the plot of equation (6):

$$lnK_0 = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad ...(6)$$

In order to obtain the quantity of ΔH^o and ΔS^o, Were drawn lnK_o against 1/T (table 7, fig. 3).

The obtained values of thermodynamic parameters (ΔG^0, ΔH^0 and ΔS^0) are listed in table 8.

Table 5: The resultant values for the studied isotherms in connection to Co^{2+} ions adsorption onto MPCL(pH = 7, tc=50 min, T=298 K, MMPCL =40 mg)

Isotherm	Parameter	Value
Freundlich	K_F /(L g^{-1})	15.9
n 0.3		
R^2 0.8786		
Langmuir	KL / (L mg^{-1})	0.102
	qm /(mg g^{-1})	15.31
	R^2	0.9775

Table 6: Separation factor for the adsorption of Co^{2+} onto MPCLin terms of initial concentration of Co^{2+}ions (pH = 7, tc=50 min, T=298 K, MMPCL =40 mg)

Xo / mg L^{-1}	10	20	30	40	50	60
R_L	0.495	0.33	0.25	0.2	0.164	0.14

Table 7: The effect of temperature on Ko values (Xo=30 mg.L-1, pH=7, MMPCL=40 mg, tc=50 min)

T/K	%A	K_0
298	90	8.62
308	82	4.56
318	78	3.57
328	76.3	3.20
338	71	2.39
348	66	1.98

Table 8: Thermodynamic parameters for adsorption Co2+ions onto MPCL(Xo=30 mg.L-1, pH=7, MMPCL =40 mg, tc=50 min)

T/K	ΔG^o/kJmol^{-1}	ΔH^o/ kJmol^{-1}	ΔS^o / kJmol^{-1} K^{-1}
298	-5.337	-23.84	-63.4
308	-3.885	-23.84	-63.4
318	-3.365	-23.84	-63.4
328	-3.172	-23.84	-63.4
338	-2.448	-23.84	-63.4
348	-1.976	-23.84	-63.4

CONCLUSION

The experimental data can be fitted with the Langmuir isotherm, thus indicating the applicability of monolayer coverage of Co^{2+} ion on MPCL surface. The calculated RL values versus initial Co^{2+} concentration that the Langmuir adsorption of Co^{2+} onto MPCL is favorable thermodynamic analysis showed that the adsorption process is exothermic and spontaneous in nature. Negative value of ΔH^0 suggests that the interaction of adsorbed Co^{2+} with MPCL is an exothermic process, which is supported by the decreasing the amount of cobalt ion adsorption with increasing temperature. The negative value of ΔS^0 indicates a decrease randomness and mobility at the adsorbent/solution interface during the adsorption of cobalt ion onto MPCL. The negative values of ΔG^0 reveals the fact that the adsorption process is spontaneous.

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