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ANALYSIS OF SOME SORPTION ISOTHERMS FOR THE REMOVAL OF Ni^{2+}, Pb^{2+} and Cu^{2+} USING ORANGE PEEL ADSORBENT

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ABSTRACT

Adsorption of Ni^{2+}, Pb^{2+} and Cu^{2+} from aqueous solution onto orange peel was studied in a batch system in which residual metal ion concentrations were measured using Shimadzu AA-650 Double Beam Digital Absorption Spectrophotometer. Equilibrium isotherms were analyzed using the Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherm models. In order to determine the type of adsorption exhibited by the metal-adsorbent systems, certain parameters like separation factor, R_L, for Langmuir isotherm; Freundlich constant, n_F, for Freundlich isotherm; and adsorption mean free energy, E, for D-R isotherm were determined and analyzed. The adsorption process was found to be physisorption with E= 1.20, 1.22 and 0.41kJ/mol for Ni^{2+}, Pb^{2+} and Cu^{2+} adsorption, respectively, as explained by the D-R isotherm model.

Keywords: Adsorption, Isotherm, Adsorbent, Orange peel, Physisorption.

INTRODUCTION

Heavy metals pollution has become an environmental problem throughout the world because they can be accumulated in the food chain and caused serious problems, not only for ecosystems, but also for human health. Ni(II), Pb(II) and Cu(II) contained in wastewaters are common as these heavy metals are found in a number of sources/or industrial activities which include electroplating, batteries manufacturing, mining, metal finishing and forging, automobile emission, pesticides, industrial aerosols, fertilizers, insecticides, mineral supplements etc. (Babel and Kurniawan, 2003).

Higher concentrations of Ni (in drinking water) above the maximum permissible level cause cancer of lungs, nose and bone. Dermatitis is the most frequent effect of exposure to Ni. High concentrations of Ni in ingested water may cause severe damage to lungs, kidneys, and gastrointestinal distress etc. (Ibrahim, 2012). High exposure to Pb causes anaemia, vomiting, and constipation etc., while higher concentrations of Cu causes kidney diseases, tuberculosis and arthritis etc. (Alluri *et al.*, 2007).

Removal of heavy metal ions from effluents can be achieved by various methods, but the existing technologies for wastewater treatment have their major problems (Das *et al.*, 2008). Technologies like electro-floatation, electro-kinetic coagulation, and coagulation combined with floatation and filtration, conventional oxidation methods by oxidizing agents, irradiation, and electrochemical processes fall under chemical methods of treatment. These chemical technologies are having many disposal problems and are very expensive to operate, hence the need for some alternative methods, which can overcome all these problems and treat the wastewater in an appropriate way. In the last few decades, biosorption process has emerged as a cost effective and efficient alternative method for water/wastewater treatment, utilizing naturally occurring and agricultural waste materials as biosorbents, as these are cheaper, renewable, and abundantly available (Davis *et al.*, 2003; Aksu, 2005; Romera *et al.*, 2006; Volesky, 2007).

The abundant natural occurrence and presence of large amount of surface functional groups make various agricultural wastes good alternatives to expensive synthetic adsorbents (Bulut and Tez, 2007). As a low-cost, orange peel is an attractive option for biosorption of dissolved metals. Ajmal *et al.* (2000*)* employed orange peel for metal ions removal from simulated wastewater. Some authors reported the use of orange peel as a precursor material for the preparation of an adsorbent by common chemical modification such as alkaline, acid, ethanol and acetone treatment (Perez *et al.*, 2008). This study reveals the importance of using an environmental pollution free approach for the removal of heavy metal ions from water/wastewater.

MATERIALS AND METHODS

All glass wares and plastic containers used were washed with detergents, rinsed with distilled water and then soaked in a 10% HNO_3 solution for 24hrs. They were then washed with deionised water and dried in an oven for 24hrs at 80°C (Ibrahim, 2012). The collected raw orange peel was extensively washed with tap water and then rinsed with distilled water. The biosorbent was cut into small pieces, oven-dried, pulverized and sieved to obtain a powdered orange peel which was used. Distilled, deionised water, AnalaR grade reagents were used without further purification for the preparation of all stock solutions, and were kept in a refrigerator. 0.1M HNO_3 was prepared from conc. HNO_3 and 1000mg/L Ni(II), Pb(II) and Cu(II) were respectively prepared by dissolving 4.95g of $NiCl_2.6H_2O$, 1.599g of $Pb(NO_3)_2$ and 3.8g of $Cu(NO_3)_2.3H_2O$ in small volumes of distilled deionised water in separate beakers and the solutions were transferred to a 1.0litre volumetric flasks each followed by the addition of $100cm^3$ of 0.1M HNO_3 and they were made to mark with more water (Svehla, 2006). Lower working concentrations were prepared daily from the stock solution by appropriate dilution.

The adsorption experiments were performed by batch equilibrium method. The experiments were carried out in $250cm^3$ conical flasks by mixing 1.0g of the adsorbent with $100cm^3$ of each metal ion solutions of concentrations, 10, 15, 30, 45, 60, 75, 90 and 105m/L and pH=6.0 at room temperature using an orbital shaker operating at 200rpm. The samples were removed from the shaker at pre-determined time intervals and the unadsorbed metal ions in the solutions were separated from the adsorbent by filtration and the filtrates were analyzed by using flame atomic absorption spectrophotometer (Perkin Elmer, Analyst 100) to determine the equilibrium metal ion concentrations. All results presented in this report are average of replicate readings. The percentage removal of metal ions and the amount of metal ions adsorbed on orange peel at equilibrium (q_e) were calculated using the following equations:

$$\%removal = \left(\frac{c_o - c_e}{c_o}\right) \times 100 \ldots\ldots\ldots\ldots \quad (1)$$

$$q_e = \frac{(c_o - c_e)v}{w} \ldots\ldots\ldots\ldots \quad (2)$$

where Co and Ce are the concentrations (mg/L) of metal ions initially and at equilibrium time, w is the weight of the adsorbent (g), while V the volume of the solution in litre (Bhattacharya *et al.*, 2008; El-Nemr *et al.*, 2008). The data obtained were tested using the linear forms of Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherm, respectively, as shown in equation (3), (4), and (5) respectively;

$$\frac{c_e}{q_e} = \frac{1}{Q_{max}b} + \frac{c_e}{Q_{max}} \ldots\ldots\ldots\ldots \quad (3)$$

$$logq_e = logk_F + \frac{1}{n}logc_e \ldots\ldots\ldots\ldots \quad (4)$$

$$lnq_e = lnq_{max} - \beta\varepsilon^2 \ldots\ldots\ldots\ldots \quad (5)$$

Where q_e is the amount of metal ions adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration (mg/L), b is a constant related to the energy of adsorption (L/mg), and Q_{max} is the Langmuir maximum adsorption capacity (mg/g), ß = activity coefficient of mean free energy (mol^2/J^2), ε = polanly potential (J/mol), which is defined by equation (6) as;

$$\varepsilon = RTln\left(1 + \frac{1}{c_e}\right) \ldots\ldots\ldots\ldots \quad (6)$$

The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless constant, separation factor or equilibrium parameter, R_L which is defined by equation (7);

$$R_L = \frac{1}{1 + bc_o} \ldots\ldots\ldots\ldots \quad (7)$$

Where b is the Langmuir energy constant (Aksu and Isoglu, 2005) and C_o is the initial adsorabte concentration (mg/L). R_L value indicates the type of isotherm. The condition, $0<R_L<1$ indicates favourable adsorption (physisorption), "n" is the Freundlich constant related to adsorption intensity. If n>1, the adsorption is favoured (physisorption) (Ibrahim and Sani, 2014).

A linearized plot of lnq_e against ε^2 (from equation 3) enables to determine the value of ß and q_{max} from the slope and intercept respectively. Using the value of ß, biosorption mean free energy, E (kJ/mol) is determined by equation (8);

$$E = \frac{1}{(-2\beta)^{\frac{1}{2}}} \ldots\ldots\ldots\ldots \quad (8)$$

If the value of E lies between 8 to 16 kJ/mol, the process is said to follow chemical ion exchange, while if the value of E < 8 kJ/mol, then the process follows physical adsorption (Ibrahim and Sani, 2014).

RESULTS AND DISCUSSION

The values of separation factor, R_L, for Ni (II), Pb(II) and Cu (II) adsorption were found to be -0.04, -0.03 and -0.15 respectively, which are all out of the range, "0 <R_L <1" for favorable physical adsorption (Ibrahim and Sani, 2014). This suggests that Langmuir model cannot be used to explain the physisorption of these metal ions onto orange peel adsorbent.

In the case of Freundlich model for Ni (II), Pb(II) and Cu (II) adsorption. The values of Freundlich constant(n) related to adsorption intensity for Ni (II), Pb(II) and Cu (II) adsorption were found to be -4.31, -1.95, and -1.74 respectively, which are all less than 1, this indicates that Freundlich model cannot be used to explain the physisorption of these metal ions onto orange peel adsorbent (Bayat, 2002).

For D-R isotherm, E (kJmol^{-1}) for Ni (II), Pb(II) and Cu (II) adsorption were found to be 1.20, 1.22 and 0.41 respectively. These values are all far less than 8kJmol^{-1} which indicated favorable physisorption. Hence D-R model can best be used to describe the adsorption of Ni (II), Pb(II) and Cu (II) ions onto orange peel adsorbent (Bayat, 2002).

In order to determine how different values for plotting each of the isotherm models agree between themselves, values of linear coefficient of determination, R^2 were compared. Table 1 shows that the linearity of the Langmuir model was highest of all the three other models (R^2 = 0.9981, 0.9993 and 0.9998 for Ni(II), Pb(II) and Cu(II) adsortion, respectively). This is followed by that of the Freundlich model, and D-R isotherm having the lowest linear coefficients of determination.

Table 1: Isotherm Parameters for Ni(II), Pb(II) and Cu(II) Adsorption onto Orange Peel.

Isotherm	Parameter	Values of parameters		
		Ni	Pb	Cu
Langmuir	R_L	-0.04	-0.03	-0.15
	R^2	0.9981	0.9993	0.9998
Freundlich	n	-4.31	-1.95	-1.74
	R^2	0.987	0.9953	0.9991
D-R	E/kJmol^{-1}	1.20	1.22	0.41
	R^2	0.9757	0.9311	0.9983

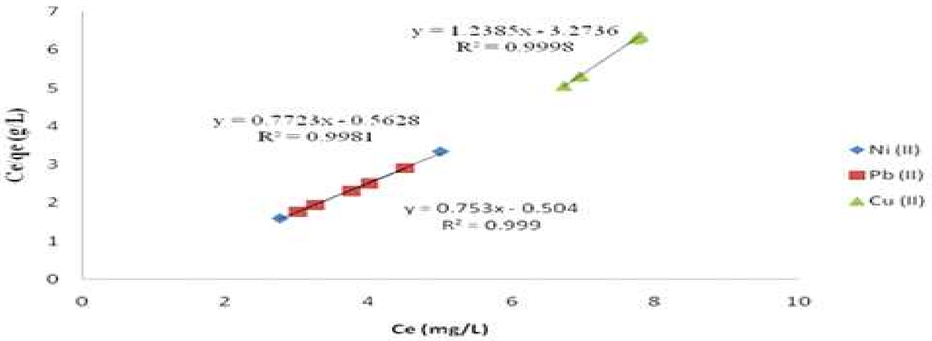

Figure 1: Langmuir Isotherms for the metal ions Adsorption onto Orange Peel Adsorbent.

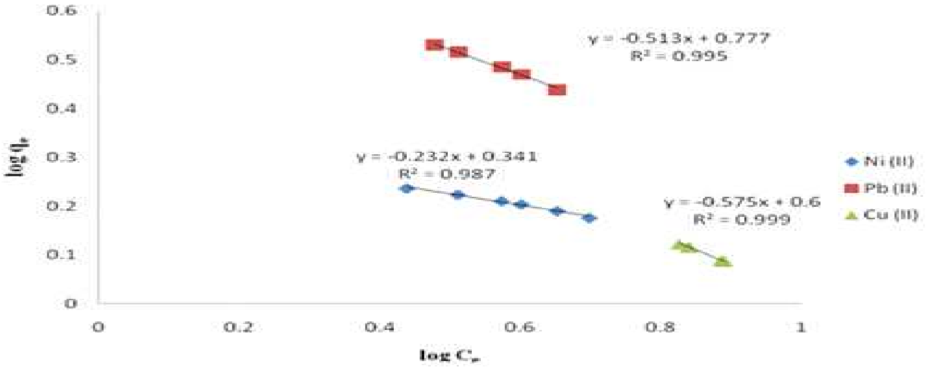

Figure 2: Freundlich Isotherms for the metal ions Adsorption onto Orange Peel Adsorbent.

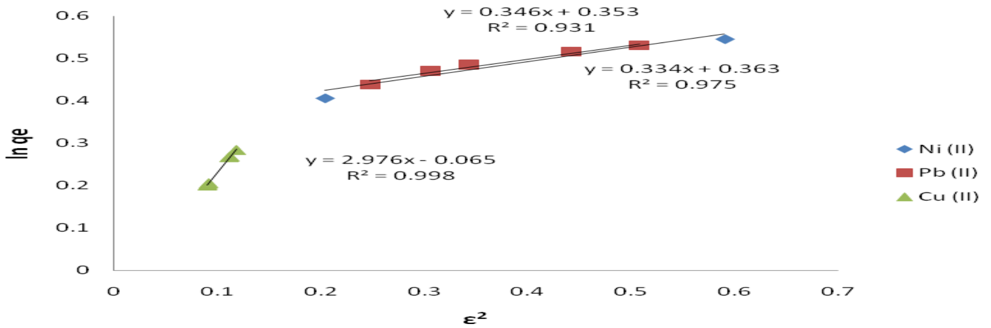

Figure 4.8: D-R Isotherms for the metal ions Adsorption onto Orange Peel Adsorbent.

CONCLUSION

Adsorption of Ni(II), Pb(II) and Cu(II) ions onto orange peel was modelled using the linear forms of Langmuir, Freundlich and D-R isotherm models. The results obtained suggested that D-R model is the best model for describing the physisorption of these metal ions onto surface of the adsorbent.

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