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Error and Regression Analysis of Some Isotherm Models and the Thermodynamic Study of Ni (II), Pb (II) and Cu (II) Adsorption from Aqueous Solution Using Orange Peel

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ABSTRACT: Adsorption of heavy metals, Ni(II), Pb(II) and Cu(II) from their aqueous solutions onto orange peel adsorbent was studied in a batch system. The concentrations of metal ions that remained in the solution were determined from the absorbance values obtained using Shimadzu AA-650 Digital Absorption Spectrophotometer. Adsorption data were modeled using the linear forms of Langmuir, Freundlich and Dubinin-Radushkevich isotherm model. The adsorption data was found to best fit Langmuir model with regression coefficient, $R^2 = 0.9981, 0.9993$ and 0.9998 for Ni(II), Pb(II) and Cu(II) adsorption respectively. Error analysis for the isotherm models was performed using *Chi-square test equation*, in which Langmuir model was found to have the lowest error value of $X^2 = 8.4 \times 10^{-3}$, 3×10^{-4} and 6.3×10^{-5} for Ni(II), Pb(II) and Cu(II) adsorption respectively, which means a better fit. Thermodynamic parameters such as ΔG° , ΔS° and ΔH° for the adsorption systems were determined at three different temperatures, 303, 313 and 323K., in which the adsorption of Ni(II) and Pb(II) ions onto orange peel was found to be exothermic in nature, while that of Cu(II) was endothermic in nature.

KEYWORDS: Adsorption, Heavy metals, Orange peel, Isotherms, Thermodynamics, Regression analysis, Aqueous solution

I. INTRODUCTION

Pollution by heavy metals has become a serious problem to the environment because they have a special ability to bio-accumulate and caused serious problems, not only for ecosystems, but also for human health. This may be as a consequence of the release of substances, which are harmful to either animals or plants, or it may be the release of energy (heat, light, radiation, or sound), which interferes with the development of animals or plants. Generally, pollution is usually harmful to one or more species of animal or plant [1]. On the other hand, a pollutant is any substance produced by human activities which, at an unacceptable level, causes damage to the environment or is harmful to living systems. As such, in order to maintain a healthy living environment, a careful study on the sources and nature of pollution and the ways of pollution control should be considered [2]. Water is one of the abundantly available substances in nature and it is distributed naturally in different forms, such as rainwater, river water, spring water and mineral water. Of these categories, rainwater though associated with some dissolved gases like CO_2 , SO_2 , and NH_3 etc is believed to be the purest. Water is an essential ingredient for the survival of any form of animal and plant life [3]. On average, a human being consumes about 2 litres of water every day. Water accounts for about 70% of the weight of a human body, while about 80% of the earth surface is covered by water. Out of the estimated 1,011 million km^3 of the total water present on earth, only 33,400 m^3 of water is available for drinking, agriculture, domestic and industrial consumption. The rest of which is locked up in oceans as salt water, polar ice-caps and glaciers and underground. Owing to increasing industrialization on one hand and exploding population on the other, the demands of water supply have been increasing tremendously. Moreover, considerable part of this limited quantity of water is polluted by sewage, industrial waste and a wide array of synthetic chemicals [4]. Water pollutants can be divided among some general classifications into organic pollutants, inorganic pollutants, suspended solids and sediments, radioactive

materials and lastly heat. Among these, inorganic pollutants are of most concern for this research. Nickel (II) containing wastewaters are common as it is used in a number of industries including electroplating, batteries manufacturing such as Ni/Fe storage batteries, mining, metal finishing and forging. Also it is used to produce ferrous steel cutlery [5]. Higher concentrations of nickel cause cancer of lungs, nose and bone. Dermatitis (Ni Itch) is the most frequent effect of exposure to Ni, such as coins and jewellery. High concentration of Ni(II) in ingested water may cause severe damage to lungs, kidneys, gastrointestinal distress, e.g., nausea, vomiting, diarrhea, pulmonary fibrosis, renal edema and skin dermatitis [6][7]. Nickel is genotoxic and mutagenic as well. In industrial wastewaters, nickel concentration varies between 6 to 12mg/L, which is above safe limit [8]. High exposure to Pb causes anemia, vomiting, and constipation etc., while a higher concentration of Cu causes kidney diseases, tuberculosis and arthritis etc. [9].

Heavy metals Removal from effluents can be achieved by various methods, but the existing technologies for wastewater treatment have their major problems [1]. 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 [10][11][12][13].

Agricultural materials contain proteins, polysaccharides and lignin which are associated with functional groups (such as -OH, -COOH and C=C) responsible for biosorption of heavy metals [14]. The abundant natural occurrence and presence of large amount of surface functional groups make various agricultural wastes good alternatives to expensive synthetic adsorbents [15].

In recent years, agricultural by-products have been widely studied for metal removal from water. These include peat, wood, pine bark, peel, soybean and cottonseed hulls, peanut shells, hazelnut shells, rice husk, sawdust, wool, and orange peel [16][17]. The use of orange peel as a biosorbent material presents strong potential due to its high content of cellulose, hemicelluloses, pectin (galacturonic acid) and lignin. As a low-cost, orange peel is an attractive option for biosorption of dissolved metals. According to a report [18], orange peel was employed 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 [19].

This study reveals the importance of using an environmental pollution free approach for the removal of heavy metal ions from water/wastewater.

II. MATERIALS AND METHODS

A. General Procedure

Glass wares and plastic containers employed in these experiments were washed with liquid detergent, rinsed with distilled water and then soaked in a 10% HNO₃ solution for a day. They were then washed with deionised water and dried in an oven for 24hrs at 80°C [20]. 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 HNO₃ was prepared from conc. HNO₃ and 1000mg/L Ni(II), Pb(II) and Cu(II) were respectively prepared by dissolving 4.95g of NiCl₂·6H₂O, 1.599g of Pb(NO₃)₂ and 3.8g of Cu(NO₃)₂·3H₂O 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 100cm³ of 0.1M HNO₃ and they were made to mark with more water [21]. 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 250cm³ conical flasks by mixing 1.0g of the adsorbent with 100cm³ of each metal ion solutions of concentrations, 10, 15, 30, 45, 60, 75, 90 and 105mg/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 ion solutions were separated from the adsorbent by filtration and the filtrates were analyzed by using Atomic Absorption Spectrophotometer (Shimadzu AA 650) 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 equation (1) and (2) below;

$$\%removal = \left(\frac{C_0 - C_e}{C_0}\right) 100 \dots\dots\dots (1)$$

$$q_e = \frac{(C_0 - C_e)V}{W} \dots\dots\dots (2)$$

where C_0 and C_e 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 [22][23]. The data obtained were tested using the linear forms of Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherm, respectively, as shown below:

$$\frac{C_e}{q_e} = \frac{1}{Q_{max} b} + \frac{C_e}{Q_{max}} \dots\dots\dots (3)$$

$$\log q_e = \log k_F + \frac{1}{n} \log C_e \dots\dots\dots (4)$$

$$\ln q_e = \ln q_{max} - \beta \epsilon^2 \dots\dots\dots (5)$$

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), β = activity coefficient of mean free energy (mol²/J²), ϵ = polyanly potential (J/mol), which is defined by;

$$\epsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \dots\dots\dots (6)$$

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:

$$R_L = \frac{1}{1 + bC_0} \dots\dots\dots (7)$$

Where b is the Langmuir energy constant and C_0 is the initial adsorbate concentration (mg/L). R_L value indicates the type of isotherm. "n" is the Freundlich constant related to adsorption intensity [24].

A linearized plot of $\ln q_e$ against ϵ^2 (from equation 5) enables to determine the value of β and q_{max} from the slope and intercept respectively. Using the value of β , biosorption mean free energy, E (kJ/mol) is determined by the following equation:

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

1) Error Analysis for the Isotherm Models

The traditional methods of determining the isotherm parameters by linear regression equations appear to give very good fits to experimental data. However, the use of R^2 is limited to solve linear forms of isotherm equation, but not the errors in isotherm curves. To evaluate the fit of isotherm equations to the experimental data, error function of non-linear regression basin was used to measure the isotherm constants and compare them with less accurate linearized analysis values. To do this, Chi-Square Test was employed. According to a report [25], chi-square test is given as;

$$X^2 = \sum_{i=1}^n \left[\frac{(q_{e,exp} - q_{e,calc})^2}{q_{e,exp}} \right] \dots\dots\dots (9)$$

The subscripts "exp" and "calc" show the experimental and calculated values, and n is the number of observations in the isotherm experiment. The small the X^2 value, the better the curve fitting and vice versa.

2) Adsorption Thermodynamic Study

Thermodynamic analysis provides valuable information on the mechanism of adsorption. The thermodynamic parameters, Gibb's free energy change, ΔG° , enthalpy change, ΔH° and entropy change, ΔS° of the adsorption processes were calculated using the following equations;

$$\Delta G^\circ = -RT \ln K \dots\dots\dots (10)$$

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \dots\dots\dots (11)$$

Where K is a constant representing the ratio, $\frac{q_e}{c_e}$, substituting in equation (7) gives;

$$\ln\left(\frac{q_e}{c_e}\right) = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \dots\dots\dots (12)$$

Where, C_e is the concentration of the metal ion (mg/L), q_e is the amount of metal ion at equilibrium in unit mass of adsorbent (mg/g), R is the gas constant (8.314J/mol/k) and T is the temperature (K). The values of ΔS° and ΔH° were obtained from the intercept and slope of the linear plot of $\ln\left(\frac{q_e}{c_e}\right)$ against $\frac{1}{T}$ respectively.

III. RESULTS AND DISCUSSION

A. RESULTS

Table 1: Adsorption Isotherm Parameters for Ni(II), Pb(II) and Cu(II) Ions Adsorption

Isotherm model	Parameter	Metal ion		
		Ni(II)	Pb(II)	Cu(II)
Langmuir	R^2	0.9981	0.9993	0.9998
	X^2	8.4×10^{-3}	3.0×10^{-4}	6.3×10^{-5}
Freudlich	R^2	0.987	0.9953	0.9991
	X^2	8.08	8.27	3.99
Dubinin-Radushkevich	R^2	0.9757	0.9311	0.9983
	X^2	2.74	112.02	0.22

Table 2: Thermodynamic Parameters for Ni(II), Pb(II) and Cu(II) Ions Adsorption

Metal Ion	ΔH° (kJ/mol)	ΔS° (kJ/molK)	ΔG° (kJ/mol)		
			303K	313K	323K
Ni(II)	-54.83	-0.17	-3.32	-1.62	0.08
Pb(II)	-43.57	-0.14	-1.15	0.25	1.65
Cu(II)	4.39	0.01	1.36	1.26	1.16

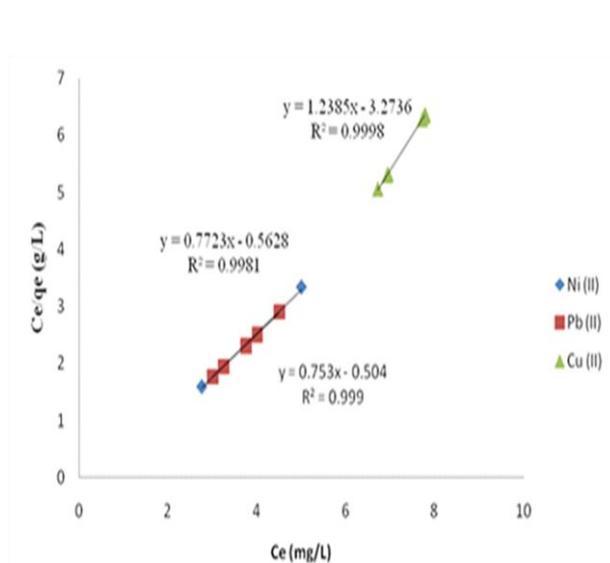


Figure 1: Langmuir Isotherms Plot

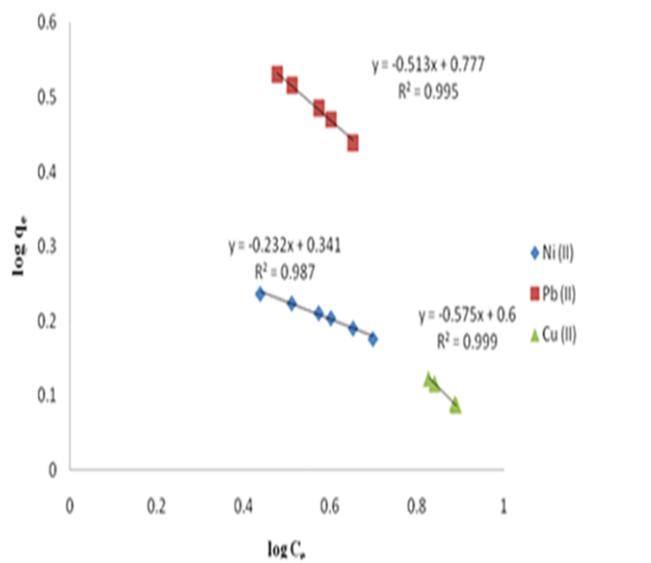


Figure 2: Freundlich Isotherms Plot

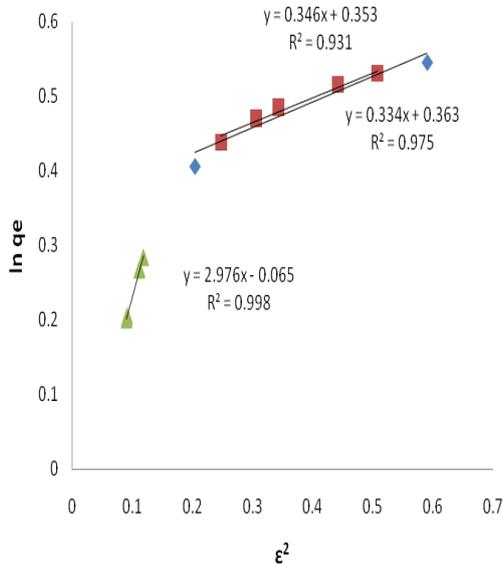


Figure 3: D-R Isotherms Plot

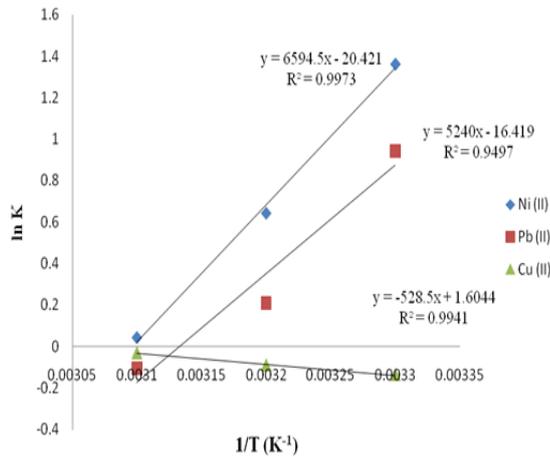


Figure 4: Thermodynamic Plots

B. DISCUSSION

From Table 1, it can be observed that the regression coefficient values (from Fig. 1), $R^2 = 0.9981, 0.9993$ and 0.9998 for Ni(II), Pb(II) and Cu(II) ions adsorption, respectively for the Langmuir isotherm are all relatively higher than those of Freundlich and D-R isotherms (Fig. 1 and 2), this indicates that the Langmuir isotherm best fit the adsorption data when compared with the Freundlich and the D-R isotherm, or in other words, the adsorption can best be described using the Langmuir isotherm model [26]. In addition, Table 1 shows that error analysis carried out further proved that the Langmuir model is the best model for describing the adsorption of Ni(II), Pb(II) and Cu(II) ions onto the adsorbent surface. This is as a result of the relatively very small error values i.e. $X^2 = 8.4 \times 10^{-3}, 3 \times 10^{-4}$ and 6.3×10^{-5} for Ni(II), Pb(II) and Cu(II) adsorption, respectively compared to Freundlich and Dubinin-Radushkevich model [25].

The calculated values of thermodynamic parameters, ΔG° , ΔH° and ΔS° obtained from Van't Hoff plot (Fig. 4) were presented in Table 2. The ΔG° values were calculated at three different temperatures (303K, 313K and 323K) for each metal ion. The negative values of ΔG° at 303 and 313K for Ni(II) adsorption and at 303K for Pb(II) adsorption suggested that the adsorption was spontaneous in nature. While the positive value of ΔG° at 303 and 323K for Pb(II) adsorption and at three different temperatures for Cu(II) adsorption showed that a chemical sorption process occurred under the experimental conditions [27].

In the case of entropy change of the system, ΔS° , the negative values of ΔS° for Ni(II) and Pb(II) adsorption confirmed the decreased randomness at the adsorbent-adsorbate interface during adsorption. The positive values of ΔS° during Cu(II) adsorption indicated that there is increased randomness at the adsorbent-adsorbate interface during the adsorption of Cu(II) ions onto orange [28]. For Ni(II) and Pb(II) adsorption, the negative values of ΔH° indicate the exothermic nature of these metal ions onto orange peel. While in the case of Cu(II) adsorption where ΔH° is positive, this implies that the adsorption process was endothermic in nature [29].

IV. CONCLUSION AND FUTURE WORK

Adsorption of Ni(II), Pb(II) and Cu(II) ions onto orange peel was studied. The modeling of the experimental data was performed using the linear forms of Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherm model. The results obtained suggested that Langmuir model is the best model for describing the adsorption of these metal ions onto the surface of the adsorbent. Adsorption of Ni(II) and Pb(II) ions onto orange peel was exothermic in nature, while



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that of Cu(II) was endothermic in nature. Many different other isotherm models should be applied in future adsorption studies for the removal of Ni(II), Pb(II) and Cu(II) ions from aqueous solution using orange in order to find whether there is any model that will fit the adsorption data better than the Langmuir model.

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