

Equilibrium Isotherm Models for Adsorption of Zinc (II) ion from Aqueous Solution on Pulp Waste

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Abstract: - The present investigation deals with the utilization of pulp waste as an adsorbent for the removal of zinc (II) ion from aqueous solution. A series of experiments were conducted in a batch system to evaluate the performance of the pulp waste for zinc removal. The effects of pH, adsorbent dosage, initial concentration and temperature were evaluated. The optimum pH value for zinc (II) adsorption on the pulp waste was found to be pH 6.0. The equilibrium sorption data were analyzed using Freundlich, Langmuir, Temkin, Halsay, Hurkins-Jura, Redlich-Peterson, Dubinin-Radushkevich and Jovanovich isotherm models, and the Langmuir and Temkin models were found to be adequate in describing the zinc (II) adsorption onto the pulp waste.

Key-Words: - Adsorption, Equilibrium isotherm, Pulp waste, Zinc (II) ion, Langmuir, Temkin, Halsay, Hurkins-Jura, Redlich-Peterson, Dubinin-Radushkevich, Jovanovich

1. Introduction

Zinc is involved in numerous aspects of cellular metabolism. It is required for the catalytic activity of approximately 100 enzymes [1, 2] and it plays a role in immune function [3,4], protein synthesis [4], wound healing [5], DNA synthesis [2, 4], and cell division [4]. Zinc also supports normal growth and development during pregnancy, childhood, and adolescence [6-8] and is required for proper sense of taste and smell [9]. A daily intake of zinc is required to maintain a good health because the human body has no specialized zinc storage system [10]. A wide variety of foods contain zinc [2]. Oysters contain more zinc per serving than any other food, but red meat and poultry provide the majority of zinc in the American diet. Other good food sources include beans, nuts, certain types of seafood (e.g., crab and lobster), whole grains, fortified breakfast cereals, and dairy products [2].

However, excess amounts of heavy metals are toxic and harmful to human being. Zinc is most often found in plating and galvanizing operations. In plating shops, the zinc often complexes with cyanide and the cyanide must be treated to free the zinc before precipitation can occur. Traditional cyanide destruct systems use sodium hypochlorite to oxidize the cyanide. Like copper, zinc can be precipitated as hydroxide which can be removed by ion exchange.

The removal of zinc ions from wastewater can be done using different methods, such as ion exchange, chemical precipitation, reverse osmosis, electrochemical treatment, evaporative recovery, and adsorption [11-13]. However, these treatment methods are costly and also suffer from incomplete removal. The search for new cost effective technologies involving the removal of heavy metals has been oriented to adsorption based on metal binding capacities of different low cost materials. Several adsorbents, such as bagasse fly ash [14], fly ash [15], wheat shell [16], spent activated clay [17], modified goethite [18], pineapple and paper waste [19] have been used for treatment of heavy metal ions adsorption.

Adsorption is defined as a process where solute is removed from a liquid phase through contact with a solid adsorbent which has a special affinity to that particular solute. The main advantages of adsorption process are low operating cost, easily available sorbent sources, minimization of the volume of sludge to be disposed of, recovery of the metal from the adsorbents and regeneration of the adsorbents for reuse. A number of natural and synthetic adsorbents have been studied by various researchers for the removal of heavy metal ions.

In the present investigation pulp waste has been used as an adsorbent for the removal of zinc (II), with an objective to explore the possibility of

utilizing pulp waste for the adsorptive removal of zinc (II) from waste water solutions. The effects of initial pH, adsorbent doses, initial metal concentration and temperature were investigated. The experimental equilibrium adsorption data were fitted to the Freundlich, Langmuir, Temkin, Hurkins-Jura, Halsay, Redlich-Peterson, Dubinin-Radushkevich and Jovanovic isotherm equations to determine the best-fit isotherm.

2. Materials and Methods

2.1 Preparation of Adsorbent

The pulp waste was obtained from the Berli Jucker Public Co. Ltd. (Thailand). The waste was produced from the final recycle pulp process of the pulp processing facility. The pulp waste was washed with distilled water to remove suspended materials and the dried in an oven at 105 °C for 48 h. The dried sludge was sieved into particle size ranges 150-300 µm. The so prepared pulp waste was kept in desiccators prior to adsorption experiments.

2.2 Chemical Reagents

All reagents used in this study were of analytical grade. A stock solution of zinc (II) was prepared by dissolving a predetermined amount of zinc chloride in 1 L of distilled water. All solutions used in the adsorption experiments were prepared by diluting the stock solution to the required concentrations. The pH of each feed solution was adjusted to a given initial pH value using 1 M HCl or 1 M NaOH. The concentration of residual zinc (II) in the liquid solution was determined with an atomic absorption spectrophotometer (Varian AA220).

2.3 Batch Adsorption Experiments

Adsorption experiments for zinc (II) ion on the adsorbents were carried out using a batch method. The initial pH of the solution was adjusted with hydrochloric acid or sodium hydroxide before addition of the adsorbent; the pH was monitored using a pH meter throughout the experiments. 1 g of adsorbent was added to 100 mL of the zinc (II) solution at a pH maintained in a range of 2 to 13. The solution was stirred in a digital shaker at 110 rpm and at a constant temperature (30 °C). The samples were filtrated and the zinc (II) concentration in the solution was analyzed using the atomic absorption spectrophotometer.

The zinc (II) adsorption capacity was determined at different zinc (II) concentrations

ranging from 50-200 ppm and a fixed amount (1 g) of adsorbent in 100 mL solution was used to calculate the adsorption constant by using different isotherms. The adsorption capacities of the adsorbent were calculated. After the sorption equilibrium was attained, the zinc (II) uptake capacity was calculated to based on mass balance

$$q_e = \frac{(C_i - C_e) V}{m} \quad (1)$$

where C_i = initial zinc (II) concentration; C_e = equilibrium zinc (II) concentration; V = volume of the solution (L) and m = weight of pulp waste (g).

The zinc (II) removal efficiency of sorption is calculated using the equation

$$\text{Zinc (II) removal efficiency(\%)} = \frac{(C_i - C_e)}{C_i} \times 100 \quad (2)$$

2.4 Adsorption Equilibrium Isotherm

2.4.1 Freundlich adsorption isotherm

The Freundlich adsorption isotherm is based on the equilibrium sorption on heterogeneous surfaces. This isotherm is derived from the assumption that the adsorption sites are distributed exponentially with respect to heat of adsorption. The adsorption isotherm is expressed by the following equation [20-21]:

$$q_e = K_F C_e^{1/n_F} \quad (3)$$

which can be linearized as

$$\ln q_e = \ln K_F + \frac{1}{n_F} \ln C_e \quad (4)$$

where q_e is the amount of zinc (II) adsorbed at equilibrium (mg/g) and C_e is the concentration of zinc (II) in the aqueous phase at equilibrium (ppm). K_F (L/g) and $1/n_F$ are the Freundlich constants related to adsorption capacity and sorption intensity, respectively.

2.4.2 Langmuir adsorption isotherm

The Langmuir adsorption isotherm is based on the assumption that all sorption sites possess equal affinity to the adsorbate. The Langmuir isotherm in a linear form can be represented as [22-23]:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (5)$$

where q_e is the amount of zinc (II) adsorbed at equilibrium (mg/g) and C_e is the concentration of zinc (II) in the aqueous phase at equilibrium (ppm). q_m is the maximum zinc (II) uptake (mg/g), and K_L is the Langmuir constant related to adsorption capacity and the energy of adsorption (g/mg).

2.4.3 Temkin adsorption isotherm

The Temkin adsorption isotherm assumes that the heat of adsorption decreases linearly with the sorption coverage due to adsorbent-adsorbate interactions [24-25.] The Temkin isotherm equation is given as:

$$q_e = \frac{RT}{b_T} \ln (K_T C_e) \quad (6)$$

which can be represented in the following linear form

$$q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e \quad (7)$$

where K_T (L/g) is the Temkin isotherm constant, b_T (J/mol) is a constant related to heat of sorption, R is the ideal gas constant (8.314 J/mol K), and T is absolute temperature (K).

2.4.4 Hurkins-Jura adsorption isotherm

The Hurkins-Jura adsorption isotherm can be expressed as [26-27]:

$$q_e = \sqrt{\frac{A_H}{B_H + \log C_e}} \quad (8)$$

which can rearranged as follows:

$$\frac{1}{q_e^2} = \frac{B_H}{A_H} - \frac{1}{A_H} \log C_e \quad (9)$$

where A_H (g²/L) and B_H (mg²/L) are two parameters characterizing the sorption equilibrium.

2.4.5 Halsay adsorption isotherm

The Halsay adsorption isotherm can be given as [28-29]:

$$q_e = \exp\left(\frac{\ln K_{Ha} - \ln C_e}{n_{Ha}}\right) \quad (10)$$

and a linear form of the isotherm can be expressed as follows:

$$\ln q_e = \frac{\ln K_{Ha}}{n_{Ha}} - \frac{\ln C_e}{n_{Ha}} \quad (11)$$

where K_{Ha} (mg/L) and n_{Ha} are the Halsay isotherm constants.

2.4.6 Radlich-Peterson adsorption isotherm

The Radlich-Peterson adsorption isotherm contains three parameters and incorporates the features of Langmuir and Freundlich isotherms into a single equation. The general isotherm equation can be described as follows [30-31]:

$$q_e = \frac{K_R C_e}{1 + a_R C_e^g} \quad (12)$$

The linear form of the isotherm can be expressed as follows:

$$\ln \frac{C_e}{q_e} = g \ln C_e - \ln K_R \quad (13)$$

where K_R (L/g) and a_R (L/mg) are the Radlich-Peterson isotherm constants, and g is the exponent between 0 and 1. There are two limiting cases: Langmuir form for $g = 1$ and Henry's law for $g = 0$.

2.4.7 Dubinin-Radushkevich adsorption isotherm

The Dubinin-Radushkevich adsorption isotherm is another isotherm equation [32]. It is assumed that the characteristic of the sorption curve is related to the porosity of the adsorbent. The linear form of the isotherm can be expressed as follows [33-34]:

$$\ln q_e = \ln Q_D - B_D \left[RT \ln \left(1 + \frac{1}{C_e} \right) \right]^2 \quad (14)$$

where Q_D is the maximum sorption capacity (mol/g), and B_D is the Dubinin-Radushkevich constant (mol²/kJ²).

2.4.8 Jovanovic adsorption isotherm

The model of an adsorption surface considered by Jovanovic [35] is essentially the same as that considered by Langmuir. The Jovanovic model leads to the following relationship [29]:

$$q_e = q_{\max} (1 - e^{-K_J C_e}) \quad (15)$$

The linear form of the isotherm can be expressed as follows:

$$\ln q_e = \ln q_{\max} - K_J C_e \quad (16)$$

where K_J (L/g) is a parameter. q_{\max} (mg/g) is the maximum zinc (II) uptake.

2.5 Error Analysis

The traditional methods of determining the isotherm parameters by linear regression appear to give a good fit to experimental data. However, the R^2 is based on the linear forms of the isotherm equations, but does not represent the errors in the isotherm curves. To evaluate the fit of the isotherm equations to the experimental data, different error functions of non-linear regression were used here to determine the constants model parameters, and they were compared with those determined from the less accurate linearized data fitting. The residual root mean square error (RMSE) and chi-square test were used. RMSE can be defined as [36, 37]

$$RMSE = \sqrt{\frac{1}{n-2} \sum_{i=1}^n (q_{e,exp} - q_{e,cal})^2} \quad (17)$$

The subscripts "exp" and "cal" show the experimental and calculated values and n is the number of observations in the experimental isotherm. The smaller the RMSE value, the better the curve fitting. The chi-square test (38) is given as

$$\chi^2 = \sum_{i=1}^n \frac{(q_{e,exp} - q_{e,cal})^2}{q_{e,exp}} \quad (18)$$

If the data from the model calculation are close to the experimental data, χ^2 will be a small number; the χ^2 value can be used to measure how well the model fits.

3. Results and Discussion

3.1 Effect of initial pH on zinc (II) adsorption

pH is an important parameter influencing heavy metal adsorption from aqueous solutions. It influences not only the surface charge of the adsorbent, the degree of ionization of material present in the solution, but also the dissociation of functional groups on the active sites of the adsorbent [39]. Fig. 1 shows the effects of initial pH of the solution on the adsorption of zinc (II) onto pulp waste at an initial zinc chloride concentration of 100 ppm. As shown in Fig 1, the sorption uptake of zinc (II) depends on pH. It increases with pH from 2.0 to 6.0, and above these levels, a further increase in pH will decrease the sorption uptake. At low pH values, there is a competition between the protons and zinc ions on the sorption sites. At a higher pH, insoluble zinc hydroxide starts to precipitate from the solutions. The maximum removal efficiency was 60 % at pH 6.0, corresponding to a maximum adsorption capacity (q_e) of 2.82 mg/g under the experimental conditions. Consequently, the working pH for zinc (II) removal by adsorption onto pulp waste was chosen as 6.0 for subsequent adsorption experiments.

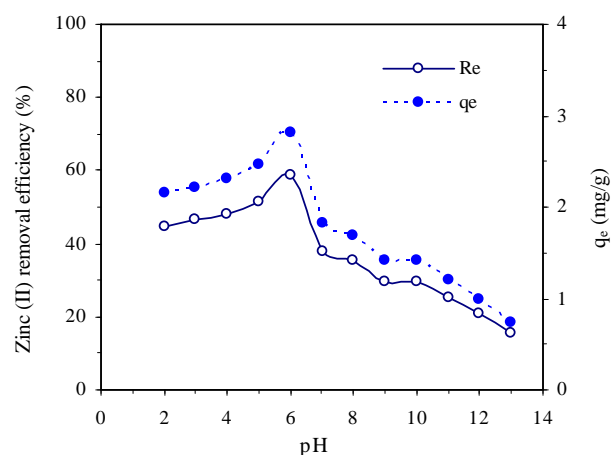


Fig. 1 Effect of pH on zinc (II) adsorption onto pulp waste (conditions: initial $ZnCl_2$ concentration 100 ppm, adsorbent dose 1 g/100 mL, agitation speed 110 rpm, contact time

3.2 Effect of Temperature

The effect of temperature on adsorption of zinc onto pulp waste was investigated at three different temperatures (30, 40 and 50 °C). Fig. 2 shows the adsorption occurred rapidly in the first 60 min, after which the adsorption gradually slowed down. The adsorption appeared to have reached equilibrium with 120 min.

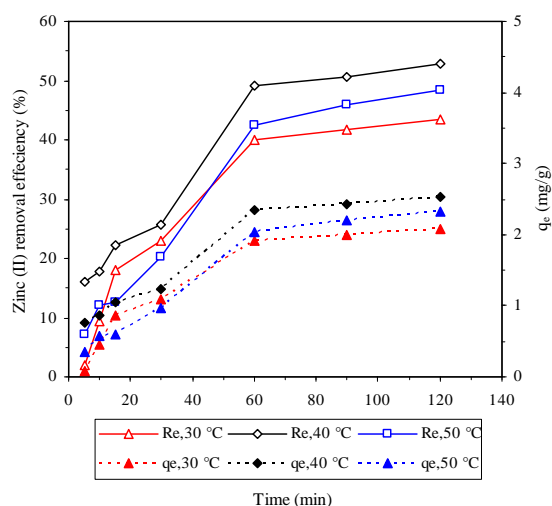


Fig. 2 Effect of temperature on percentage of zinc (II) removal (R_e) and adsorption capacity (q_e) onto pulp waste (conditions: initial $ZnCl_2$ concentration 100 ppm, adsorbent dose 1 g/100 mL, agitation speed 110 rpm, contact time 120 min, pH 6.0)

From Fig. 2, the sorption uptake increases with an increase in temperature from 30 to 40°C. At an initial zinc chloride concentration of 100 ppm, the equilibrium uptake increased from 2.08 to 2.54 mg zinc (II) per gram of adsorbent with increasing temperature from 30 to 40 °C. However, a further increase in temperature to 50°C decreased the equilibrium uptake to 2.32 mg zinc (II) per gram of adsorbent. Zinc sorption was exothermic, and thus the extent of sorption increased with a decrease in temperature. The adsorption of zinc on dried pulp waste may involve mainly physical sorption. The decrease in sorption capacity of dried pulp waste at higher temperature (50°C) may be attributed to the deactivation of the adsorbent surface or the destruction of some active sites on the adsorbent surface due to bond rupture.

3.3 Effect of Adsorbent dosage

The effect of adsorbent dose on the removal of zinc (II) was investigated by changing the quantity of adsorbent in the test solution, as shown in Fig 3. The removal of zinc (II) increased with an increase in the adsorbent dosage up to a certain level and then it remains almost constant. This is expected because of the increase in the adsorbent surface area and the availability of more adsorption sites [40]. In contrast, the adsorption capacity of zinc (II) onto pulp waste decreased with the increase in dose of adsorbent. It was decreased from 2.54 to 1.35 and

0.84 mg/g with an increase in the dose of adsorbent from 1 to 3 and 5 g, respectively.

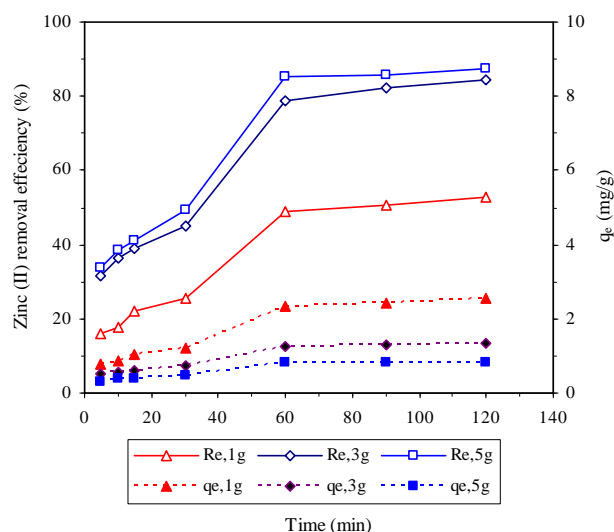


Fig. 3 Effect of adsorbent dose on percentage of zinc (II) removal (R_e) and adsorption capacity (q_e) onto pulp waste (conditions: initial $ZnCl_2$ concentration 100 ppm, agitation speed 110 rpm, contact time 120 min, temperature 40 °C, pH 6.0)

3.4 Effect of initial zinc concentration

The adsorption capacity was determined at different $ZnCl_2$ concentrations ranging from 50 to 200 ppm. Fig. 4 shows the adsorption uptake at different contact time at different initial zinc chloride concentrations. It is shown that the adsorption was fast during the early period of sorption but began to slow down gradually at the end. The initial faster rates of adsorption may be attributed to the presence of a larger number of binding sites available for adsorption, and the gradually reduced adsorption rates at the end were caused by the saturation of the binding sites and attainment of equilibrium. The adsorption appeared to have reached equilibrium within 60 min irrespective of initial $ZnCl_2$ concentration.

It is also observed that as the initial $ZnCl_2$ concentration increased from 50 to 200 ppm, the adsorption capacity of the adsorbent increased. This is easy to understand because a higher metal concentration means a greater driving force for mass transfer from the aqueous solution to the solid adsorbent. However, for a given adsorbent dosage, the percentage removal of zinc (II) decreased with an increase in the initial $ZnCl_2$ concentration, as shown in Fig. 5. This can be explained by the fact that the adsorbent has a limit number of active sites, and fewer of them are available at equilibrium

sorption at a higher zinc loading levels. This indicates that the overall adsorption uptake will increase with an increase in the initial ZnCl₂ concentration but the percentage of zinc that can be adsorbed decreases.

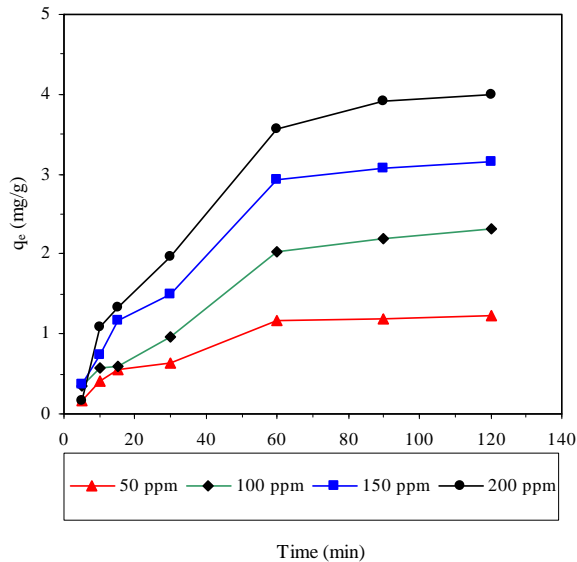


Fig. 4 Effect of initial ZnCl₂ concentration on the adsorption capacity onto pulp waste (conditions: adsorbent dose 1 g/100 mL, agitation speed 110 rpm, contact time 120 min, temperature 40 °C, pH 6.0)

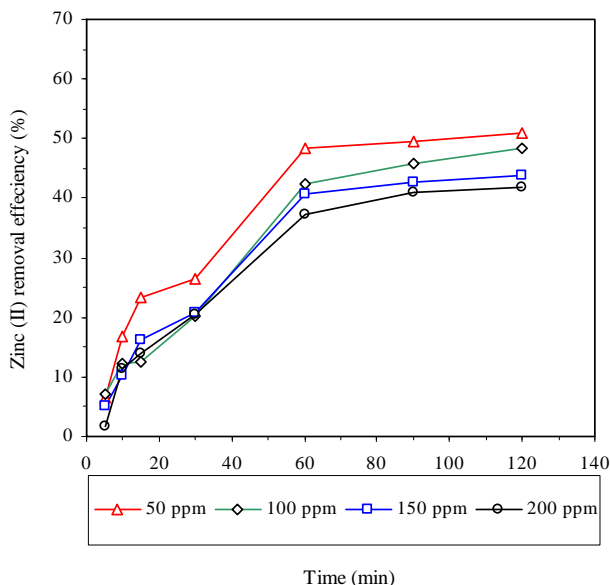


Fig. 5 Effect of initial ZnCl₂ concentration on percentage of zinc (II) removal efficiency onto pulp waste (conditions: adsorbent dose 1 g/100 mL, agitation speed 110 rpm, contact time 120 min, temperature 40 °C, pH 6.0)

3.5 Adsorption Equilibrium Isotherm

It is important to determine the most appropriate correlation for equilibrium adsorption isotherm, to optimize the design of a sorption system. The Freundlich, Langmuir, Temkin, Hurkins-Jura, Halsay, Redlich-Peterson, Dubinin-Radushkevich and Jovanovich isotherm models were used to analyze the adsorption equilibrium. Experimental isotherm data were obtained at an adsorption time of 120 min at different temperatures.

3.5.1 Freundlich adsorption isotherm

The Freundlich constants K_F and $1/n_F$ were calculated from the slope and intercept of the $\ln q_e$ versus $\ln C_e$ plot, as shown in Fig. 6, and the model parameters are shown in Table 1. The magnitude of K_F showed that pulp waste had a high capacity for zinc (II) adsorption from the aqueous solutions studied. The Freundlich exponent, n_F , should have values in the range of 1 and 10 (i.e., $1/n_F < 1$) to be considered as favorable adsorption [23]. A $1/n_F$ value of less than 1 indicated that zinc (II) is favorably adsorbed by pulp waste. As shown in Fig. 7, the Freundlich isotherm did not show a good fit to the experimental data as indicated by RMSE and Chi-square statistics in Table 1.

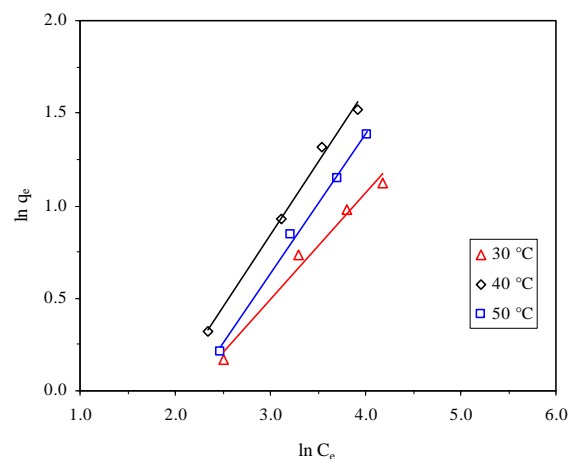


Fig. 6 Freundlich isotherm at different temperatures

Table 1 Isotherm constants for zinc (II) adsorption onto pulp waste at different temperatures

Isotherm Model	Parameters	Temperature (°C)		
		30 °C	40 °C	50 °C
1. Freundlich	K_F (L/g)	0.578	0.780	0.751
	$1/n_F$	0.289	0.224	0.198
	R^2	0.982	0.995	0.995
	RMSE	0.393	0.737	0.611
	χ^2	0.145	0.419	0.321
2. Langmuir	q_m (mg/g)	5.050	11.822	9.765
	K_L (g/mg)	0.025	0.013	0.012
	R^2	0.999	0.998	0.999
	RMSE	0.054	0.119	0.074
	χ^2	0.002	0.009	0.004
3. Temkin	K_T (L/g)	0.230	0.176	0.1640
	b_T (J/mol)	2221.729	1269.705	1548.645
	R^2	0.999	0.980	0.986
	RMSE	0.012	0.245	0.173
	χ^2	0.0001	0.051	0.022
4. Hurkins-Jura	A_H (g ² /L)	1.174	1.386	1.129
	B_H (mg ² /L)	1.849	1.679	1.739
	R^2	0.890	0.909	0.893
	RMSE	2.558	3.800	3.290
	χ^2	4.981	7.606	6.597
5. Halsay	K_{Ha} (mg/L)	0.116	0.147	0.116
	n_{Ha}	1.731	1.282	1.332
	R^2	0.982	0.995	0.995
	RMSE	3.283	4.628	4.027
	χ^2	8.660	12.069	10.557
6. Redlich-Peterson	g	0.422	0.220	0.249
	K_R (L/g)	2.236	1.953	1.854
	a_R (L/mg)	7.729	8.187	9.067
	R^2	0.967	0.943	0.957
	RMSE	2.171	0.193	0.112
χ^2	0.027	0.018	0.011	
7. Dubinin-Radushkevich	B_D (mol ² /kJ ²)	23.630	19.696	23.184
	Q_D (mol/g)	2.865	4.086	3.578
	R^2	0.951	0.904	0.926
	RMSE	0.285	0.675	0.528
	χ^2	0.065	0.273	0.174
8. Jovanovic	K_J (L/g)	-0.017	-0.030	-0.026
	q_{max} (mg/g)	1.115	1.155	1.048
	R^2	0.868	0.923	0.925
	RMSE	2.582	3.710	3.210
	χ^2	5.477	7.717	6.692

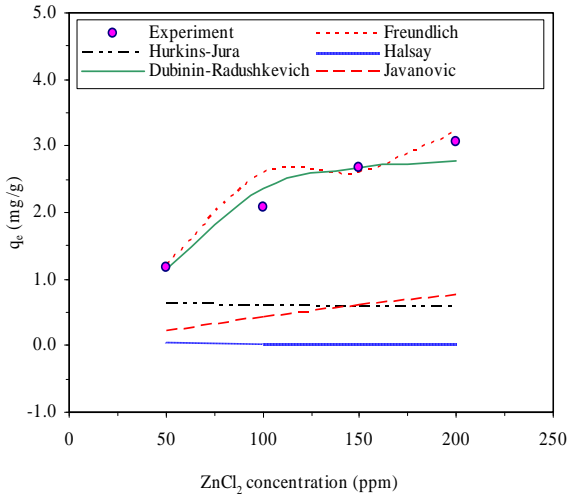


Fig. 7 Comparison between the experimental ($q_{e, \text{exp}}$) and calculated ($q_{e, \text{cal}}$) data for the Freundlich, Hurkins-Jura, Halsay, Dubinin-Radushkevich, and Jovanovic adsorption isotherms of zinc (II) at 30 °C onto pulp waste

3.5.2 Langmuir adsorption isotherm

A linear plot of C_e/q_e versus C_e was employed to determine the value of q_m and K_L , as shown in Fig. 8, and the data so obtained were also presented in Table 1. The model predicted a maximum value that could not be reached in the experiments. The value of K_L decreased with an increase in the temperature. A high K_L value indicates a high adsorption affinity. The monolayer saturation capacity, q_m , is shown to be 5.05, 11.82 and 9.77 mg/g at a temperature of 30, 40 and 50 °C, respectively.

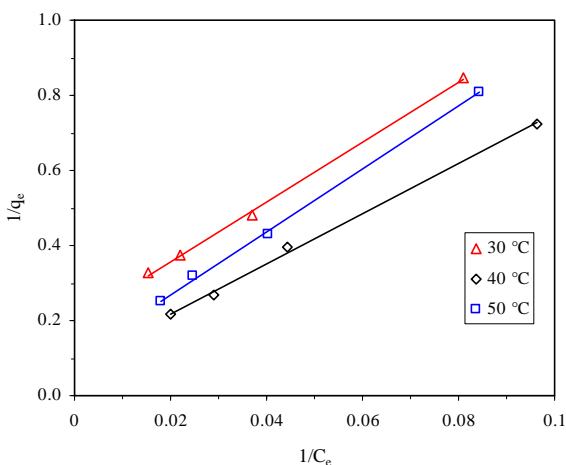


Fig. 8 Langmuir isotherm at different temperatures

Weber and Chakraborti [41] expressed the Langmuir isotherm in term of dimensionless constant separation factor or equilibrium parameter (R_L) defined in the following equation:

$$R_L = \frac{1}{1 + K_L C_0} \tag{19}$$

where C_0 is the initial zinc (II) concentration (ppm). Four scenarios can be distinguished: 1) The sorption isotherm is unfavorable when $R_L > 1$, 2) the isotherm is linear when $R_L = 1$, 3) the isotherm is favorable when $0 < R_L < 1$ and 4) the isotherm is irreversible when $R_L = 0$. The values of dimensionless separation factor (R_L) for zinc (II) removal were calculated at different concentrations and temperatures. As shown in Table 2, at all concentrations and temperatures tested, the values of R_L for zinc (II) adsorption on the pulp waste were less than 1 and greater than zero, indicating favorable adsorption.

Table 2 dimensionless constant separation factor (R_L)

Initial ZnCl ₂ concentration	Temperature		
	30 °C	40 °C	50 °C
50 ppm	0.00333	0.00396	0.00348
100 ppm	0.00077	0.00092	0.00084
150 ppm	0.00031	0.00040	0.00035
200 ppm	0.00016	0.00021	0.00019

The Langmuir isotherm showed a better fit to the adsorption data than the Freundlich isotherm as shown in Fig. 7 and Fig. 9. The fact that the Langmuir isotherm fits the experimental data well may be due to homogeneous distribution of active sites on the pulp waste surface, since the Langmuir equation assumes that the adsorbent surface is energetically homogeneous.

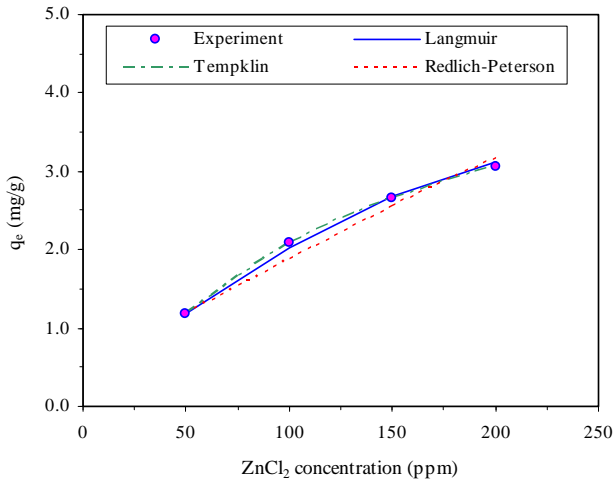


Fig. 9 Comparison between the experimental ($q_{e, \text{exp}}$) and calculated ($q_{e, \text{cal}}$) data for the Langmuir, Temkin and Redlich-Peterson adsorption isotherms of zinc (II) at 30 °C onto pulp waste

3.5.3 Temkin adsorption isotherm

A plot of q_e versus $\ln C_e$ enables the determination of isotherm constants K_T and b_T from the slope and intercept, as shown in Fig. 10. The model parameters are listed in Table 1. The Temkin isotherm appears to provide a good fit to the zinc (II) adsorption data. The non-linear error analysis results are also presented in Table 1.

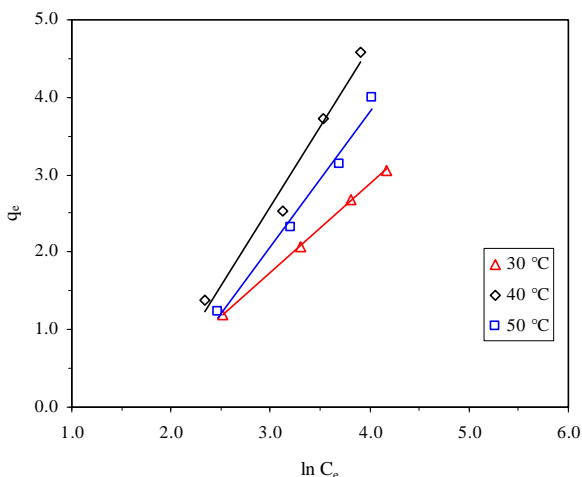


Fig. 10 Temkin isotherm at different temperatures

The adsorption energy in the Temkin model, b_T , is positive for zinc (II) adsorption from the aqueous solution, which indicates that the adsorption is exothermic. Temkin isotherm is compared with the corresponding experimental data

in Fig. 9, and the RMSE and χ^2 values are presented in Table 1. The experimental equilibrium curve is close to that predicted by Temkin model. Consequently, the adsorption isotherm of zinc (II) on pulp waste can be described reasonably well by the Temkin isotherm.

3.5.4 Hurkins-Jura adsorption isotherm

A plot of $1/q_e^2$ versus $\log C_e$ enables the determination of model parameters A_H and B_H from the slope and intercept in Fig. 11. The isotherm equation accounts for multilayer adsorption and can be explained by the existence of a heterogeneous pore distribution.

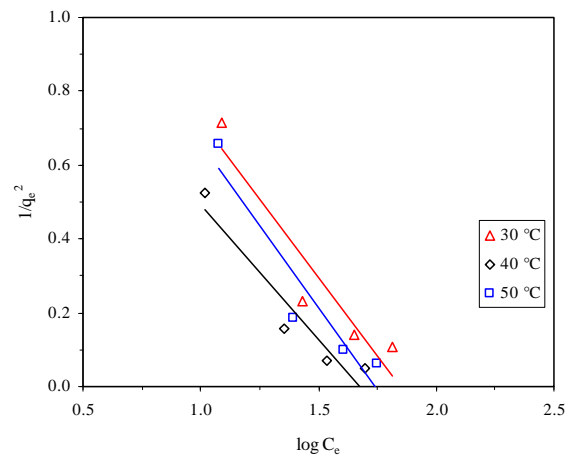


Fig. 11 Hurkins-Jura isotherm at different temperatures

3.5.5 Halsay adsorption isotherm

A plot of $\ln q_e$ versus $\ln C_e$, shown in Fig. 12, enables the determination of n_{Ha} and K_{Ha} from the slope and intercept. This equation is suitable for multilayer adsorption and the fitting of the experimental data to this equation attest to the heteroporous nature of adsorbent. Fig. 7 also shows that the experimental data and the model predictions based on the non-linear form of the the Hurkins-Jura and Halsay models. The model parameters are listed in Table 1.

The values of RMSE and χ^2 for the Hurkins-Jura model are considerably big in comparison with other models, suggesting that the Harkins-Jura model could not describe the experimental data satisfactorily for the adsorption of zinc (II) on pulp waste. This result also shows that the adsorption of zinc (II) on pulp waste was not based on significant multilayer adsorption. The Halsay model is also not suitable to describe the adsorption of zinc (II) on

pulp waste either, because this model also assumes a multilayer behavior for the adsorption of adsorbate onto adsorbent. This is in agreement with large RMSE and χ^2 values (Table 1).

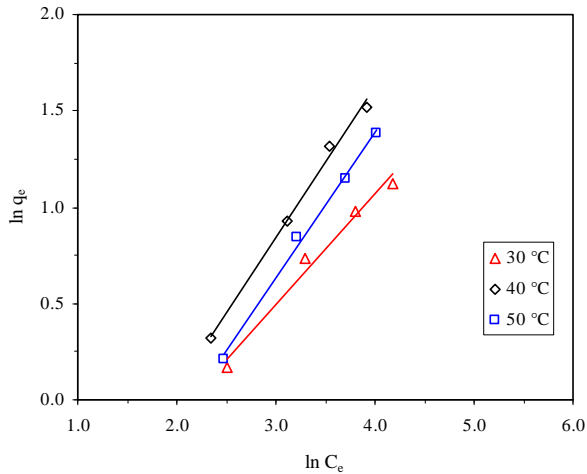


Fig. 12 Halsay isotherm at different temperature

3.5.6 Radlich-Peterson adsorption isotherm

A plot of $\ln C_e/q_e$ versus $\ln C_e$ (shown in Fig. 13) enables the determination of isotherm constants g and K_R from the slope and intercept. The values of K_R , presented in Table 1, indicate that the adsorption capacity of the pulp waste decreased with an increase temperature. Furthermore, the value of g lies between 0 and 1, indicating favorable adsorption.

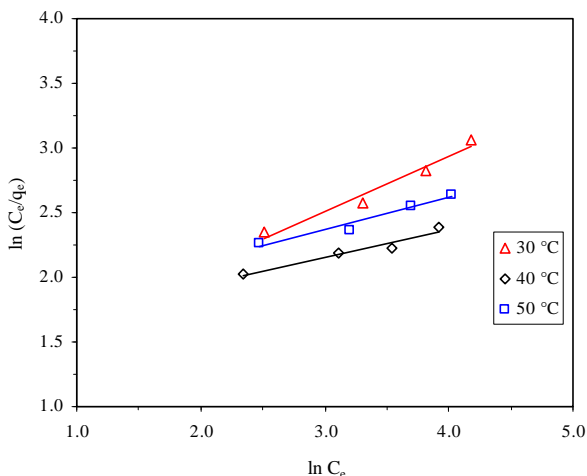


Fig. 13 Radlich-Peterson isotherm at different temperatures

3.5.7 Dubinin-Radushkevich adsorption isotherm

A plot of $\ln q_e$ versus $RT \ln (1+1/C_e)$ enables the determination of isotherm constants B_D and Q_D from the slope and intercept, as shown in Fig. 14.

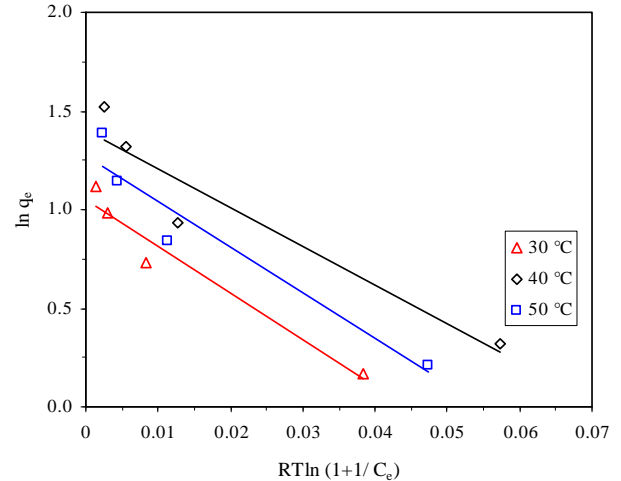


Fig. 14 Dubinin-Radushkevich isotherm at different temperature

The mean energy of sorption, E (kJ/mol) can be calculated by the following equation

$$E = \frac{1}{\sqrt{2B_D}} \quad (20)$$

The calculated Dubinin-Radushkevich constants and mean free energy for adsorption are shown in Table 1. The mean adsorption energy (E) was found to be of 0.146, 0.160 and 0.147 kJ/mol at 30 °C, 40 °C and 50 °C, respectively. As shown in Table 1, Dubinin-Radushkevich model provides worse agreement with experimental data in comparison with Langmuir and Temkin model. This is also evident in Fig. 7 and Fig. 9.

3.5.8 Jovanovic adsorption isotherm

The q_{max} is obtained from a plot of $\ln q_e$ and C_e , as shown in Fig. 15. Comparison of the experimental data and Jovanovic model is also shown in Fig. 7. Their related parameters are listed in Table 1. The RMSE and χ^2 values for the Jovanovic model were higher than all other models.

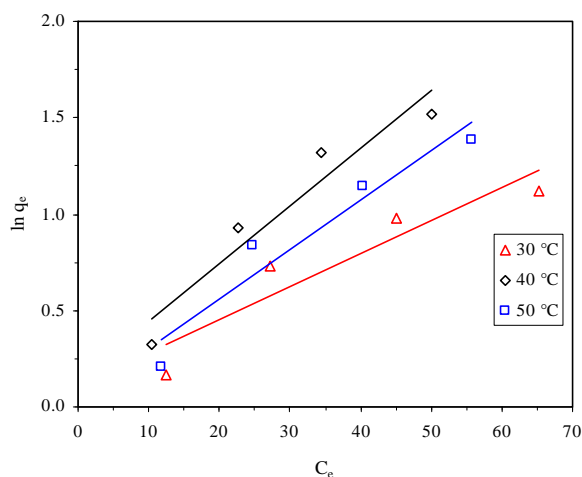


Fig. 15 Jovanovic isotherm at different temperatures

By comparing the values of the error functions, it was found the Langmuir and Temkin models are best to fit the zinc (II) adsorption on the pulp waste. Both models show a high degree of correlation with low root mean square error (RMSE) and chi-square (χ^2) values. This is clearly shown in Fig. 9, confirming the good fit of Langmuir and Temkin models with the experimental data for removal of zinc (II) from the solution.

4. Conclusions

Pulp waste was used as an adsorbent for removal of zinc (II) from aqueous solutions. The adsorption was influenced by such parameters as initial pH, initial zinc (II) concentration, adsorbent dosage and adsorption temperature. The maximum uptake of zinc (II) occurred at pH 6.0. The zinc (II) removal efficiency was increased with an increase in the adsorbent dosage and initial zinc (II) concentrations. It was shown that the pulp waste could be used as an adsorbent to remove zinc from waste water by adsorption. Studies of the adsorption isotherms revealed that zinc adsorption on the pulp waste followed the Langmuir and Temkin models.

References:

[1] H.H. Sandstead, Understanding zinc: recent observations and interpretations, *Journal of Laboratory and Clinical Medicine*, Vol.124, 1994, pp. 322-327.
 [2] Institute of Medicine, *Food and Nutrition Board*. Dietary Reference Intakes for Vitamin

A, Vitamin K, Arsenic, Boron, Chromium, Copper, Iodine, Iron, Manganese, Molybdenum, Nickel, Silicon, Vanadium, and Zinc Washington, DC: National Academy Press (2001).

- [3] N.W. Solomons, Mild human zinc deficiency produces an imbalance between cell-mediated and humoral immunity, *Nutrition Reviews*, Vol. 56, 1998, pp. 27-28.
 [4] A.S. Prasad, Zinc: an overview, *Nutrition*. Vol. 11, 1995, pp. 93-99.
 [5] C.A. Heyneman, Zinc deficiency and taste disorders, *Annals of Pharmacotherapy*, Vol. 30, 1996, pp. 186-187.
 [6] K. Simmer, R.P. Thompson, Zinc in the fetus and newborn, *Acta Paediatrica Scandinavica Supplement*, Scand Suppl. Vol.319, 1985, pp. 158-163.
 [7] N. Fabris, E. Mocchegiani, Zinc, human diseases and aging, *Aging (Milano)*, Vol. 7, 1995, pp. 77-93.
 [8] W. Maret, H.H. Sandstead, Zinc requirements and the risks and benefits of zinc supplementation, *Journal of Trace Elements in Medicine and Biology*, Vol.20, 2006, pp. 3-18.
 [9] A.S. Prasad, F.W. Beck, S.M. Grabowski, J. Kaplan, R.H. Mathog, Zinc deficiency: changes in cytokine production and T-cell subpopulations in patients with head and neck cancer and in noncancer subjects, *Proceedings of the Association of American Physicians*, Vol.109, 1997, 68-77.
 [10] L. Rink, P. Gabriel, Zinc and the immune system, *Proceedings of the Nutrition Society*, Vol.59, 2000, pp.541-52.
 [11] C. Gakwisiri, N. Raut, A. Al-Saadi, S. Al-Aisri, A. Al-Ajmi, A Critical Review of Removal of Zinc from Wastewater, *Proceedings of the World Congress on Engineering*, Vol.1, 2012, pp. 627-630.
 [12] F. Fu, Q. Wang, Removal of heavy metal ions from wastewaters: A review *Journal of Environmental Management*, Vol.92, 2011, pp. 407-418.
 [13] N.K. Srivastava, C.B. Majumder, Novel biofiltration methods for the treatment of heavy metals from industrial wastewater, *Journal Hazardous Materials*, Vol.177, 2008, pp. 70-80.
 [14] V.K. Gupta I. Ali, Utilization of bagasse fly ash (a sugar industry wastes for the removal of copper and zinc from wastewater, *Separation and Purification Technology*, Vol.18, 2000, pp. 131-140.

- [15] L. Bois, A. Bonhomme, A. Ribes, B. Pais, G. Raffin, F. Tessier, Functionalized silica for heavy metals ions adsorption, *Colloids and Surfaces. A, Physicochemical and Engineering Aspects*, Vol.221, 2003, pp. 221-230.
- [16] N. Basci, E. Kocadagistan, B. Kocadagistan, Biosorption of copper (II) from aqueous solutions by wheat shell, *Desalination*, Vol.164, 2004, pp. 135-140.
- [17] C.H. Weng, C.Z. Tsai, S.H. Chu, Y.C. Sharma, Adsorption characteristics of copper (II) onto spent activated clay, *Separation and Purification Technology*, Vol.54, 2007, pp. 187-197.
- [18] W. Li, S. Zhang, X-q. Shan, Surface modification of goethite by phosphate for enhancement of Cu and Cd adsorption, *Colloids and Surfaces. A, Physicochemical and Engineering Aspects*, Vol.293, 2007, pp. 13-19.
- [19] P. Sampranpiboon, P. Charnkeitkong, Equilibrium Isotherm, Thermodynamic and Kinetic Studies of Lead adsorption onto pineapple and paper wastes, *International Journal of Energy and Environment*, Vol.4, 2010, pp. 88-97.
- [20] G. Crini, H.N. Peindy, F. Gimbert, C. Robert, Removal of C.I. Basic Green 4 (Malachite Green) from aqueous solutions by adsorption using cyclodextrin-based adsorbent: Kinetic and equilibrium studies, *Separation and Purification Technology*, Vol.53, 2007, pp. 97-110.
- [21] D.I. Mall, V.C. Srivastava, N.K. Agarwal, Removal of Orange-G and methyl violet dyes by adsorption onto bagasse fly ash kinetic study and equilibrium isotherm analysis, *Dyes and pigments*, Vol.69, 2006, pp. 210-223.
- [22] H.M.F. Freundlich, Over the adsorption in solution, *Journal of Physical Chemistry*, Vol.57, 1906, pp. 385-470.
- [23] M. Ghorbani, H. Eisazadeh, A.A. Ghoreyshi, Removal of zinc ions from aqueous solution using polyaniline nanocomposite coated on rice husk, *Iranica Journal of Energy & Environment*, Vol.3, 2012, pp. 66-71.
- [24] I. Langmuir, The constant and fundamental properties of solids and liquids, *Journal of the American Chemical Society*, Vol.38, 1916, pp. 2221-2295.
- [25] A. Jusoh, W.J.H. Hartini, N. Ali, A. Endut, Study on the removal of pesticide in agricultural run off by granular activated carbon, *Bioresource Technology*, Vol.102, 2011, pp. 5312-5318.
- [26] M.J. Tempkin, V. Pyozhev, *Acta Physicochim USSR*, Vol.12, 1940, pp. 327-352.
- [27] A.U. Itodo, H.U. Itodo, Sorption energies estimation using Dubinin-Radushkevich and Temkin adsorption isotherms, *Life Science Journal*, Vol.7, 2010, pp. 31-39.
- [28] W.D. Hurkins, E.J. Jura, The decrease of free surface energy as a basis for the development of equations for adsorption isotherm: and the existence of two condensed phases in films on solids, *Journal of Chemical Physics*, Vol.12, 1944, pp. 112-113.
- [29] E. Malkoc, Y. Nuhoglu, Determination of kinetic and equilibrium parameters of the batch adsorption of Cr(VI) onto waste acorn of *Quercus ithaburensis*, *Chemical Engineering and Processing*, Vol.46, 2007, pp. 1020-1029.
- [30] G. Halsay, Physical adsorption on non-uniform surface, *Journal of Chemical Physics*, Vol.16, 1948, pp. 931-937.
- [31] M.R. Samarghandi, M. Hadi, S. Moayedi, F.B. Askari, Two parameter isotherms of methyl orange sorption by pinecone derived activated carbon" *Iranian Journal of Environmental Health Science & Engineering*, Vol.6, 2009, pp. 285-294.
- [32] O. Redlich, D.L. Peterson, A Useful adsorption isotherm, *Journal of Physical Chemistry*, Vol.63, 1959, pp. 1024-1026.
- [33] O. Abdelwahab, Kinetic and isotherm studies of copper (II) removal from wastewater using various adsorbents, *Egyptian Journal of Aquatic research*, Vol. 33, 2007, pp. 125-143.
- [34] M.M. Dubinin, The potential theory of adsorption of gases and vapors for adsorbents with energetically non-uniform surface, *Chemical Reviews*, Vol.60, 1960, pp. 235-266.
- [35] Y.S. Ho, J.F. Porter, G. McKay, Equilibrium isotherms studies for the sorption of divalent metal ions onto peat: copper, nickel and lead single component systems, *Water, Air and Soil Pollution*, Vol.141, 2002, pp. 1-33.
- [36] S. Chowdhury, P. Saha, Adsorption thermodynamics and kinetics of Malachite Green onto Ca(OH)₂-treated fly ash, *Journal of Environmental Engineering*, Vol. 137, 2011, pp. 388-397.

- [37] D.S. Jovanovic, Physical adsorption of gases I: isotherms for monolayer and multilayer adsorption, *Colloid and Polymer Science*, Vol.235, 1969, pp. 1203-1214.
- [38] Y.C. Wong, Y.S. Szeto, W.H. Cheung, G. McKay, Adsorption of acid dyes on chitosan-equilibrium isotherm analyses, *Process Biochemistry*, Vol.39, 2004, pp. 693-702.
- [39] K. Vijayaraghavan, T.V.N. Padmesh, K. Palanivelu, M.Velan, Biosorption of nickel (II) ions onto *Sargassum wightii*: Application of two-parameter and three-parameter isotherm models, *Journal of Hazardous Materials*, Vol.B133, 2006, pp. 304-308.
- [40] Y.S. Ho, W.T. Chiu, C.C. Wang, Regression and analysis for the sorption isotherms of basic dyes on sugarcane dust, *Bioresource Technology*, Vol.96, 2005, pp. 1285-1291.
- [41] T.W. Webi, R.K. Chakravort, Pore and solid diffusion models for fixed-bed adsorbers, *Journal of American Institute of Chemical Engineers*, Vol.20, 1974, pp. 228-238.