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Kinetics Study on the Removal of Cu(II) from Aqueous Solution using Raw and Modified Pumpkin Seed Hulls-Low Cost Biosorbents

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ABSTRACT

Raw pumpkin seed hull (RPSH) was modified using sodium hydroxide to improve adsorption capacity for the removal of Cu(II) from aqueous solutions. The RPSH and MPSH were evaluated through SEM and FTIR. The biosorption studies were carried out under various parameters, such as average biosorbent particle size, solution acidity, biosorbent dosage, contact time, initial Cu(II) concentration and temperature. The Langmuir, Freundlich, Temkin, Dubinin-Radushkevich isotherm models were applied to describe the equilibrium isotherms. The data were also fitted to kinetic models such as pseudo-first order, pseudo-second order and intraparticle diffusion kinetic models. The adsorption data were found to follow the Langmuir better than other models. Uptake of Cu(II) increased with increasing temperature indicating the endothermic nature of the adsorption process. Thermodynamic parameters such as ΔG, ΔH and ΔS have also been evaluated. The results demonstrate that the MPSH has higher affinity for Cu(II) than that RPSH.

Key words: Pumpkin Seed Hull ; Copper; Kinetics; Thermodynamic

Introduction

Heavy metal ions such as copper, zinc, cadmium, lead, nickel, etc, are considered as hazardous to the environment due to their toxicity and non-biodegradability even at low concentrations (Jorgetto *et al.,* 2013 and Yafei *et al.,* 20 Yafei1 Yafei4 Yafei). Therefore, it is important to take effective precautions to prevent water, soil and air pollutions. Copper is present in the wastewater of several industries, such as metal cleaning and plating baths, refineries, paper and pulp, fertilizer, and wood preservatives and it is highly toxic. Copper, among these heavy metals, it is potentially hazardous because of its toxicity and mobility in soil, also it is essential and healthy to humans. The excessive intake of copper results in its accumulation in the liver and produces gastrointestinal problems, kidney damage, anaemia and continued inhalation of copper-containing sprays which is linked with an increase in lung cancer (Bruce *et al.,*2015). Therefore, it is important to eliminate traces of copper from drinking water, or to remove copper from wastewater before they are discharged into receiving bodies (Gunnar *et al.,*2015).

Various treatment techniques have been employed to eliminate or reduce copper in wastewater including precipitation, adsorption on activated carbon and other adsorbents, ion exchange and reverse osmosis ((Kumar *et al.,*2013; Karunakaran *et al.,* 2013; Yuan and Yangsheng, 2013). Among these mentioned processes, adsorption is a very effective technique and now it is an economical and efficient method for the removal of metal ions present at low concentrations from wastewater. In recent years, attention has been taken on the utilization of unmodified or modified low-cost potential adsorbents for the treatment of wastewater laden with heavy metals (Gustavo *et al.,* 2014; Lidiany *et al.,* 2015; Muhammad *et al.,* 2014 and Yao *et al.,* 2015).

In this work, we are attempt to use Egyptian pumpkin seed hulls, which are described as waste material from the food industry, as an alternative low-cost sorbent in the removal of copper ions from aqueous solutions. Pumpkin fruits are dehulled before they enter in the industrial processes. Thus a huge load of pumpkin hulls is generated with no commercial values and become disposal problems for the environment owing to their low bulk density. To our knowledge, the utilization of such pumpkin seed hulls in adsorption processes for heavy metal ions was little studied (Mohammad, 2010). For this reason, we treated the adsorbent with sodium hydroxide to investigate the potential of pumpkin seed hulls, waste material, and analysed their property as an adsorbents in the removal of copper ions from aqueous solutions. The adsorption capacity of raw (RPSH) and modified (MPSH) to remove copper ions from aqueous solution as a function of initial pH, different initial concentrations, adsorbent dose and particle size, was tested, and the adsorption equilibrium was expressed using different adsorption isotherms such as, Langmuir and Freundlich, Temkin and, Dubinin-Radushkevich models. Furthermore, three adsorption kinetic models were calculated to analyse the reaction mechanisms provides information for the design and operation of wastewater treatment reactors or equipments through different

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kinetics models, namely, pseudo first- and second order, Weber-Morris and Boyed models. Thermodynamic parameters of these adsorption processes were also investigated.

Experimental

Materials and methods

Chemicals

Analytical grade reagents were used for copper chloride solution, sodium hydroxide and hydrochloric acid

Adsorbate solution

Synthetic stock solution of copper chloride was prepared by dissolving required quantity of Analar grade salts in the distilled water. The stock solution was further diluted with distilled water to desired concentration for obtaining the test solutions.

Adsorbents

Egyptian pumpkin seed hulls (PSH) are obtained by removing it from the pumpkin seeds, washed several times by hot tap water to remove any adherent dirt and finally with distilled water and oven dried at 60^{o}C for 48 h to constant weight. The dried material (RPSH) was ground and sieved to obtain the different particle sizes (0.8, 0.2 and 0.08 mm) and stored in plastic bottles for further studies.

Chemical modification of the pumpkin seed hulls

Surface functional groups on the adsorbent surface substantially influence the adsorption characteristics of metal ions (Lasheen and Ammar, 2012). Consequently, the raw pumpkin seed hulls (0.8 mm) were divided into two sections, first section 100 g was completely immersed in NaOH solution, stirred for 30 min and left overnight. It was then filtered and washed several times with distilled water to remove excess lignin-containing alkali. This material will be referred as alkali- treated pumpkin seed hulls. After this, the treated adsorbent materials were dried at 60^{o} C for 48 h and stored in desiccators for use as a adsorbent (MPSH), as well as the sample of 0.2 mm (M_1PSH). While the second part of 0.8 mm (RPSH) and the sample of 0.08 mm no treated with NaOH (R_1PSH).

Adsorbent characterization

The function groups of RPSH and MPSH, were characterized by a Fourier transform infrared (FTIR) spectrophotometer (UV Perkin Elmer, 101Nin 50507) using KBr disc to prepare unmodified and modified PSH. The chemical structures of the two samples were analyzed.

Procedures

The adsorption of copper ions on RPSH, R_1PSH, MPSH and M_1PSH was studied by batch technique. The general method used for this study is described as follows, A known weight of adsorbent (e.g. 0.5) was equilibrated with 25 ml of Cu(II) solution of known concentration (1.5-9.0 mmol/L) in a stopper glass Erlenmeyer's flasks at a fixed temperature in a thermostatic shaker for a known period (150 min) of time. The copper ion concentration was determined by AAS varion 6 (Analytik Jena AG Konrad-Zuse-StraBe 1 07745 Jena), and the measured concentration was used to calculate the amount of Cu(II) adsorbed at different times. Equilibrium or adsorption capacity, q_e (mmol/g), was calculated by;

$$q_e = \frac{(Co-Ce)V}{Wx1000}$$

where C_o and C_e (mmol/L), are the liquid-phase concentrations of the heavy metal at initial and equilibrium, respectively, v is the volume of the solution (L) and W is the mass of dry adsorbent used (g).

The % heavy metal removal was calculated using the following equation;

$$\% \text{ metal ion removal} = \frac{(Co-Ce)x100}{Co}$$

Results and discussion

Characterization of pumpkin seed hull

FTIR spectrum (Fig.1a and b) of RPSH and MPSH was used to characterization the adsorbents. The spectra indicated a number of adsorption peaks showing the complex nature of this adsorbent. Major intense bands around 590, 1048, 1264, 1424, 1514, 1658, 2926, 3358, 3398 and 3440 cm^{-1} are observed in the spectrum of the raw pumpkin seed hull (RPSH). The broad and strong band at 3398 cm^{-1}can be related to overlapping of O-H stretching of H-bonded –OH groups with N-H stretching from primary/secondary amines or amides. The bands appearing at 1658 cm^{-1} were related to the formation of oxygen bearing functional groups like highly conjugated C=O stretching in carboxyl groups, and carboxylate moieties, respectively (Zhou *et al.,* 2011). The peaks at 1048 – 1658 cm^{-1} indicating the presence of C-H and S=O groups, respectively. The C=O and S=O functional groups generally exhibit very high coordination with heavy metals.

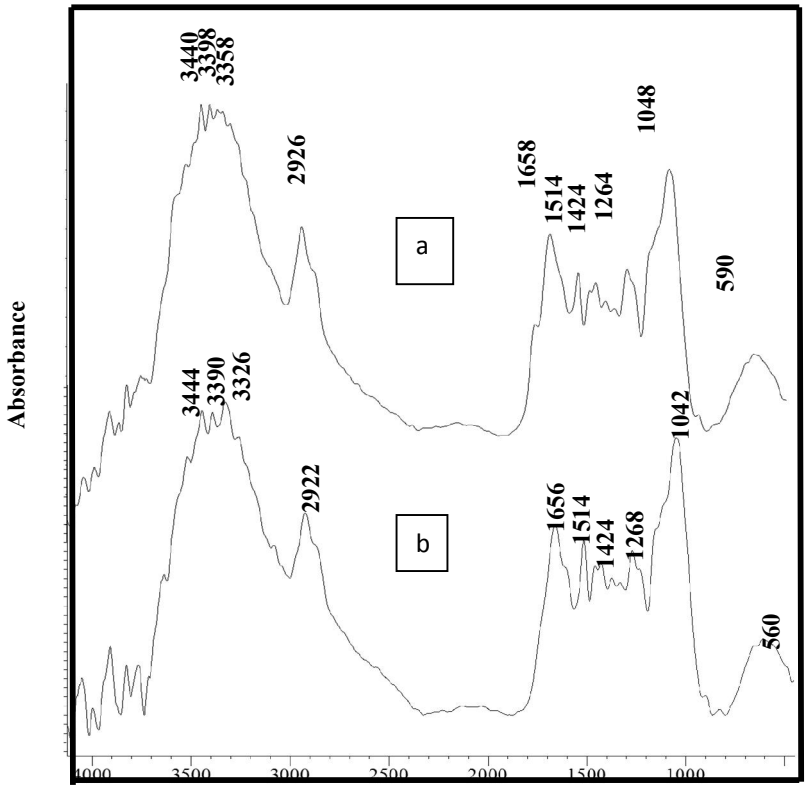


Fig.1 FTIR of a-RPSH and b-MPSH

Hence, the good sorption properties of the pumpkin seed hull towards Cu(II) can be attributed to the presence of these functional groups.

The adsorbent also exhibit typical stretching vibration of C=C at 1658 and 2926 cm^{-1}. The bands between 2926 and 1424 cm^{-1} indicated the presence of aliphatic species such as $–CH_3$ and $–CH_2$ ions through weak complex formation.

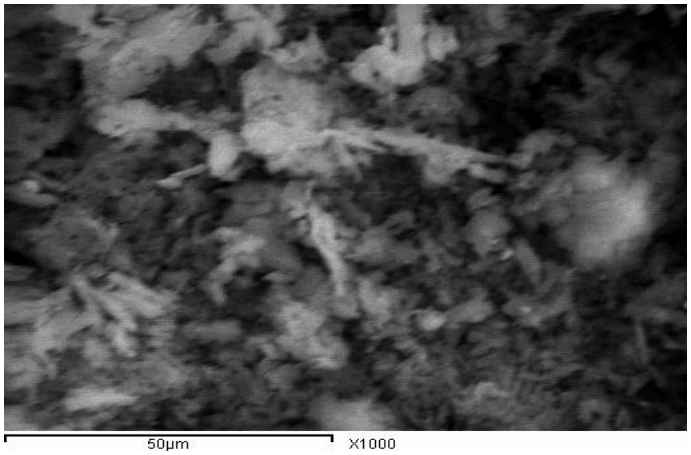
Due to the presence of amino groups (stretching at 3440 cm), the surface of RPSH exhibited a basic nature which was apparent from the FTIR determination. The amino and amide groups provide additional sites for anchoring Cu(II).

Compared to RPSH with MPSH, the latter has been accepted surface with higher basic nature which leads to higher copper ions uptake. The FTIR spectroscopy results of the samples showed some differences for both the absorbents (RPSH and MPSH) in shapes of the bands and in their location.

SEM

The scanning electron micrographs of Pumpkin seed hulls samples before (RPSH) and after modification (MPSH)

a



b

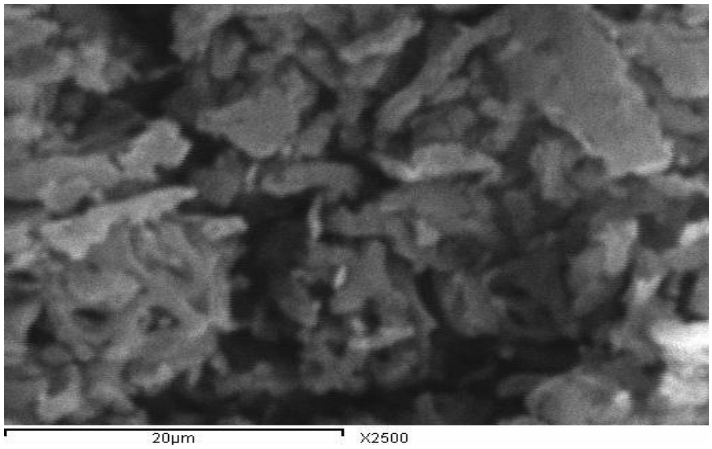


Fig.2. Scanning electron micrograph (SEM) of a- RPSH and b- MPSH

shows the surface texture and morphology of the two biosorbents (Fig.2a and b).
It is evident from the micrograph, presence of asymmetric pores and open pores structure in both the two adsorbents that might be the reason of high metal ions adsorption due to providing high internal surface area. However, after modification the micrographs revealed the presence of more dense of pores number and surface charges over the adsorbent surface.

Effect of P^H values

Acidic conditions of the metal ions solution is an important parameter that can be affect the form and the quantity of ions in water, the form and quantity of an adsorbent's surface sites , and the interaction of the adsorbent and the metal ions, thus the experiments were conducted at acidity range of 0.0 to 2.0. Such study helps in designing the appropriate acidity of the effluent/waste water for achieving maximum efficiency in the removal of Cu(II).

The effect of acidity on the removal of Cu(II) from aqueous solution can be explained considering the surface charge on the adsorbent material. Carboxyl and hydroxyl groups are the main exchangeable functional groups that take part in the adsorption of metal ions onto the adsorbent. With decreasing of acidity solution, these functionalities dissociate, i.e., become deprotonated and negatively charged.

It is known that the metal cations in the aqueous solution convert to different hydrolysis products, i.e., there are three species present in solution, copper ions exist as Cu^{2+} (in very small quantity), $Cu(OH)^{+}$, and as neutral compound $Cu(OH)_2$ (in large quantity).

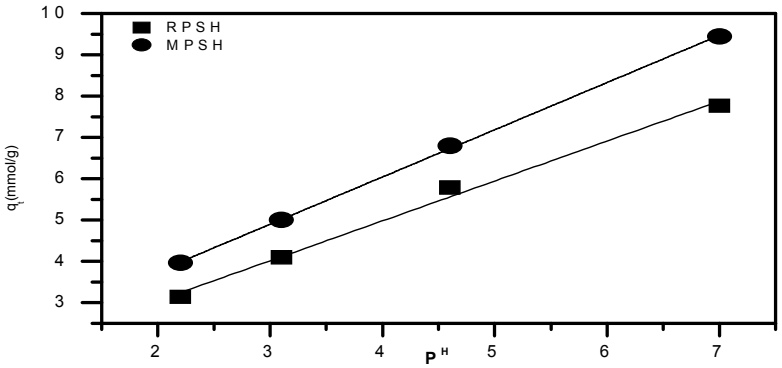


Fig.3 Effect of P^H values on the uptake of Cu(II) onto RPSH and MPSH

Based on the results presented in Fig. 3, it is obvious, in general that, as the acidity decreased and, especially for the alkali pre-treated pumpkin seed hulls, the amount of Cu(II) adsorbed per adsorbent mass unit, as well as the Cu(II) % removal increased.

Hydrogen ions induce metal complexation because they have great affinity for many complexing and ion exchange sites. At high acidity (2.0) functional groups (hydroxyl, carboxyl, phenol, methoxyl, etc.) of the PSH are protonated. Equilibrium reaction of metal adsorption can be considered as follows:

$PSH - COOH = PSH - COO^- + H_{(aq)}^+$ ---------- (1)

$Cu_{(aq)}^{+2} + 2\ PSH - COO^- = (PSH - COO)_2Cu$ ---------- (2)

$Cu_{(aq)}^{+2} + 2\ OH^- = Cu(OH)_2$ ---------- (3)

Due to high concentration of H^+ ions equilibrium of the Reaction (1) will be shifted to the left side according the equilibrium law. Since sites of ion exchange on the PSH are mainly protonated, less available groups for ion exchange become available. As expected, the efficiency generally increases with decreasing acidity, while the effect of acidity is indistinctive or even reverse. The increase of the adsorption efficiency is the most explicit for acidity of 0.0 values probably reflecting progressive deprotonation of carboxylic groups. Namely, in mentioned acidity range, the carboxyl groups (− COOH) from the PSH can lose H^+ and be appreciably deprotonated and induces replacement of hydrogen ions from the surface of the PSH with the copper ions resulting in improvement of the adsorption efficiency extent. That will shift the reaction (2) to the right, while the decrease of the acidity solution increases copper ion removal. In this acidity range, process of ion exchange is the major mechanism for the removal of copper ions from the aqueous solution. As already mentioned, hydrolysis reaction (3) happened pure aqueous solution (pH 7.0). It is obvious that optimum condition for Cu(II) adsorption will occur in absence of HCl.

On the other hand, at higher acidity values 2.0, the surface of the adsorbent is surrounded by hydronium ions leads to high positive charge density on the surface sites, accordingly, electrostatic repulsion between metal ions and H^+ ions, which are characterized by high mobility, will be high during uptake of metal ions resulting in lower removal efficiency of the adsorbent for copper ions. It is attributed to competition the H^1 ions with the Cu(II) on the exchange sites in the adsorbent (Mouni *et al.,* 2011), hence H^1 occupied the sites on adsorbents, leaving heavy metals in solution. With higher pH values, there is a gradual reduction in the degree of protonation, thus, electrostatic repulsion decreases attributed to reduction of positive charge density of H^1 ions on the sorption sites, leading to an enhancement of Cu(II) adsorption.

Owing to modification of RPSH with NaOH, the figure also shows the comparison for the effect of acidity on the uptake of Cu(II) on RPSH and MPSH, since, q_e are higher with MPSH. This is due to increases of basic nature of MPSH surface. Similar observation was reported by earlier researchers (Zheng *et al.,* 2010; Pellera *et al.,* 2012).

Effect of initial concentration of metal ions and contact times

The influence of contact time on the adsorption of Cu(II) onto both RPSH and MPSH was investigated at various initial concentrations of Cu(II), 95, 190, 302, 381 and 553 mg/L is shown in Fig.4. Our experiments were carried out at a fixed adsorbent dose 0.5g, pure aqueous media and 29^0C. It can be seen that by increasing the initial concentration of Cu(II) from 95 to 553 mg/L, an increase of adsorption capacity occurs from 4.75 to 10.15 and 4.75 to 14.96 mg/g for RPSH and R_1PSH, respectively, and from 4.75 to 11.73 and 4.75 to 14.32 (mmol/g) for MPSH and M_1PSH respectively. This may be attributed by the initial concentration which provides an important driving force to overcome all mass transfer resistances of Cu(II) between the aqueous and solid phases, hence a higher initial concentration of Cu(II) will enhance the adsorption process (Gupta and A.

Nayak, 2012), while the percentage removal of Cu(II) showed the opposite trend. When the initial concentration increased from 95 to 553 mg/L, removal percentage decreased from 100% to 42.36% , 100% to 54.03%, 100% to 47.78%, and from 100% to 51.72% for both RPSH, R_1PSH, MPSH and M_1PSH respectively, this is due to the saturation of the active sites in the solution. It was also observed from the Figure that the adsorption capacity is more for modified adsorbents (MPSH and M_1PSH) when compared to unmodified adsorbents (RPSH, R_1PSH). This is due to the fact that modification with NaOH saturated solution can cause an increase in internal surface area, a decrease in the degree of polymerization, separation of structural linkages between lignin and carbohydrates, disruption of the lignin structure (Demirbas, 2008) increase of carboxyl groups after hydrolyzation and made the surface charge of the adsorbents becomes more negative which alters the adsorbate functions leading quick saturation sites (Milicevic *et al.,* 2012).

This strongly suggested that adsorption of Cu(II) onto the four adsorbents ((RPSH, R_1PSH, MPSH and M_1PSH) was fast and significantly practical important, as it will facilitate the use of small adsorbent volumes in order to ensure efficiency and economy.

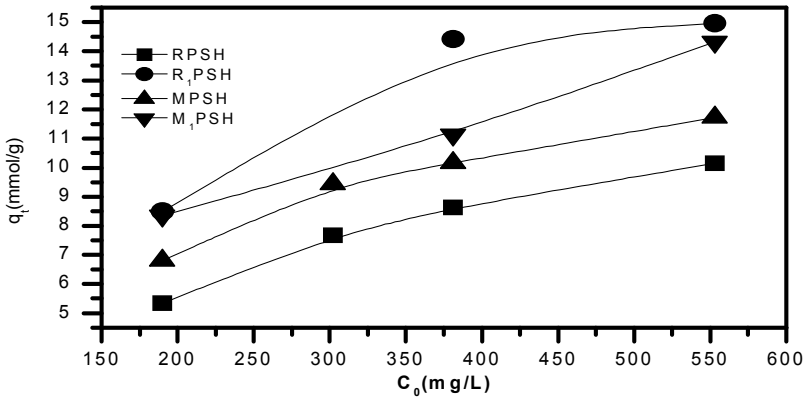


Fig.4 Effect of different initial concentrations of Cu(II) on the uptake onto RPSH, R_1PSH, MPSH and M_1PSH

Effect of adsorbent dose

The biosorbent dosage is an important parameter because this determines the capacity of a biosorbent for a given initial concentration (190 mg/L) and at pH 7 for the four adsorbents (RPSH, R_1PSH, MPSH, and M_1PSH) over the range 0.5 – 2.0 g/0.025 L. The biosorption efficiency for Cu(II) as a function of biosorbent dosage was investigated. The percentage of the metal ions biosorption steeply increases with the biosorbent loading up to 2.0 g/0.025 L. This result can be explained by the fact that the biosorption sites remain unsaturated during the biosorption reaction whereas the number of sites available for biosorption site increases by increasing the biosorbent dose. Moreover, the maximum biosorption, 100 % (complete sorption) for Cu(II) was attained at biosorbent dosage, 1.0 and 2.0 g/0.025 L with different contact times. Therefore, the optimum biosorbent dosage was taken as 1.0 g/0.025 L. From the results obtained, we can observe that the Cu(II) uptake steeply increases with the biosorbent loading up to 2g. On the other hand the results obtained reveal order of the equilibrium uptake of Cu(II) with dosage 0.5 g/0.025 L as follows that, RPSH < R_1PSH < MPSH < M_1PSH, respectively.

Effect of particle size

Kinetics of copper ions biosorption were carried out for different particle sizes of the raw pumpkin seed hulls varying from 0.8 to 0.08 mm. The results are illustrated in Fig. 4. The figure indicates that the amount of Cu(II) uptake at equilibrium increased and the equilibrium time was decreased by decreasing the particle size. Similar trend was observed when particle sizes of modified pumpkin seed hulls varying from 0.8 to 0.2 mm. The fast and higher adsorption capacity with smaller adsorbent particles could be attributed to the fact that smaller particles provided a larger and easily accessible surface area. The figure also indicates that affinity of modified pumpkin seed hulls for Cu(II) is higher than unmodified pumpkin seed hulls.

Adsorption isotherms

Isotherm or adsorption equilibrium data are essential for designing an adsorption system. The adsorption isotherm for the Cu(II) removal were studied using initial concentration between 95.48 and 553.76 mg/L at adsorbent dosage level of 0.5g and at 29^{o}C, keeping the other conditions remain same.

The Freundlich isotherm is used for non-ideal adsorption on heterogeneous surface (Freundlich, 1926; Wang *et al.,* 2013). The heterogeneity is caused by the presence of different functional groups on the surface, and also by various mechanisms of adsorbent-adsorbate interactions. Freundlich equation is given by

$\log q_e = \log k_F + (1/n) \log C_e$ ---------- (4)

where k_F is an indicative constant for adsorption capacity of the sorbent (mg/g) and the constant n indicates the intensity of the adsorption. The values of k_F and n were obtained from intercept and slope of the plot log q_e against logC_e (Fig is hidden). The data obtained shows that the values of n between 1 and 10, this is represent a favourable adsorption (Table 1).

The Langmuir adsorption model (Langmuir, 1918; Boluda and Aguilar, 2013) assumes uniform adsorption on the surface and is used for describing monolayer adsorption on a surface containing a finite number of identical sites (homogeneous surface). The linear form of the Langmuir model is expressed by

$$\frac{Ce}{qe} = \frac{1}{Qob} + \frac{1}{Qo} Ce$$ ---------- (5)

The linear plot of specific adsorption (C_e/q_e) against the equilibrium concentration (C_e, mmol/L). Langmuir constants Q_o and b were determined from the slope and intercept of the plot (Fig.is hidden). The essential characteristics of the Langmuir
isotherm can be expressed in terms of a dimensionless constant separation factor (R_L)
that it given by Eq.6.

$$R_L = \frac{1}{1+bCo}$$ ---------- (6)

Where C_o is the highest initial concentration of adsorbate (mmol/L) and b (L/mg) is Langmuir constant. It is found that the parameter R_L ($0 < R_L < 1$) shows favourable adsorption. Correlation coefficient (R^2) has been found to be 0.9977 for RPSH and 0.9982 for MPSH (Table 1), indicating, also that adsorption of Cu(II) on RPSH or MPSH is favourable at operation.

Table.1: Adsorption isotherm parameters of Cu(II) in aqueous solution.

	Freundlich			Langmuir				Temkin			D-R			
	n	K_F (mg/g)	R^2	Q_O (mmol/g)	b (L/mg)	R_L	R^2	K_T (L/g)	B_T (J/mol)	R^2	X_m (mmol/g)	β (mg^2/j^2)	E (kJ/mol)	R^2
RPSH	2.28	4.08	0.9964	13.73	0.007	0.20	0.9977	8.54	3.73	09953	7.27	$3.57x10^{-4}$	38.46	0.9464
MPSH	1.90	1.60	0.9969	14.16	0.016	0.11	0.9982	9.92	2.25	0.9993	6.24	$0.22x10^{-4}$	28.57	0.9863

The Temkin isotherm (Temkin and Pyzhev, 1940; Kumar *et al.,* 2013) has commonly been applied in the following form;

$q_e = (RT/b) \ln(A_T Ce)$ ---------- (7)

Eq. 7 can be expressed in its linear form as

$q_e = (RT/b) \ln A + (RT/b) \ln C_e$ ---------- (8)

where, $B_T = RT/b$

where A_T and B_T are Temkin isotherm constants, R is the gas constant (8.314 j/mol K) T is the absolute temperature. The Temkin isotherm constants are given in Table 1. The constant, B_T which related to heat of sorption, is 8.54 and 9.92 kJ/mol, for RPSH and MPSH, respectively. These values show strong interaction between metal ions, indicated chemisorptions process.

D-R isotherm (Dubinin and Radushkevich, 1947; Abdel wahab *et al.,* 2013) was employed to find out the adsorption mechanism based on the potential theory assuming a heterogeneous surface. D-R isotherm is expressed as follows

$q_e = X_m e^{-\beta \varepsilon^2}$ ---------- (9)

the linear form was;

$\log q_e = \log X_m - \beta \varepsilon^2$ ---------- (10)

Where X_m is the D-R monolayer capacity (mmol/g),β is a constant related to sorption energy, and Ɛ is the Polanyi potential which is related to the equilibrium concentration as follows

$\varepsilon = RT \ln (1 + 1/C_e)$ ---------- (11)

Where R is the gas constant (8.314j/mol K) and T is the absolute temperature. The constant β gives the mean free energy, E, of sorption per molecule of the adsorbate when it is transferred to the surface of the solid from infinity in the solution and can be computed using the relationship.

$$E = \frac{1}{\sqrt{2\beta}}$$ ---------- (12)

A plot of q_e vs. ε^2 (Fig. is hidden) gave a straight line of slope, β and intercept, X_m of different systems were evaluated.

The difference in the free energy between the adsorbed phase and the saturated liquid adsorbate is referred to as the Polanyi potential. Thus the sorption space in the vicinity of the solid surface may be characterized by a series of equipotential surfaces with a given sorption potential. The sorption potential is independent of temperature but varies according to the nature of the adsorbent and adsorbate. In the present study, D-R

isotherm constants, monolayer capacity (X_m) and sorption energy (β) were found to be 7.27 mg/g and $3.57x10^{-4}$ mg^2/j^2,respectively, for RPSH, while for MPSH was found to be 6.94 mg/g and $6.22x10^{-4}$ mg^2/j^2 (Table 1). The magnitude of E is used to determine the type of adsorption mechanism (Abdel wahab *et al.,* 2013)), the calculated values of E for the present study is 38.46 and 28.57 kJ/mol for the adsorption of Cu(II) ions onto RPSH and MPSH adsorbent respectively, which suggest that adsorption process of Cu(II) onto the surface of both adsorbents is following chemical adsorption type.

Comparison of adsorption isotherms

The experimental data on the effect of an initial concentration of copper ions on the RPSH and MPSH surface of the test medium were fitted to the different four isotherm models, namely, Langmuir, Freundlich, Temkin and D-R isotherms. The constants obtained from Langmuir and Freundlich isotherms had very high correlation coefficients (R^2) (Table 1). Comparisons between correlation coefficients, with the adsorption correlation values for RPSH and MPSH, fit the Langmuir model better than the Freundlich model. These values indicated a strong positive correlation.

From the fitting results of Langmuir isotherms, the maximum Q_o and minimum b value of the Langmuir constants were 13.73 and 0.007, respectively, for RPSH and 14.16 and 0.0155 for MPSH. In comparing the b value of the two biosorbents, each demonstrated differing adsorption results for copper ions. Q_o represents the maximum biosorption capacity of the adsorbent. While the b value indicates the affinity of a biosorbent toward the adsorbat.

From the fitting results of the Freundlich model, higher k_F values, and n values are 4.08 mg/g and 2.28 for RPSH respectively, while for MPSH were 1.6 mg/g and 1.9 in the adsorption of copper ions. A high value (n > 1) indicated high adsorption strength. Table 1 shows a comparison of correlation coefficients for various biosorbents in the adsorption of copper ions. The results indicated that MPSH is a better biosorbent material than RPSH.

It was observed from Table 1 that the best fitted adsorption isotherms considering the correlation coefficient obtained were to be in the order of prediction precision; Langmuir > Temkin > Freundlich > D-R isotherms. Comparing the correlation coefficients were obtained from the adsorption isotherms which shows the best fits to the experimental values using the different isotherm equations and were also generally very good for Langmuir and Temkin isotherm equations. The applicability of Langmuir and Temkin isotherm equations to the copper ions-RPSH system, as well as copper ions-MPSH system, indicated that both the monolayer adsorption and heterogeneous surface conditions exist under the studied experimental conditions. The adsorption of copper ions onto RPSH and MPSH surface is thus complex, involving more than one mechanism (Gunay et al, 2007). The comparison of maximum monolayer adsorption capacity of copper ions onto various adsorbents was presented in Table 1. It shows that, in general, the MPSH studied in this work has larger adsorption capacity than RPSH.

Mechanism of adsorption (Adsorption kinetics)

In order to investigate the adsorption mechanism such as mass transfer and chemical reaction, kinetic models were used to examine the rate of the adsorption process and to propose potential rate-controlling step. In this paper kinetic studies are carried out in batch experiments using variable initial sorbate concentrations, along with raw and modified pumpkin seed hulls.

Lagergren (Lagergren, 1898; Wang *et al.,* 2013) proposed a method for adsorption analysis which is the pseudo-first-order kinetic equation of Lagergren

$$\frac{dqt}{dt} = k_1(q_e - q_t) \quad \text{---------- (13)}$$

Integrating this for the boundary conditions t=0 to t=t and q_t=0 to q_t=q_t, gives;

$$\text{Log}(q_e - q_t) = \log q_e - \frac{k1}{2.303}t \quad \text{---------- (14)}$$

Where k_1 is the equilibrium rate constant (1/min), q_e the amount of copper ions adsorbed on the surface at equilibrium (mmol/g), q_t the amount of copper ions adsorbed at any time (mmol/g). The value of the adsorption rate constant (k_1) for copper ions sorption by RPSH and MPSH was determined from the plot of log ($q_e - q_t$) against t (Fig. is hidden). The parameters of pseudo-first-order model are summarized in Table 2.

The pseudo-second-order kinetics (McKay and Ho, 2000) may be expressed as;

$$\frac{dqt}{dt} = k_2(q_e - q_t)^2 \quad \text{---------- (15)}$$

Where k_2 is the rate constant of adsorption, q_e is the amount of copper ions adsorbed on the surface at equilibrium (mmol/g), q_t the amount of copper ions adsorbed at any time (mmol/g). Separating the variables in Eq. 15, gives;

$$\frac{dqt}{d(qe - qt)2} = k_2 dt \quad \text{---------- (16)}$$

Integrating this for the boundary conditions t=0 to t=t and q_t=0 to q_t=q_t, gives

$$\frac{1}{(qe - qt)} = \frac{1}{qe} + k_2 t \quad \text{---------- (17)}$$

This is the integrated rate law for a pseudo-second-order reaction. Eq.15 can be rearranged to obtain;

$$qt = \frac{t}{\left(\frac{1}{k2qe2}\right) + \left(\frac{t}{qe}\right)} \quad \text{---------- (18)}$$

This has a linear form of;

$$\frac{t}{qt} = \left(\frac{1}{k2qe2}\right) + \frac{1}{qe}t \quad \text{----------(19)}$$

Where the equilibrium adsorption capacity (q_e), and the second-order constants k_2 (g/mg min) can be determined experimentally from the slope and intercept of plot t/q_t, versus t (Fig. Is hidden)

The coefficients of the pseudo-first-order and pseudo-second-order models obtained were presents in Table 2a. The R^2 values of the pseudo-second-order model exceeded 0.99 and the $q_{e,cal}$ values calculated from pseudo-second-order model were more consistent with experimental $q_{e,exp}$ values than those calculated from the pseudo-first-order model. Hence, the pseudo-second-order model better represented the adsorption kinetics and this suggests that the overall rate of the copper ions adsorption process appeared to be controlled by chemical process.

Table. 2a: Kinetic models parameters for the adsorption of copper ions at 302 K and different initial concentrations, (k_1,1/min, k_2,g/mg min)

C_0 (mg/L)	Pseudo-first-order						Pseudo-second-order					
	RPSH			MPSH			RPSH			MPSH		
	$q_{e,1,cal}$ (mmol/g)	K_1 (min^{-1})	R^2	$q_{e,1,cal}$ (mmol/g)	K_1 (min^{-1})	R^2	$q_{e,2,cal}$ (mmol/g)	K_2 (g/mg min)	R^2	$q_{e,2,cal}$ (mmol/g)	K_2 (g/mg min)	R^2
90	6.02	0.0407	0.9935	8.23	4.68	0.9657	7.86	3.33	0.9989	9.20	3.55	0.9910
302	6.77	0.0460	0.9873	6.65	0.029	0.7828	8.69	9.03	0.9966	10.43	5.59	0.9905
381	6.52	0.0522	0.9905	7.44	0.0481	0.9682	9.51	12.23	0.9983	10.54	11.58	0.9970
553	4.83	0.0670	0.9959	5.46	0.0897	0.9246	10.36	33.52	0.9982	12.01	37.11	0.9960

For the process design and control of adsorption systems, it is important to understand the dynamic behaviour of the system. At the present time Weber and Morris ((Weber and Morris, 1963) and Boyd's film-diffusion (Boyd *et al.,* 1947) are the two most widely used models for studying the mechanism of adsorption. Both models usually show a multilinear nature in their plots, and the conventional method is that the researcher inspects the plots visually to decide the start and end of each linear segment.

On the other hand, Weber and Morris' s pore-diffusion model expressed as;

$$q_t = k_i t^{0.5} + C \quad \text{---------- (20)}$$

where q is the amount adsorbed (mmol/g) at time t.

In the present studies, the k_{id} values were obtained from the slope of the linear portions of the curve of different initial concentrations of copper ions in aqueous solution and tabulated in Table 2b (Fig. is hidden).

Table. 2b. Intraparticle and film diffusion prameters for different initial Cu(II) concentrations

C_0 (mg/L)	Intraparticle						Film diffusion			
	RPSH			MPSH			RPSH		MPSH	
	k_{id} (mg/g $min^{-0.5}$)	C (mg/g)	R^2	k_{id} (mg/g $min^{-0.5}$)	C (mg/g)	R^2	$D_i x10^{-3}$ (cm^2/s)	R^2	$D_i x10^{-3}$ (cm^2/s)	R^2
90	0.6736	0.5299	0.9917	0.7787	0.0268	0.9975	1.26	0.9965	2.11	0.8441
302	0.7141	1.6253	0.9911	0.8040	1.5855	0.9928	1.23	0.9515	1.83	0.9060
381	0.6748	3.0206	0.9744	0.7551	3.7260	0.9922	2.45	0.9890	1.48	0.9814
553	0.7218	5.4893	0.9957	0.6668	7.4709	0.9994	1.41	0.9995	1.71	0.8489

According to this model, the plot of uptake, q_t against the square root of time ($t^{0.5}$) must give a straight line and intercept equal to zero if intraparticle diffusion is the rate controlling step. When the plots do not pass through the origin, this is indicative of some degree of boundary layer control and these further shows that the intraparticle diffusion is not the only rat-limiting step, but also other kinetic models may control the rate of adsorption, all of which may be operating simultaneously. The values of intercept give an idea about the boundary layer thickness such as the larger the intercept, the greater the boundary layer effect.

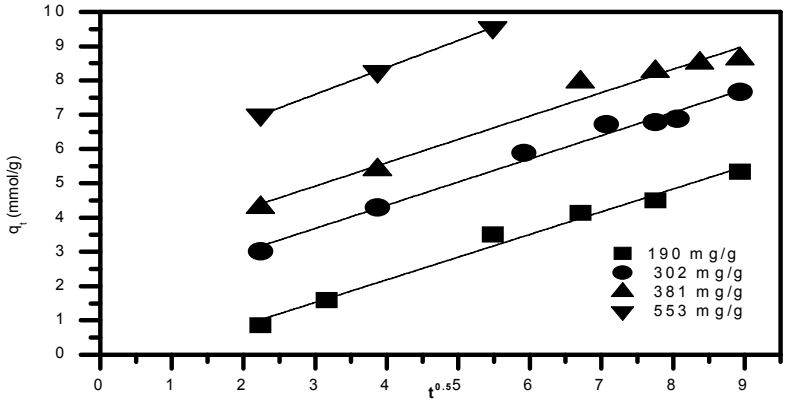


Fig.5 Weber and Morris's plots for the adsorption of Cu(II) onto RPSH

For the proper understanding of experimental data it is necessary to identify the rate controlling step of the adsorption process. Boyd (Boyd *et al.,* 1947) gave the expression (Eq.21) for the treatment of kinetic data, which is in accordance with the observation of Reichenberg (Reichenberg, 1953)

$$F=1-\frac{6}{\pi 2}\sum_{1}^{\infty}\left(\frac{1}{n2}\right)e^{(-n2Bt)} \quad \text{---------- (21)}$$

In this study, the film diffusion model of Boyd assumes that the main resistance to diffusion is in the thin film (boundary layer) that surrounds the adsorbent particle; this model is expressed as;

$$F=\frac{qt}{qe} \quad \text{---------- (22)}$$

Where F is the fractional attainment of equilibrium, at different times, t, and is obtained by using Eq.22 and n is Freundlich constant of the ongoing adsorption process. For every value of F, corresponding calculated values of Bt was derived from Reichenberg's Table. Thereafter time versus Bt plots were drawn at different concentrations for both the systems. Linearity in the time versus Bt plots at higher concentrations of copper ion indicate that the particle diffusion process is operative in both the adsorbents, while film diffusion process is more pronounced at lower concentration due to deviation in linearity at all concentrations.

To further evaluate the data, slops of the straight lines obtained at different concentrations of Cu(II) for both systems was taken as B, the time constant, which was subsequently used for the evaluation of the values of D_i using Eq.23

$$B=\frac{(\pi 2Di)}{r2}= \text{time constant} \quad \text{---------- (23)}$$

Where D_i (cm^2/s) is the effective diffusion coefficient of adsorbate in adsorbent phase, r is the radius of the adsorbent particle assuming spherical shape (Table 2b). Our experiments agree well with other researchers (Senthil *et al.,* 2011; Hameed and El-Khaiary, 2008).

Effect of temperature

The experimental results obtained from a series of contact time studies for metal ion adsorption with an initial concentration of 190 mg/L at PH 7.0 in which temperature was varied from 302 to 322 K. The adsorption of metal ions has been found to increase with an increase in temperature from 302 to 322 K (Fig. is hidden). The increase in adsorption capacity of RPSH and MPSH with temperature indicates an endothermic process. The increase in adsorption with temperature may be attributing to either change in pore size of the adsorbent causing inter-particle diffusion within the pores or to enhancement in the chemical affinity of the metal cations to the surface of adsorbent leading to some kind of chemical interaction to take during adsorption process which results into increase in adsorption capacity. At higher temperatures, the possibility of diffusion of solute within the pores of the adsorbent may not ruled out. Since diffusion is an endothermic process, greater adsorption will be observed at higher temperature. Thus the diffusion rate of ions in the external mass transport process increases with temperature. The above results were further substantiated by the various thermodynamic parameters evaluated for adsorption.

Activation energy

The activation energy E_a was calculated by the linearized Arrhenius equation.

$$Ln(k)= ln(A) - (E_a/RT) \quad \text{---------- (24)}$$

Where E_a is the activation energy of adsorption (kJ/mol), k is the rate constant which control the process, A is Arrhenius constant, R is the ideal gas constant (8.314J/mol K), and T is the absolute temperature (K).

From the pseudo-second-order kinetic studies, k_2 is the rate constant which control the process, i.e. k. In this study, activation energy value (Table 3) of 42.40 and 69.42 (kJ/mol) was obtained from the plot of lnk_2 versus 1/T (Fig. is hidden) indicating chemical adsorption process (Aksu, and Karabbayir, 2008). Li (*et al.,* 2009) noted that chemical adsorption includes activated and nonactivated forms. Activated chemical adsorption means that the rate varies with temperature according to finite activation energy (between 8.4 and 83.7 kJ/mol) in the Arrhenius equation, but the activation energy for nonactivation chemical adsorption is near zero. The results shows that the process is one of activated chemical adsorption and the positive value of the activation energy suggested that the rise in solution temperature favours Cu(II) adsorption onto RPSH and MPSH.

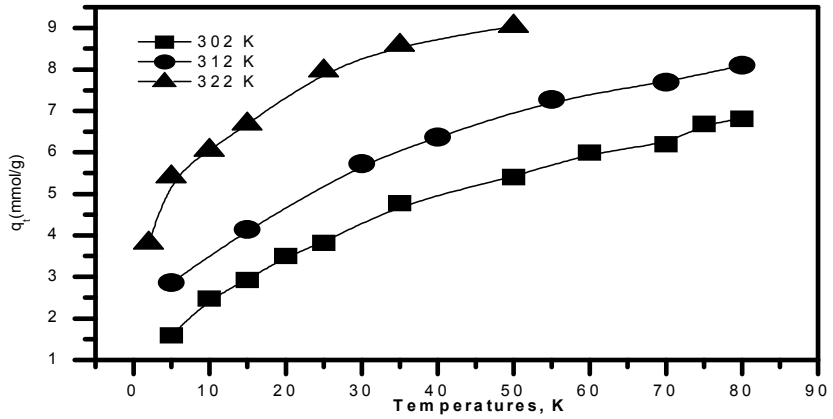


Fig.6 Effect of temperatures for the adsorption of Cu(II) onto a-RPSH and b-MPSH

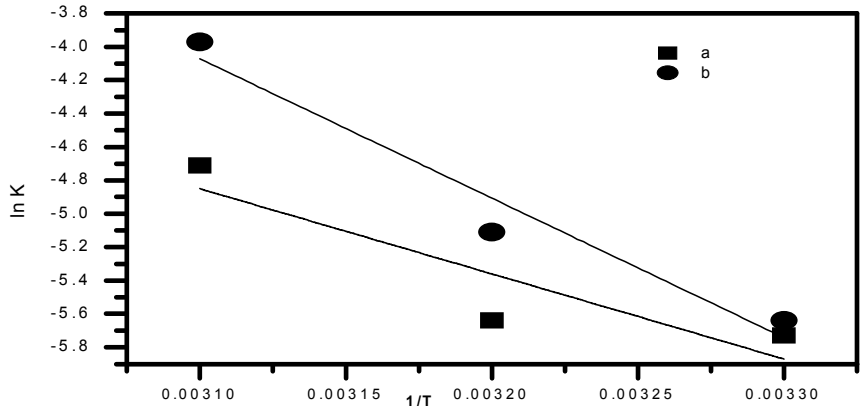


Fig.7 Arrheneus plots for the adsorption of Cu(II) at different concentrations onto a-RPSH and b-MPSH

The effect of temperature on sorption is further confirmed by the van't Hoff plots based on the equations

$K_D = q_e/C_e$ ---------- (25)

$\Delta G = -RT\ln K_D$ ---------- (26)

$\ln K_D = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$ ---------- (27)

Where T is absolute temperature in Kelvin (K), R is the gas constant (8.314×10^{-3}) and K_D is the distribution coefficient (ml/g). The thermodynamic parameters namely enthalpy change (ΔH) and the entropy change (ΔS) can be calculated from the slope and intercept of the straight line plotted by $\ln K_D$ versus 1/T, (Fig. is hidden) respectively. The Gibbs free energy change was determined at 302, 312 and 322 K. The obtained thermodynamic parameters were listed in Table 3.

By adsorption abundant Cu(II) onto the surface of RPSH and MPSH, the number of H(I) ions attached to activated sites of the adsorbent decreased. Therefore the positive value of ΔS suggested some structure changes in the adsorbent and adsorbate. In fact, the positive value of enthalpy ΔH further confirmed the endothermic nature of the processes, so increasing temperature supplied with a more favourable adsorption of Cu(II) onto RPSH and MPSH. On the other hand, the positive Gibbs free energy value for copper adsorption process on the

adsorbents at different temperatures indicates the no spontaneity of process as a result of presence of an energy barrier in the adsorption process. The positive values for these parameters are quite common because the activated complex in the transition state is in an excited form (Ugurlu, 2009).

Table. 3: Calculated thermodynamic parameters for adsorption of Cu(II) onto RPSH and MPSH at C_o,190 (mg/L)

ΔS (j/mol)		ΔH kj/mol)		E_a (kJ/mol)		ΔG (kj/mol)					
						302K		312K		322K	
RPSH	MPSH	RPSH	MPSH	RPSH	MPSH	RPSH	MPSH	RPSH	MPSH	RPSH	MPSH
305.46	251.0	99.77	81.48	42.40	69.42	7.52	5.65	4.47	3.14	1.41	0.63

Equilibrium distribution coefficient, K_d

Distribution coefficients (K_d) for different metal ions were determined by batch method at different temperatures systems. The distribution coefficient, K_d, is defined as the ratio of metal ion concentration on the resin to that in the aqueous solution and can be used as a valuable tool to study metal cation mobility.

$$K_d = \frac{\text{amount of metal ion in adsorbent}}{\text{mount of metal ion in solution}} \text{ x } \frac{ml\ of\ solution}{g\ of\ dry\ resin} \text{ ---------- (28)}$$

Various portions of (500 mg each) the exchanger in H^+ form were taken in Erlenmeyer flasks and mixed with 50 mL of different metal ion solutions in the aqueous medium and subsequently shaken for 24 h in temperatures controlled shaker at 28, 40 and 50^0C to attain the equilibrium. The amount of metal ion before and after the equilibrium was determined by EDTA titration (AL-Othman and Inamuddin,2011). The distribution coefficients were calculated using the equation.

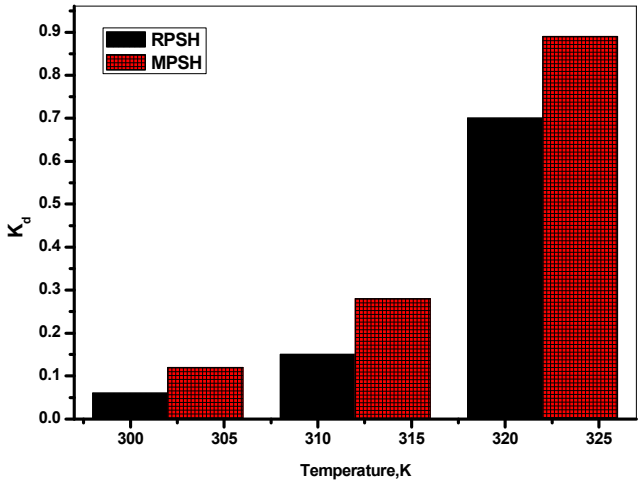


Fig. 8. Distribution coefficients of Cu(II) at different temperatures

High values of distribution coefficient, K_d indicate that the metal has been retained by the solid phase through sorption reactions, while low values of K_d indicate that a large fraction of the metal remains in solution. Fig. 8 show that the distribution coefficient K_d values increase with the increase in temperatures of metal solutions. The rapid metal sorption has significant practical importance, as this will facilitate with the small amount of resins to ensure efficiency and economy.

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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