

Performance comparison of individual adsorbents and mixed adsorbent for the removal of copper (II) from waste water

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ABSTRACT


Removal of Cu (II) metal ions from wastewater using borassus flabellifer coir and ragi husk mixed adsorbent is studied in a batch fashion to find out the effect of several process parameters like the agitation time (0-120 min), the mixed adsorbent size (0.1 to 1.0 g in 50 mL solution), concentration of copper ion (20-100 mg/L), temperature (273-323 K) and pH (2-10) as because of copper ions present in water causes severe affect on aquatic life, animals and humans. The Langmuir isotherm for copper adsorption onto mixed adsorbent is proved to be the best fit followed by Freundlich and Tempkin isotherms for the experimental data. The adsorption kinetic models follow the second order. As the equilibrium agitation time is achieved at 60 min, the batch process time for the removal of Cu (II) metal ions from wastewater is less. The thermodynamic parameters such as change in Gibb's free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) reveals the feasibility, irreversibility, spontaneity and endothermic nature. The results obtained in this study illustrate that mixed adsorbent is expected to be an effective and economically viable adsorbent for copper removal from industrial wastewater whereby the quality of water may be improved.

Keywords: Adsorption, Adsorption isotherms, Cu (II), Kinetics, Mixed adsorbent powder, Thermodynamic parameters.

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1. INTRODUCTION

India is the second most populous country in the world and also under developing stage which generates large quantity of industrial, domestic, medical wastes etc, having toxic, carcinogenic and disease causing heavy metals. Various industries discharge heavy metals which contaminate water bodies and severely affect on aquatic life, human health and environment (Krim et al., 2006). Largely various human activities such as weathering of rocks and volcanic activities release heavy metals which are primary concern about pollution (Yisa, 2010; Ong and Kamruzzaman, 2009). Heavy metals such as manganese (Mn), mercury (Hg), lead (Pb), cadmium (Cd), copper (Cu) are treated as toxic due to their non-biodegradability and oxidation nature (Ghalay et al., 2008; Omar and Al-Itawi, 2007). Out of these heavy metals, copper is treated as one of the most toxic one. Industries like electroplating industries, paper and pulp, fertilizer, wood preservatives, refineries and metal cleaning are primary source of copper metal ion discharges into the environment. The intake of copper beyond limit leads to renal failure and hepatic damage, severe mucosal, irritation of nose, mouth and eyes, wide spread capillary damage, gastrointestinal irritation, headaches, stomachaches, dizziness, vomiting, diarrhea etc. and high consumption of copper may also cause necrotic changes in kidney and liver, damaging these vital organs. World Health Organization (WHO) has recommended that maximum acceptable limit for Cu (II) concentration in drinking water

should be 1.5 mg/L (WHO, 2004). It is necessary that water bodies containing heavy metals are treated for domestic use.

There are several methods for removal of copper metal ion from water bodies such as reduction followed by chemical precipitation, ion exchange, reduction, electrochemical precipitation, solvent extraction, membrane separation, evaporation and foam separation etc. (Zhou et al., 1993; Tiravanti et al., 1997; Seaman et al., 1999; Kongsricharoern and Polprasert, 1996; Pagilla and Canter, 1999; Chakravathi et al., 1995; Aksu et al., 1996; Huang et al., 1982). Above cited conventional copper elimination processes are costly or ineffective at small concentrations. Presently biosorption research on removal of heavy metals using readily available agriculture waste is acquiring importance. This process can be applied as a cost effective way for purifying industrial wastewater before its discharge. So far, several bio-materials have been used as adsorbents to remove Cu (II) from aqueous solutions (Park et al., 2010). These include low cost adsorbents prepared with paddy straw powder (Varma and Misra, 2016), tea waste adsorbent (Thapak et al., 2015), onion and garlic skin (Chowdhury et al., 2012), natural clay (Veli and Alyuz, 2007) coconut shell and neem leaves (Singha and Das, 2013), Ceiba pentandra hulls (Rao et al., 2006), walnut shell (Kamar and Nechifor, 2015), saw dust (Ho and McKay, 2003) and Chromolaena leaf powder (Krishna, D. and Shende, 2018).

Though process industries have not focused on use of these naturally available adsorbents, various investigators have been exploring ways to find out the naturally available adsorbents for removal of heavy metals in effective manner and which can be used by industries in coming days. In this regard, mixed adsorbents have been used for the removal of copper from wastewater. This work addresses the use of borassus flabellifer coir and ragi husk mixed adsorbent powder as an effective and inexpensive material for the removal of copper from wastewater in batch experimentation.

2. MATERIALS AND METHODS

2.1 Preparation of Synthetic Copper Solution

Stock solution of 1000 mg/L was prepared by adding distilled water in known quantity of copper (II) sulfate placed in 1 L volumetric flask up to the mark. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, sodium hydroxide (NaOH) and hydrochloric acid (HCl) were purchased from Merck and analytical reagents (AR) and pure. Various concentrations of test solution of Cu (II) ranging from 20-100 mg/L were prepared by subsequent dilution of the stock solution

2.2 Preparation of Borassus Flabellifer Coir Powder and Ragi Husk Powder

Borassus flabellifer coir and ragi husk, collected from agriculture farms in the close region of college were used for the preparation of mixed adsorbents. These materials were washed with pure water and dried to increase the purity

of material by removal of moisture. After this process, materials have been crushed in a roll crusher. The powders so obtained were screened through British Standard Screen (BSS) meshes of required particle sizes. The powders so obtained without any pre-treatment were kept in air tight bottles for carrying out experiments.

2.3 Batch Experimental Procedure

Batch mode adsorption studies for individual metal ions were carried out to investigate the effect of different parameters such as initial metal ion concentration, adsorbent dosage, adsorbent size, agitation time, temperature and pH. The range of different parameters studied in the present work has been given in Table 1. Solution containing adsorbate and adsorbent was taken in 250 mL capacity conical flasks and agitated at 200 mg/L in a mechanical shaker at known time intervals as shown in Table 1. The adsorbate was decanted and separated from the adsorbent using Whatman filter paper.

Final residual metal concentration after adsorption was quantified using atomic absorption spectrophotometer (PinAAcle, 500, Perkin Elmer Pvt Ltd). To find out the percentage removal of copper (II) from wastewater, the given below equation was used.

$$\text{Removal of Copper} = \frac{\text{Initial} - \text{Final metal ion concentration}}{\text{Initial metal ion concentration}} \times 100 \quad (1)$$

2.4 Characterization of Mixed Adsorbent (Ragi Husk and Borassus Flabellifer Coir Powders)

The components present in the mixed adsorbent was evaluated and analyzed as organic nature which represents unoccupied spaces to the mixed adsorbent as identified in SEM photographs shown in Fig. 1. The Fig. 1 indicates that mixed adsorbent surface has the nature of most irregular and unoccupied spaces between sites and thus it promotes the adsorption of metal ions on the surface of mixed adsorbent. Furthermore, the EDS spectra of selected zone of mixed adsorbent before adsorption and after adsorption has indicated the chemical components present in the adsorbent (refer to Fig. 2). It was observed from Fig. 2a that mixed adsorbent contains the components such as carbon, oxygen and silica on its surface before interaction with Cu (II) ions, whereas in Fig. 2b new copper peak has been found along with the surface bearing groups of carbon, oxygen and silica, which indicated the adsorption of Cu (II) on mixed adsorbent.

3. RESULTS AND DISCUSSION

3.1 Effect of Contact Time at Various Mixed Adsorbent Dosages

Fig. 3 represents the agitation time profile for adsorption of Cu (II) metal for solution of 20 mg/L for various dosages

Table 1. Various parameters and its ranges for the removal of copper (II)

Various Parameters	Its ranges
Agitation time, minute	5, 10, 15, 20, 25, 30, 40, 50, 60, 90 and 120
Mixed adsorbent dosage, gram	0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1
Copper ion concentration, mg/L	20, 40, 60, 80 and 100
pH	2, 3, 4, 5, 6, 7, 8, 9 and 10
Absolute temperature, K	273, 283, 293, 303, 313 and 323
Mixed adsorbent particle size, μm	63, 89 and 125

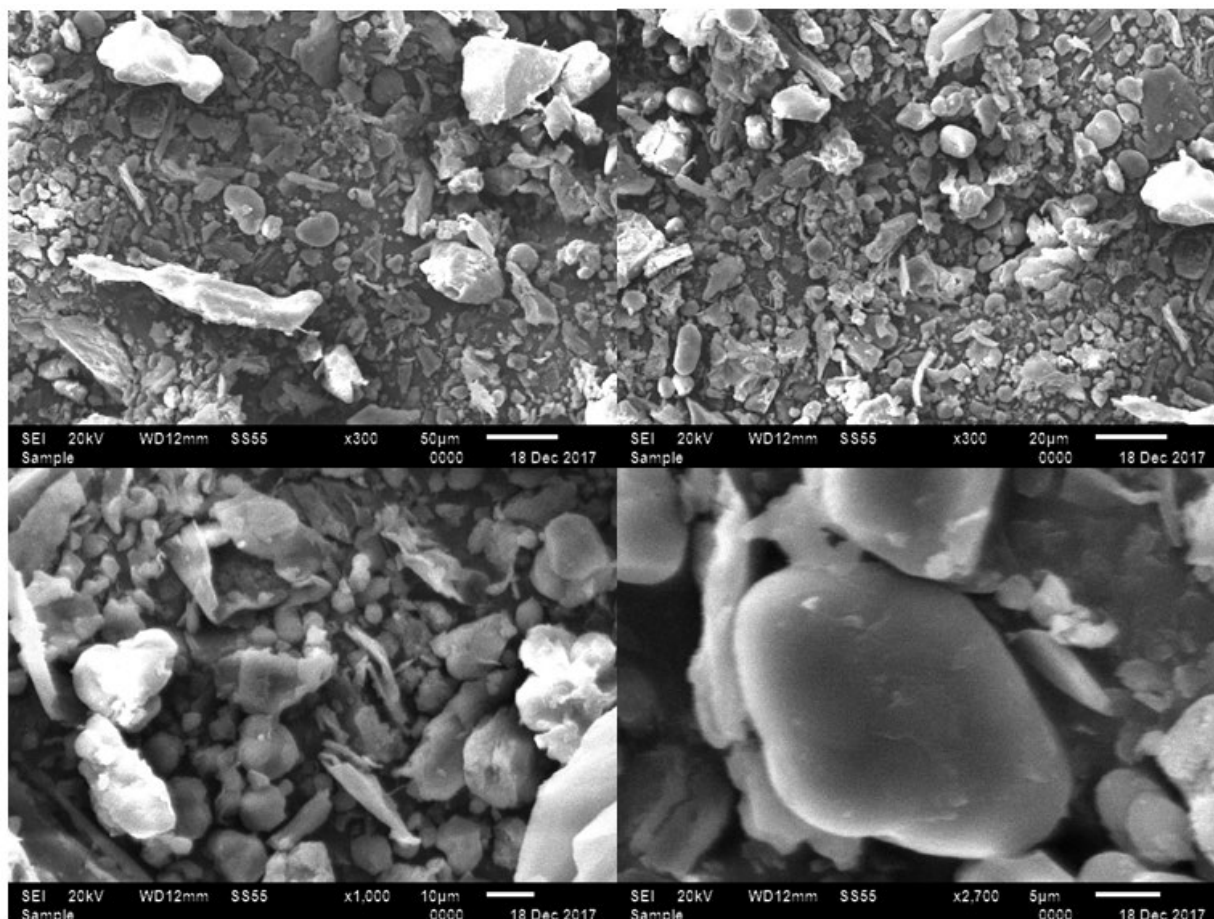


Fig. 1. Scanning Electron Micrograph (SEM) of mixed adsorbent at different frequencies

of mixed adsorbent and also equilibrium time at 60 minute at optimum pH value of 6 for the percentage removal of Cu (II). After equilibrium time, no further change in percentage removal of copper metal is observed. Adsorption process shows that percentage removal of copper increases from 95.34 to 96.11 with increase in dosage of mixed adsorbent from 0.6 g to 0.8 g afterwards it decreases from 96.11 to 94.36 with increase in dosage of mixed adsorbent from 0.8 g to 1.0 g. It conforms that adsorption reaches its saturation capacity at 0.8 g of mixed adsorbent. In present investigation mixed adsorbents i.e. (Ragi husk powder + Borasus flabellifer coir powder) in different proportions have been tested for the removal of copper (II) metal ion from waste water. The d_p is the particle size, in microns.

3.2 Effect of pH

pH is one of the important adsorption parameter for controlling the adsorption process as it changes the degree of ionization, the surface charge of the adsorbents and the species of the adsorbate. Fig. 4 shows the effect of pH on adsorption of copper at different initial concentrations. There was increase in adsorption of copper with increase in pH values from 1 to 6, when pH is greater than 6, adsorption of copper decreases. The maximum percentage removal of copper was noticed at pH 6. The main driving force for any metal ion adsorption is the electrostatic interaction, viz., attraction between the adsorbate and adsorbent. The higher the adsorption of metal ion was investigated at pH value of 6 as greater the interaction among the adsorbate and adsorbent.

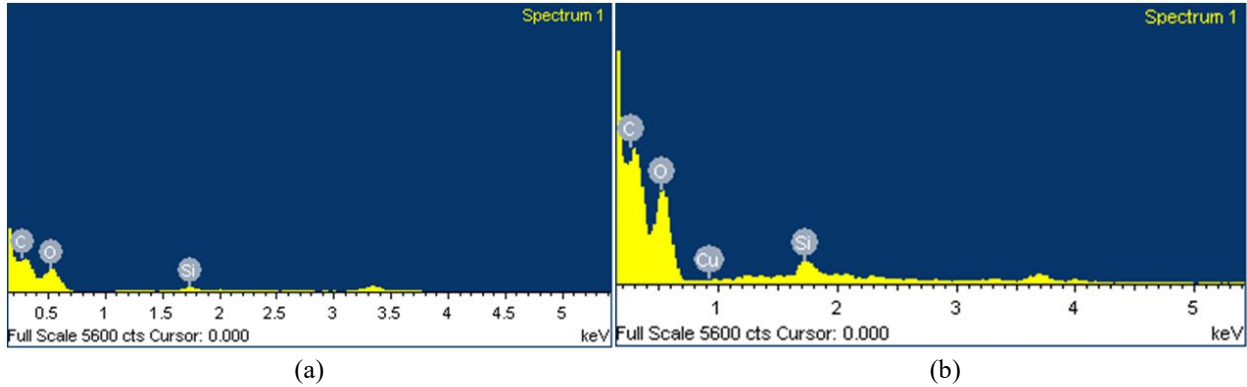


Fig. 2. Energy disperse spectra of mixed adsorbent (a) before copper (II) adsorption (b) after copper (II) adsorption

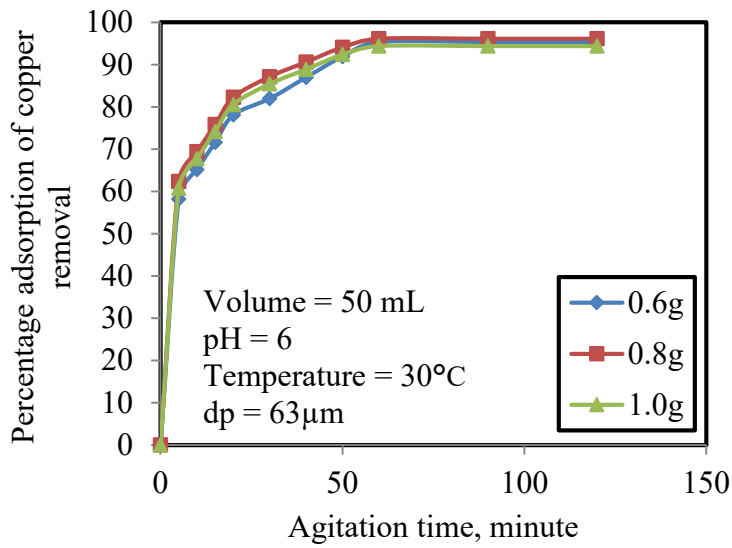


Fig. 3. Effect of agitation time on adsorption of Cu (II) by mixed adsorbent

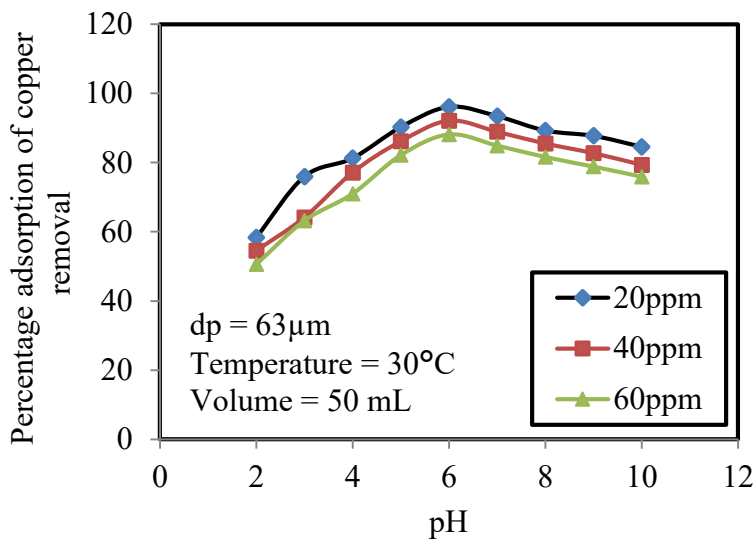


Fig. 4. Effect of pH on adsorption of Cu (II) at different initial concentrations by mixed adsorbent

In this adsorption process, the extent of reaction is affected by both the concentration and pH of the solution while metal ions gets precipitated over a range of pH values.

3.3 Effect of Mixed Adsorbent Dosage and Size in an Aqueous Solution

The variations in percentage removal of Cu (II) and also metal uptake (mg/g) with dosage of mixed adsorbent are depicted in Fig. 5. The percentage removal of copper (II) increases from 72.53% to 96.11% and also metal uptake decreases from 7.253 to 0.9437 mg/g with an increase in the mixed adsorbent dosage from 0.1 g to 0.8 g in 50 mL solution at 313 K for 63 μm mixed adsorbent size. Afterwards, adsorption process reveals that further increase in mixed adsorbent dosage does not result in increase of percentage removal of Cu (II). This may be due to unavailability of binding sites and also due to the blockage of binding site with the excess mixed adsorbent dosage. The percentage removal of copper (II) from wastewater with mixed adsorbent size is reported in Table 2. The percentage removal of copper (II) increases from 91.18 (1.1398 mg/g) to 96.11% (1.2014 mg/g) with decrease in the mixed adsorbent size from 125 to 63 μm. This phenomenon is expected as the decrease in size of adsorbent results in the increase of the surface area of it, thereby the number of active sites are better exposed to the adsorbate.

In present investigation, metal uptake of borassus flabellifer coir powder as adsorbent is 1.369 mg/g whereas metal uptake of borassus flabellifer coir and ragi husk as

mixed adsorbent is 1.2014 mg/g. The performance of mixed adsorbent in comparison with individual adsorbent such as borassus flabellifer coir powder and ragi husk powder are shown in Table 3. The percentage removal of copper from wastewater using mixed adsorbent is 96.1. When the performance of mixed adsorbent is compared with the borassus flabellifer coir powder, the percentage removal of copper using mixed adsorbent seems little bit low because of that ragi husk powder or borassus flabellifer coir powder reduces the pathway for mass transport and internal diffusion of adsorbate inside the adsorbents after both are mixed in some proportion as a mixed adsorbent.

3.4 Effect of Temperature

The effect of temperature on adsorption of copper metal ion on mixed adsorbent at different initial concentrations is depicted in Fig. 6. The maximum percentage removal of copper (II) for various initial concentrations is reported at temperature 323 K. It is confirmed that adsorption of Cu (II) increases with increase in temperature for all concentrations; adsorption process reveals that the present process is endothermic in nature. Further, low initial metal ion concentrations of the solution shows favorable adsorption in comparison with higher metal ion concentration solutions. The percentage removal of copper is increased from 78.09% to 97.56% for a temperature range of 283-323 K. Maximum adsorption of 97.56% was observed at 323 K. This increase in binding might be due to increase in surface activity and increased kinetic energy of the Cu (II) metal ions.

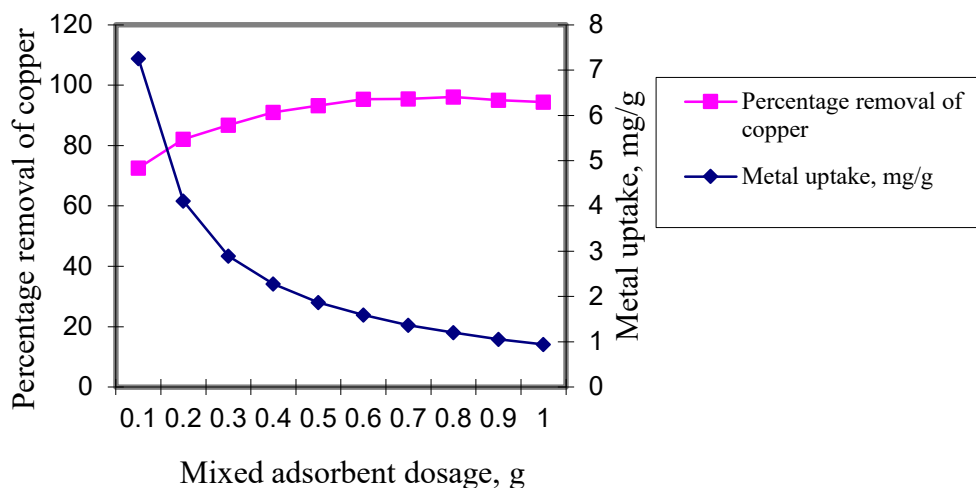


Fig. 5. Effect of mixed adsorbent dosage on percentage removal of copper and metal uptake

Table 2. Effect of mixed adsorbent particle size, C₀ = 20 mg/L; Temperature = 303 K; V = 50 mL; t = 60 min; pH = 6

S.No.	Mixed adsorbent average particle size, μm	Final metal ion concentration, mg/L	Percentage removal of Cu(II)	Metal uptake (mg/g)
1	63	0.778	96.11	1.201
2	89	0.924	95.38	1.192
3	125	1.764	91.18	1.139

Table 3. Comparison of performance of individual adsorbents against mixed adsorbent

S.No.	Name of adsorbent	pH	Percentage removal of copper (II)	References
1	Borassus flabellifer coir powder	6	97.92	Krishna (2013)
2	Ragi husk powder	10	97.97	Rudre et al. (2012)
3	Mixed adsorbent powder	6	96.1	Present study

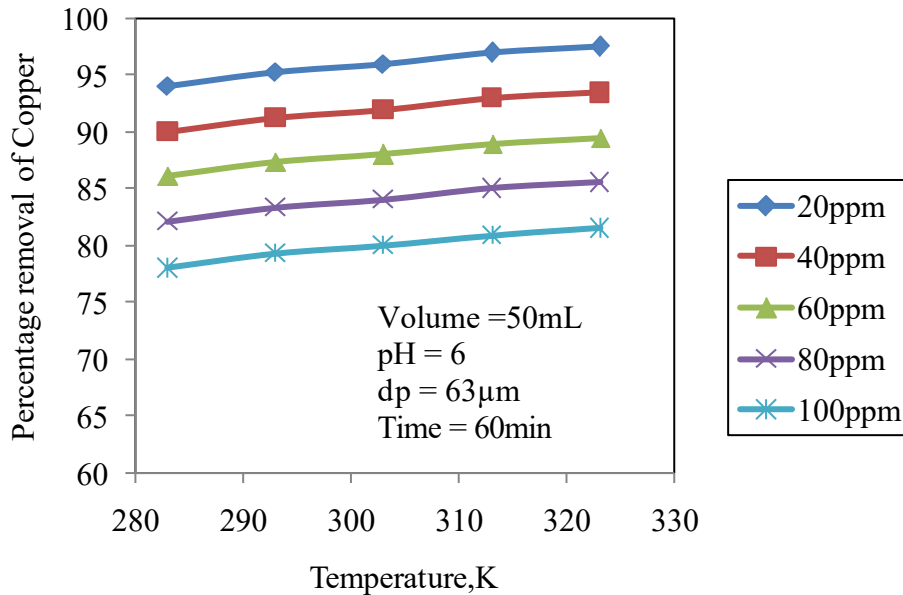


Fig. 6. Effect of temperature on percentage removal of Cu (II) by mixed adsorbent

3.5 Adsorption Isotherms

An applicability of Langmuir, Freundlich and Tempkin isotherms for mixed adsorbents of borassus flabellifer coir powder and ragi husk powder was tested to characterize the interaction of the metal ions with the mixed adsorbent. This provides a relationship between the concentration of metal ions in the solution and the amount of metal ions adsorbed to the solid phase when the two phases are at equilibrium.

3.5.1 Langmuir Model

The applicability of Langmuir isotherm (Langmuir, 1918) was tested to estimate the maximum metal uptake which occurs on a homogeneous surface by monolayer sorption. The model of this is given below

$$q_e = \frac{q_{max} b C_e}{1 + b C_e} \tag{2}$$

q_e is the metal uptake (mg/g), C_e is the equilibrium metal ion concentration (mg/L). q_{max} is the maximum metal uptake (mg/g), and b is the ratio of sorption rates. The linear form of Langmuir isotherm is given below

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{q_{max} b C_e} \tag{3}$$

Fig. 7 depicts the linearity for Langmuir isotherm for the adsorption of copper metal ion on mixed adsorbent powder.

Their equations along with the q_{max} and b calculated from the slope and the intercept are depicted in Table 4. It is noticed that there was strong binding of copper metal ions onto the surface of mixed adsorbent powder. The separation factor, R_L determined from Table 5 at temperature 303 K and pH 6 is in between 0.0433-0.1844 for various concentrations shows favorable adsorption ($0 < R_L < 1$).

3.5.2 Freundlich Model

The applicability of Freundlich isotherm (Freundlich, 1907) was tested for nonlinear multilayer adsorption model with heterogeneous energetic distribution active sites and reversible adsorption, followed by interaction between adsorbed molecules. The general of this model is given below

$$q_e = K_f C_e^{\frac{1}{n}} \tag{4}$$

K_f and n are the adsorption capacity and adsorption intensity respectively. q_e is the equilibrium metal uptake (mg/g) and C_e is concentration of copper at equilibrium. The linear equation representing the Freundlich model is given below.

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{5}$$

The values of K_f and n obtained from intercept and slope of a plot of $\log q_e$ versus $\log C_e$ is shown in Table 6. Fig. 8

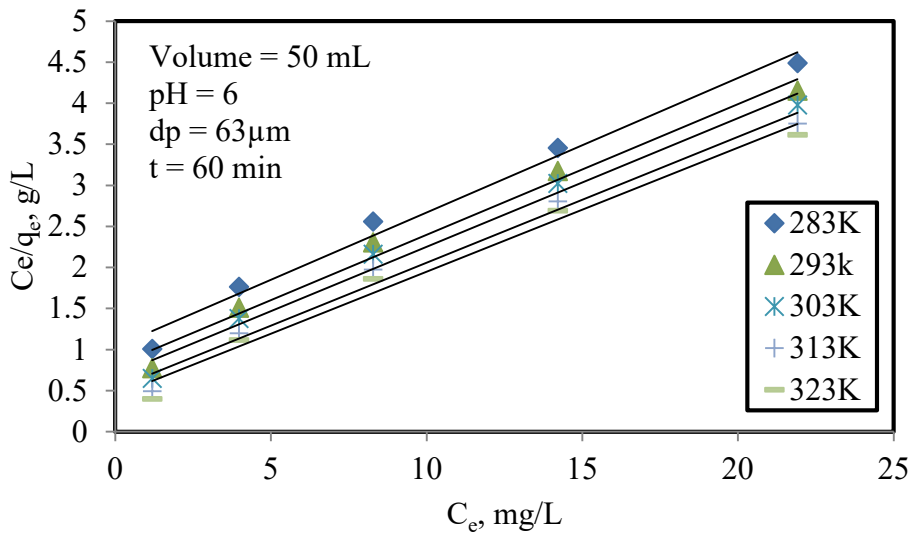


Fig. 7. The Langmuir isotherm for adsorption of Cu (II) by mixed adsorbent

Table 4. Langmuir isotherm parameters for removal of Cu (II) by mixed adsorbent

S.No.	Parameters	Model Equations	q_{max}	b	R_L	R^2
1	T = 283K	$\frac{C_e}{q_e} = 0.163C_e + 1.031$	6.1349	0.1581	<1	0.985
2	T = 293K	$\frac{C_e}{q_e} = 0.167C_e + 0.854$	5.988	0.1955	<1	0.981
3	T = 303K	$\frac{C_e}{q_e} = 0.168C_e + 0.760$	5.952	0.2211	<1	0.980
4	T = 313K	$\frac{C_e}{q_e} = 0.171C_e + 0.641$	5.848	0.2668	<1	0.978
5	T = 323K	$\frac{C_e}{q_e} = 0.173C_e + 0.576$	5.7803	0.3003	<1	0.976

Table 5. Separation factor $R_L = \frac{1}{1 + bc_i}$ values at pH = 6; T = 303K

Initial concentration, C_i (mg/L)	R_L
20	0.1844
40	0.1016
60	0.0701
80	0.0535
100	0.0433

Table 6. Freundlich isotherm parameters for removal of Cu (II) by mixed adsorbent

S.No.	Parameters	Model Equations	K_f	n	R^2
1	T = 283K	$\log q_e = 0.49 \log C_e + 0.046$	1.1117	2.041	0.997
2	T = 293K	$\log q_e = 0.461 \log C_e + 0.101$	1.2618	2.1692	0.998
3	T = 303K	$\log q_e = 0.442 \log C_e + 0.134$	1.3614	2.2624	0.999
4	T = 313K	$\log q_e = 0.415 \log C_e + 0.179$	1.5101	2.4096	0.999
5	T = 323K	$\log q_e = 0.396 \log C_e + 0.208$	1.6143	2.5252	0.999

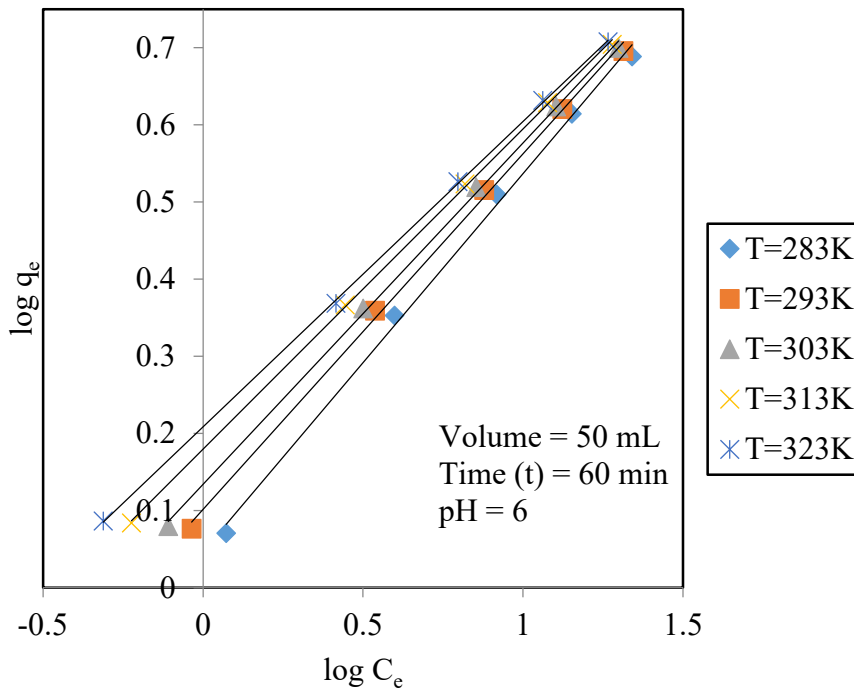


Fig. 8. The Freundlich isotherm for adsorption of Cu (II) by mixed adsorbent

depicts good linearity with high regression coefficient for Freundlich isotherm for the adsorption of copper metal ion on mixed adsorbent powder and linearity of the relationship reveals strong binding of copper metal ion on to surface of the mixed adsorbent. As the slope of isotherm (n) is greater than 1, it favors for the adsorption of copper metal ion on mixed adsorbent.

3.5.3 Tempkin Model

The applicability of Tempkin isotherm model (Tempkin and Pyzhev, 1940) was tested for direct/indirect adsorbent-adsorbate interactions. Both the nonlinear and linear form of Tempkin equations are given below.

$$q_e = \frac{RT}{b_T} \ln(A_T C_e) \tag{6}$$

$$q_e = B_T \ln A_T + B_T \ln C_e \tag{7}$$

$B_T = (RT/b_T)$. T is the temperature (K) and R is the universal ideal gas constant. The constant b_T represents the heat of

adsorption. A_T is the equilibrium binding constant at the maximum binding energy. A plot of q_e versus $\ln C_e$ at a fixed temperature will give Tempkin isotherm constants, A_T and b_T .

Fig. 9 depicts the linearity for Tempkin isotherm for the adsorption of Cu (II) metal ion on mixed adsorbent. Their equations with regression coefficients are given in Table 7 and linearity relationship of figure reveals that strong binding of Cu (II) on to surface of the mixed adsorbent.

3.6 Studies on Kinetics of Adsorption

Reaction rate, pathways and time to obtain equilibrium are evaluated by adsorption kinetic models, viz, pseudo first and second order kinetic models. Based on high or low regression coefficient, the approaches of experimental data to predicted values from the model will be decided. A relatively high regression coefficient (close or equal to one) is always chosen for better adsorption of Cu (II) metal ions on to the mixed adsorbent.

Table 7. Tempkin isotherm parameters for removal of Cu (II) by mixed adsorbent

S.No.	Parameters	Model Equations	b_T	A_T	R^2
1	T = 283K	$q_e = 1.262 \ln C_e + 0.757$	1864.39	1.8117	0.977
2	T = 293K	$q_e = 1.201 \ln C_e + 1.065$	2028.31	2.427	0.973
3	T = 303K	$q_e = 1.159 \ln C_e + 1.255$	2173.55	2.953	0.969
4	T = 313K	$q_e = 1.097 \ln C_e + 1.522$	2372.18	4.004	0.964
5	T = 323K	$q_e = 1.049 \ln C_e + 1.698$	2559.98	5.0464	0.958

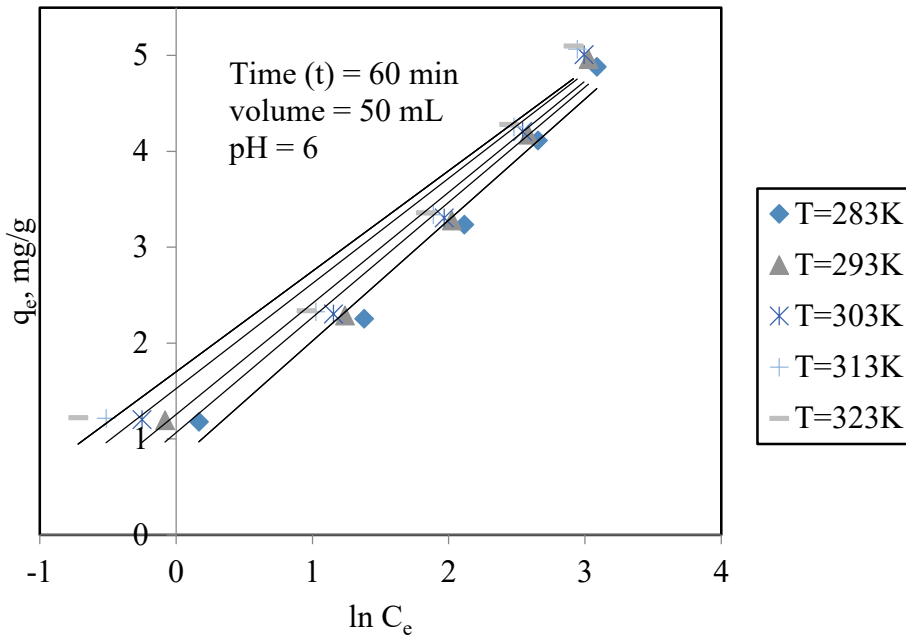


Fig. 9. The Tempkin isotherm for adsorption of Cu (II) by mixed adsorbent

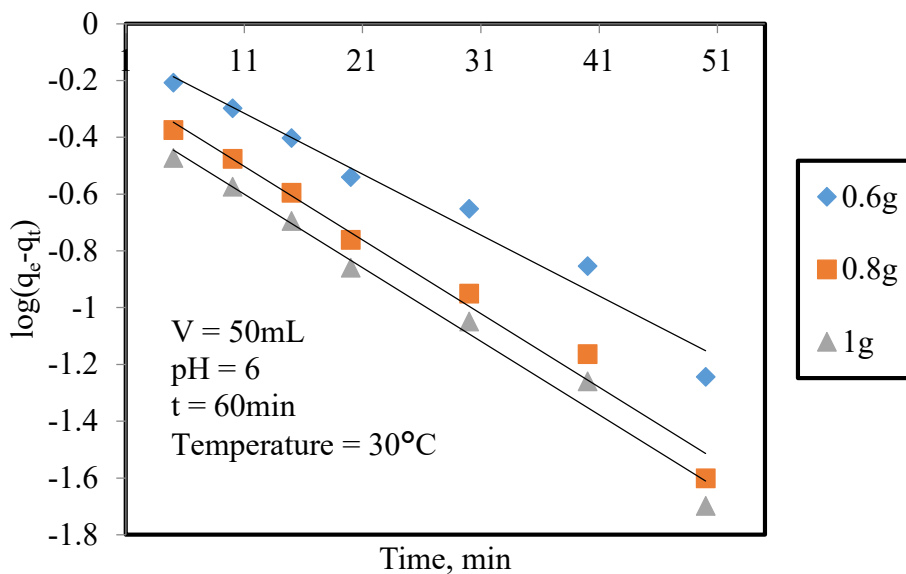


Fig. 10. Testing the first order kinetics for adsorption of Cu (II) by mixed adsorbent

3.6.1 Pseudo-First Order Kinetic Model

The pseudo first order kinetic model is given below

$$\frac{dq}{dt} = k_1(q_e - q_t) \tag{8}$$

q_e and q_t are the metal uptake at equilibrium and time t , respectively (mg/g) and k_1 is the rate constant of pseudo first order adsorption (min^{-1}). Equation (8) is arranged as follows

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t \tag{9}$$

The plot of $\log (q_e - q_t)$ vs t is linear from which k_1 can be determined from the slope. Fig. 10 depicts the first order kinetics for adsorption of Cu (II) metal ion on mixed adsorbent. The model equations with regression coefficients are shown in Table 8. From the graph, the q_e is estimated for different process parameters and the estimated values are checked with the experimental values. From Table 8, it is observed that q_{ecal} and q_{exp} are not the same. Therefore, first order kinetics may not represent the first order kinetic model. The above model is not fit for Cu (II) removal on mixed adsorbent.

3.6.2 Pseudo-Second Order Kinetic Model

The pseudo-second-order kinetic model rate equation is expressed as

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \tag{10}$$

k_2 is the rate constant ($g\ mg^{-1}min^{-1}$). The linear form of Equation (10) after integration is given by

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e} \tag{11}$$

And k_2 is obtained from the intercept of the plot of t/q_t vs t . Fig. 11 shows the second order kinetic model for adsorption of Cu (II) metal ion on mixed adsorbent. At the same adsorption parameters, comparison between metal uptake q_e values of the second order kinetic model and experimental q_e values is made in Table 9. It is observed that q_{ecal} and q_{eexp} are almost the same. Therefore, the second order kinetic model is fit for Cu (II) removal by mixed adsorbent.

Table 8. Kinetic data of pseudo first order coefficients for removal of Cu (II)

Kinetics	Mixed adsorbent dosage, g	Model Equations	q_{ecal}	q_{eexp}	R^2	Rate constants, k_1, min^{-1}
1 st order	0.6	$\log(q_e - q) = -0.021t - 0.078$	0.836	1.589	0.971	0.0484
	0.8	$\log(q_e - q) = -0.039t + 0.753$	0.608	1.201	0.982	0.0575
	1.0	$\log(q_e - q) = -0.036t + 0.920$	0.484	0.9437	0.982	0.0575

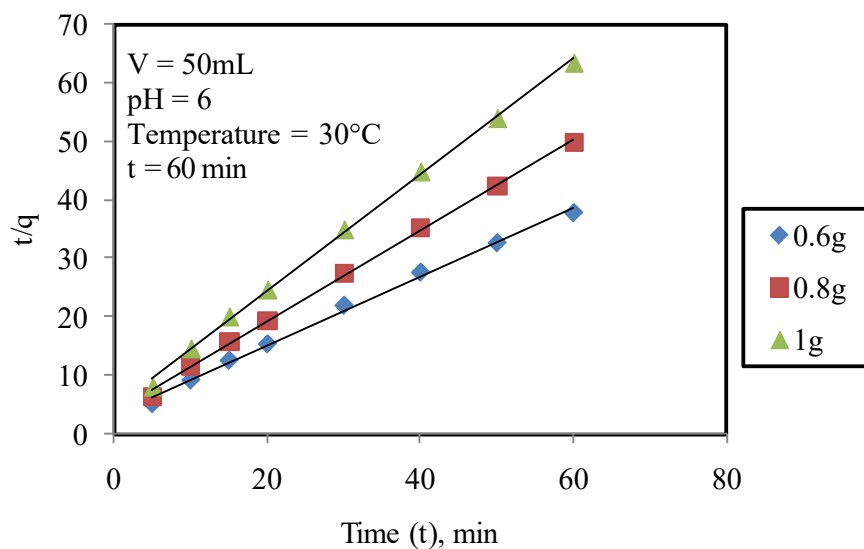


Fig. 11. Testing the second order kinetics for adsorption of Cu (II) by mixed adsorbent

Table 9. Kinetic data of pseudo second order coefficients for removal of Cu (II)

Kinetics	Mixed adsorbent dosage, g	Model Equations	q_{ecal}	q_{eexp}	R^2	Rate constants, $k_2, g\ mg^{-1}\ min^{-1}$
2 nd order	0.6	$\frac{t}{q} = 0.587t + 3.385$	1.7035	1.589	0.996	0.1018
	0.8	$\frac{t}{q} = 0.781t + 3.597$	1.2804	1.201	0.998	0.1687
	1.0	$\frac{t}{q} = 0.083t + 0.603$	1.007	0.9437	0.998	0.2111

3.6.3 Intra-Particle Diffusion Model

The combination of four consecutive steps (Baral et al., 2009), viz, diffusion in the bulk solution, diffusion across the thin film surrounding the adsorbent particles, intra-particle diffusion and adsorption within the particles are used for Cu (II) removal from wastewater. According to Weber and Moris (1963) if the rate limiting step is the intra-particle diffusion, then amount of adsorbed at any time is directly proportional to the square root of contact time t and may pass through the origin which is given mathematically in Equation (12).

$$q_t = K_{diff} t^{0.5} + C \quad (12)$$

q_t , t and K_{diff} are the metal uptake (mg/g), contact time (min) and the intra-particle diffusion coefficient respectively. A plot of q_t against $t^{0.5}$ will give a straight line with a positive intercept for intra particle diffusion. The value of K_{diff} will be calculated from slope. The higher value of K_{diff} indicates the enhancement of the rate of adsorption.

Fig. 12 depicts the linearity for intra particle diffusion model based on the regression coefficients. The R^2 values (refer to Table 10) are close to unity, conforming that the rate-limiting step is actually the intra-particle diffusion process. The values of K_{diff} calculated from slope provide

information about thickness of the boundary layer, i.e. the resistance to the external mass transfer. The larger slope indicates higher external resistance.

3.7 Thermodynamics of Adsorption

Adsorption depends on the temperature and also associated with three thermodynamic parameters like change in enthalpy (ΔH), entropy (ΔS) and Gibb's free energy (ΔG) (Hamdaoui and Naffrechoux, 2007).

The Van't Hoff equation is given below

$$K_D = \frac{C_{Ae}}{C_e} \quad (13)$$

$$\Delta G = -RT \ln K_D \quad (14)$$

K_D is the equilibrium constant and C_{Ae} and C_e (both in mg/L) are the equilibrium concentrations for solute on the mixed adsorbent and in the solution, respectively. The K_D values calculated from Equation (13) are used in Equation (14) to find out the ΔG , ΔH and ΔS . Then K_D is expressed below as function of ΔH (KJ/mol) and ΔS (KJ/mol K) and absolute temperature (K).

$$\ln K_D = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (15)$$

Table 10. Intra particle diffusion model parameters for removal of Cu (II)

S.No.	Mixed adsorbent dosage, g	Model equations	R^2	K_{diff}	Constant, C
1.	0.6	$q_t = 0.114t^{0.5} + 0.736$	0.983	0.114	0.736
2.	0.8	$q_t = 0.082t^{0.5} + 0.618$	0.972	0.082	0.618
3.	1.0	$q_t = 0.065t^{0.5} + 0.479$	0.972	0.065	0.479

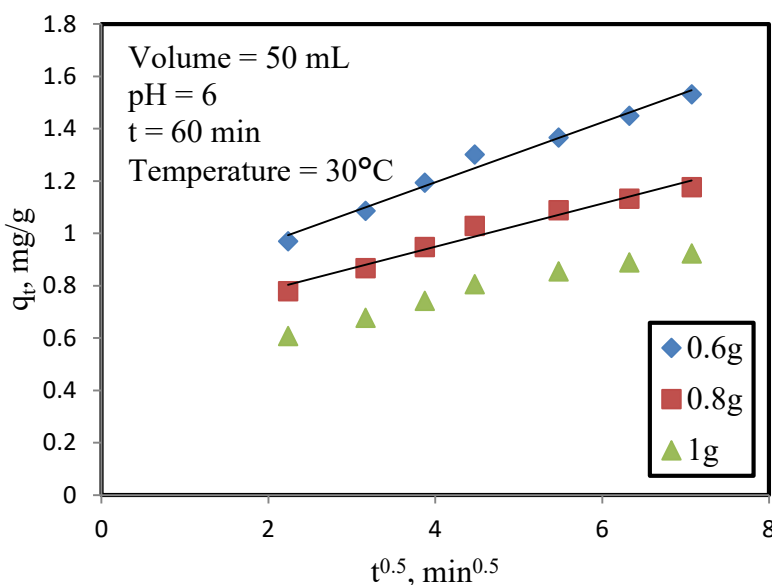


Fig. 12. Testing the intra particle diffusion model for adsorption of Cu (II) by mixed adsorbent

The values of ΔH and ΔS are calculated from the slope and intercept respectively by plotting $\ln K_D$ vs $(1/T)$.

The experimental data was plotted in Fig. 13 which indicates the linearity for Van't Hoff equation. Their equations with correlation coefficients are shown in Table 11. From values of ΔH , adsorption process is endothermic in nature as ΔH values are positive. If ΔS value is less than zero, it represents that adsorption process is highly reversible. If ΔS value is more than or equal to zero, it represents that adsorption process is irreversible. The negative value of ΔG represents the spontaneity and feasibility of the process while the positive values non spontaneity and non feasibility of the process. The thermodynamic parameters such as change in Gibbs free

energy (ΔG), enthalpy (ΔH) and entropy (ΔS) for the adsorption of Cu (II) metal ions on mixed adsorbent powder indicates the feasibility, spontaneity, irreversibility and endothermic nature.

4. CONCLUSIONS

Borassus flabellifer coir and ragi husk mixed adsorbent powder have the potential for use as cheap naturally available bio-sorbent for the removal of Cu (II) from wastewater, up to 96.11% for an initial concentration of Cu (II) 20 mg/L and at a temperature of 303 K. The Cu (II) adsorption performance by mixed adsorbent powder is

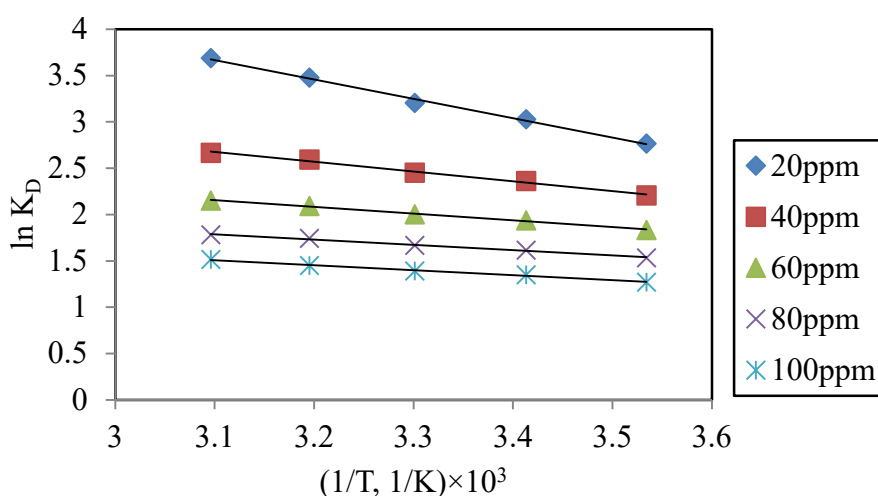


Fig. 13. Finding out the Von't Hoff equation

Table 11. Thermodynamic parameters for removal of Cu (II) by mixed adsorbent

Concentration, mg/L	Model Equations	ΔH , KJ/mol	ΔS , J/mol K	ΔG , KJ/mol				
				283	293	303	313	323
20	$\ln K_D = -2.090\left(\frac{1}{T}\right) + 10.14$ $R^2 = 0.995$	17.376	84.304	-6.482	-7.325	-8.168	-9.011	-9.854
40	$\ln K_D = -1.058\left(\frac{1}{T}\right) + 5.939$ $R^2 = 0.992$	8.796	49.376	-5.177	-5.671	-6.164	-6.659	-7.152
60	$\ln K_D = -0.726\left(\frac{1}{T}\right) + 4.407$ $R^2 = 0.995$	6.036	36.639	-4.333	-4.429	-4.796	-5.432	-5.798
80	$\ln K_D = -1.807\left(\frac{1}{T}\right) + 6.696$ $R^2 = 0.889$	4.756	29.606	-3.622	-3.918	-4.215	-4.511	-4.807
100	$\ln K_D = -1.922\left(\frac{1}{T}\right) + 7.006$ $R^2 = 0.889$	4.465	26.372	-2.998	-3.262	-3.526	-3.789	-4.053

strongly affected by parameters, viz, contact time, Cu (II) concentration, pH, mixed adsorbent dosage, mixed adsorbent particle size and temperature.

- Percentage adsorption of Cu (II) by mixed adsorbent is reached the equilibrium agitation time at 60 minutes for all initial concentration of copper solution.
- With an increase in pH from 1 to 10, the percentage adsorption of Cu (II) is increased upto pH value of 6 after that it decreases. The optimum pH is taken at pH of 6.
- With the increase in mixed adsorbent dosage from 0.1 to 1.0 g (for 50 mL of solution of 20 mg/L), the percentage adsorption of copper is increased from 72.53 to 96.1%.
- The percentage removal of Cu (II) increases from 91.88 (1.1398 mg/g) to 96.1 percentage (1.2014 mg/g) for 0.8 g of mixed adsorbent dosage in 50 mL (20 mg/L) of solution at 60 minute equilibrium agitation time.
- The percentage adsorption of Cu (II) on mixed adsorbent increases with increase in the temperature from 283 to 323 K for all initial concentrations of Cu (II).
- The Freundlich isotherm for adsorption of copper (II) onto mixed adsorbent is proved to be the best fit followed by the Langmuir isotherm and Tempkin isotherms to the experimental data.
- The adsorption kinetic model follows the pseudo second-order kinetics.
- The thermodynamic parameters such as change in Gibb's free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) reveals the feasibility, irreversibility, spontaneity and endothermic nature and an increased randomness at the surface of the mixed adsorbent powder.

The present study has been performed in the batch process as this gives a platform for the designing of continuous flow systems which enables its online measurement in industrial wastewater.

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