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Valorization of Paper Mill Sludge as Adsorbent in Adsorption Process of Copper (II) Ion from Synthetic Solution: Kinetic, Isotherm and Thermodynamic Studies

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Abstract This study investigates the process conditions of the adsorption of copper (II) ion onto paper mill sludge (PMS) in a batch process. These conditions are: concentration of initial solution, contact time, temperature and quantity of the adsorbent. Characteristic properties of PMS employed as an adsorbent in the experiments were defined using Fourier transform infrared spectroscopy (FT-IR) scanning electron microscopy (SEM) and elemental analyses. According to the obtained results, while the amount of removed copper (II) ion increased with an increase in the rate of the adsorbent and contact time, it decreased as a result of an increase in the temperature and initial solution concentration. Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherms were implemented for the determination of the most appropriate isotherm model for the experimental data, and it was found that the process is in concordance with Langmuir equation. The maximum adsorption capacity of PMS was calculated as $114.42\,\mathrm{mg\,g^{-1}}$. In kinetic studies, the adsorption process of copper (II) ion onto PMS was controlled by the pseudo-second-order kinetic model. The calculated activation value (E_a) was $38.61\,\mathrm{kJ\,mol^{-1}}$ and demonstrates that the process occurred by physical adsorption mechanism. The values of the thermodynamic parameters such as enthalpy (ΔH^O) $(-21.19\,\mathrm{kJ\,mol^{-1}})$, free energy (ΔG^O) $(-8.883\,\mathrm{kJ\,mol^{-1}})$ and entropy (ΔS^O) $(0.101\,\mathrm{kJ\,mol^{-1}\,K^{-1}})$ changes were determined to estimate the nature of the process. The results clearly showed that the process was of exothermic and spontaneous nature and that PMS could be utilized as an adsorbent for the removal of copper (II) ion from wastewater.

Keywords Adsorption · Copper (II) ion · Isotherm · Kinetic · Thermodynamic · Paper mill sludge · Heavy metal

List of symbols

C_o	Initial concentration of Cu (II) solution (mM)
C_s	Final concentration of Cu (II) solution (mM)
C_e	Cu (II) concentration in solution at equilibrium $(\mathrm{mM\,L^{-1}})$
q_e	Amount of Cu (II) ions adsorbed per unit mass of adsorbent $(\mathrm{mM\,g^{-1}})$
q_{max}	Maximum adsorption capacity $(\mathrm{mM\,g^{-1}})$
v	Volume of the solution (L)
m	Amount of adsorbent (g)
q_e	Amount of Cu (II) ions adsorbed at equilibrium $(\mathrm{mM\,g^{-1}})$
q_t	Amount of Cu (II) ions adsorbed at time t $(\mathrm{mM\,g^{-1}})$
k_1	Pseudo-first-order reaction rate constant $(\mathrm{min^{-1}})$
k_2	Pseudo-second-order reaction rate constant $(\mathrm{g\,mM^{-1}\,min^{-1}})$
k_i	Intra-particle diffusion rate constant $(\mathrm{mM\,g^{-1}\,min^{-1/2}})$
b	Adsorption energy $(\mathrm{L\,mM^{-1}})$
K_f	Adsorption capacity $(\mathrm{mg\,g^{-1}})$
n	Adsorption intensity
q_m	Maximum amount of Cu (II) ion adsorbed onto unit weight of adsorbent $(\mathrm{mg\,g^{-1}})$
β	Adsorption energy $(\mathrm{mol^2\,kJ^{-2}})$

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ε	Polanyi potential
R	Universal gas constant ($\text{kJ mol}^{-1}\,\text{K}^{-1}$)
T	Temperature (K)
r	Separation factor
b	Langmuir constant (L mM^{-1})
m/V	Adsorbent/solution ratio (g L^{-1})
b_o	A constant
ΔH^o	Enthalpy (kJ mol^{-1})
ΔS^o	Entropy ($\text{kJ mol}^{-1}\,\text{K}^{-1}$)
ΔG^o	Gibbs free energy (kJ mol^{-1})

1 Introduction

Toxic heavy metal ions from inorganic pollutants discharged into water resources cause serious health problems on many biological species and the environment, even at low concentrations [1]. It is known that the considerable amount of hazardous and toxic heavy metals are discharged into water resources without any wastewater treatment during various industrial processes such as metallurgical, batteries, mining, smelting, alloy and textile manufacturing [2–4]. In reference to water pollution regulation, the maximum permissible concentration of Cu (II) ion discharge from industrial liquid wastes is limited to $0.25\ \text{mg L}^{-1}$ [5]. Therefore, it is necessary to develop environmentally friendly and cost-effective processes in order to remove heavy metals from industrial effluents by multiple techniques, e.g., ion exchange [6], membrane filtration [7], chemical precipitation [8] electrocoagulation [9–11] and adsorption [12,13]. The adsorption process is usually preferred because it has been easier to apply and more cost-effective for the removal of contaminants as heavy metals in recent years [14,15].

The paper industry produces enormous quantities of solid waste which causes an environmental burden [16]. For this reason, the land filling, land application (composting) and incineration methods are utilized to overcome this problem all over the world [17,18]. Nowadays, particularly land filling and land application are commonly used methods for the disposal of PMS. However, utilization of these methods will have to be reduced in the future due to new stringent environmental regulations and decreasing landfill capacity [16,19]. Although PMS containing organic components is mostly incinerated to minimize its burden on the environment, this is an uneconomic and unfeasible technique [16]. Recent studies in the literature focus on PMS being indirectly used as an adsorbent for the removal of hazardous and toxic heavy metals from industrial wastewaters [17,20,21].

In this paper, we utilized PMS as a cost-effective adsorbent for the adsorption of Cu (II) ion from synthetic solutions. In this context, the adsorption experiments in a batch system were performed to investigate the heavy metal adsorption features of PMS and the affecting parameters, e.g., concentration of the initial solution, temperature, contact time and quantity of adsorbent on the adsorption of Cu (II) ion. In addition, adsorption process was also described using kinetic, equilibrium and thermodynamic inquiries.

2 Materials and Methods

2.1 Materials and Characterization

The stock solution containing Cu (II) ions (0.25 M) was prepared using distilled water and analytical grade $CuCl_2 \cdot 2H_2O$. pH values of the metal solutions were regulated using 0.1M HCl and 0.1M NaOH. PMS was provided from OYKA paper industry in the Western Black Sea Region (Zonguldak/Turkey). Firstly, PMS was air-dried, crushed and sieved in a laboratory to achieve the desired particle sizes (<100 meshes) and then kept in a plastic bottle to be used in the subsequent experiments.

Organic and inorganic compositions of PMS structure were assessed using an elemental analyzer (LECO CHNS 932). pH measurements of the supernatants were performed using a pH meter (Metler Delta 350), and then the quantity of Cu (II) ion in the supernatant was measured using an atomic absorption spectrophotometer (Perkin Elmer AAnalyst-400). To detect the presence of functional groups in the adsorbent structure, FT-IR spectra were recorded using an IR Affinity-1 with an ATR attachment (Shimadzu Inc.) in a wavelength range of $4000–400\ \text{cm}^{-1}$ with a resolution of $4\ \text{cm}^{-1}$ after 100 scans. SEM images were recorded using a TESCAN MAIA3 XM.

2.2 Adsorption Study

The solutions at various concentrations (5, 10, 15, 20 and 25 mM) were prepared by diluting with distilled water from stock solution.

All studies were performed in 300 mL. Erlenmeyer flasks in a shaker was equipped with an adjustable agitation speed and temperature (Zhcheng ZHWY-200D). After the initial pH values of the prepared solutions were measured, PMS was added and then the obtained mixtures were shaken at 200 rpm and stipulated temperature and time. The mixtures were filtered (Double Rings-203) and supernatant was collected. Finally, the quantity of Cu (II) ions in the supernatant was calculated after pH measurements.

In the preliminary experiments, PMS at different rates (0.5; 1; 2.5; 5; 7.5; 10; 15; 20; 25 and $50\ \text{g L}^{-1}$) was added to the prepared solution (5 mM) which was, then, shaken for 24 h. As a result of the analyses of the supernatants, the removal yield of Cu (II) ion from the synthetic solution was calculated and the optimum rate of PMS was determined to be $10\ \text{g L}^{-1}$ for the subsequent experiments.

The effects of the experimental variables such as the initial concentration of Cu (II) solution, temperature and time of

the adsorption process were studied within the ranges of 5 to 25 mM, at 25–55 °C and for 0–24 h, respectively. The removal rate and the quantity of Cu (II) ions adsorbed onto the PMS were calculated using the following equations:

$$\text{Removal (\%)} = (C_o - C_s) \times \frac{100}{C_o} \tag{1}$$

$$q_e = \frac{(C_o - C_s) \times V}{m} \tag{2}$$

All studies were repeated to verify the reproducibility of the results, and the mean values of the results were noted for calculations. The results of the repeated experiments were found to vary ($\pm 5\%$).

3 Isotherm, Kinetic and Thermodynamic Studies

3.1 Adsorption Kinetics

The structure of the adsorption process was elucidated by analyzing the obtained experimental data in three different kinetic models: pseudo-first-order kinetic, pseudo-second-order kinetic and intra-particle diffusion models by which the activation energy of the process was calculated. Furthermore, the adsorption data were analyzed using Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherms in order to calculate the thermodynamic parameters of the process.

The equation of the pseudo-first-order kinetic model is as follows [22]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{3}$$

q_e and k values were obtained using the intercept and slope of the plotted graphic in terms of Eq. (3), respectively.

The pseudo-second-order kinetic model is denoted by Eq. (4) [23]:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \tag{4}$$

The intra-particle diffusion equation is as follows [24]:

$$q_t = k_i t^{1/2} + I \tag{5}$$

k_i and I values were found using the slope and intercept of the plotted graphic in terms of Eq. (5), respectively.

3.2 Adsorption Isotherms

In order to affirm its validity, the experimental data on the adsoption processes at 25, 40 and 55 °C were reanalyzed using Langmuir, Freundlich and Dubinin–Radushkevich isotherm models. In adsorption processes, the Langmuir model is based on the formation of a homogenous surface by monolayer sorption. It is denoted by the equation [25];

$$\frac{C_e}{q_e} = \frac{1}{q_{max}b} + \frac{C_e}{q_{max}} \tag{6}$$

q_{max} and b values were calculated using the slope and intercept of the plotted graph of C_e/q_e versus C_e, respectively

The Freundlich isotherm equation designating the heterogeneous surface formation due to the interaction between the adsorbed ions can be written as [26];

$$\ln(q_e) = \ln K_f + \left(\frac{1}{n}\right) \ln C_e \tag{7}$$

Freundlich constants (K_f and $1/n$) were determined using the intercept and slope from a straight line of $\ln q_e$ versus $\ln C_e$.

The Dubinin–Radushkevich isotherm equation is commonly preferred to describe the chemical or physical nature of adsorption process. Below is the equation of the linear D–R model [27]:

$$\ln q = \ln q_m - \beta \varepsilon^2 \tag{8}$$

β and q_m values were found using the slope and intercept of the plotted graph of $\ln q_e$ versus $\ln C_e$, respectively.

The dimensionless separation factor (r) is used in calculations to evaluate the adsorption process corresponding to Langmuir equation as follows [28]:

$$r = \frac{1}{1 + bC_0} \tag{9}$$

The value of r is used to indicate the type, characteristic and feasibility of the isotherm. In other words, r value indicates that the process is irreversible ($r = 0$), favorable ($0 < r < 1$), linear ($r = 1$) or unfavorable ($r > 1$) [28]. In addition, it is well known that higher adsorbent/solution ratio in solutions is required for a higher amount of metal removals. Therefore, the following equation is expressed mathematically as:

$$\frac{m}{V} = \frac{(C_0 - C_e)(1 + bC_e)}{q_{max}bC_e} \tag{10}$$

3.3 Thermodynamic Parameters

Thermodynamic parameters related to enthalpy (ΔH^o), entropy (ΔS^o) and free energy (ΔG^o) of process were also calculated using the equations [29]:
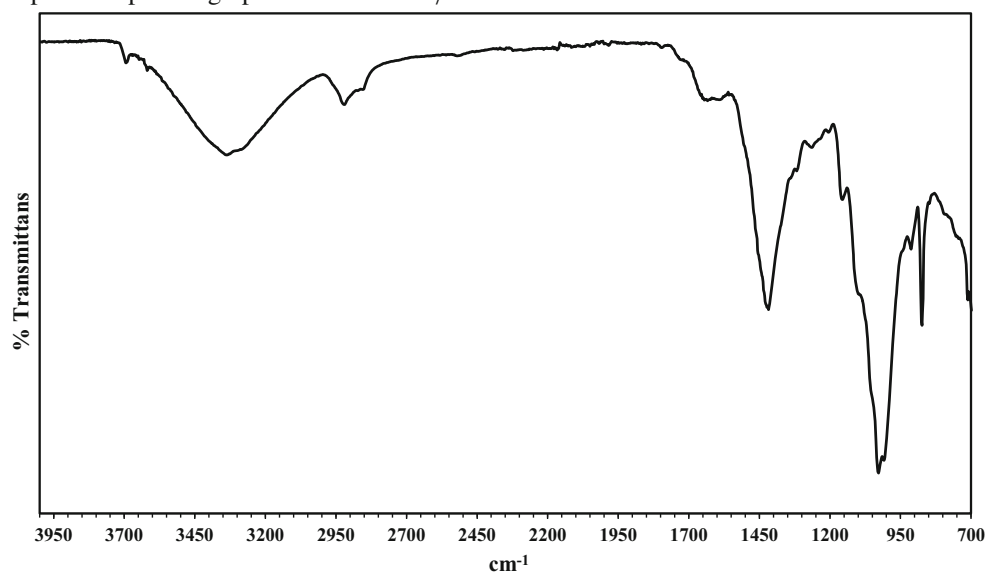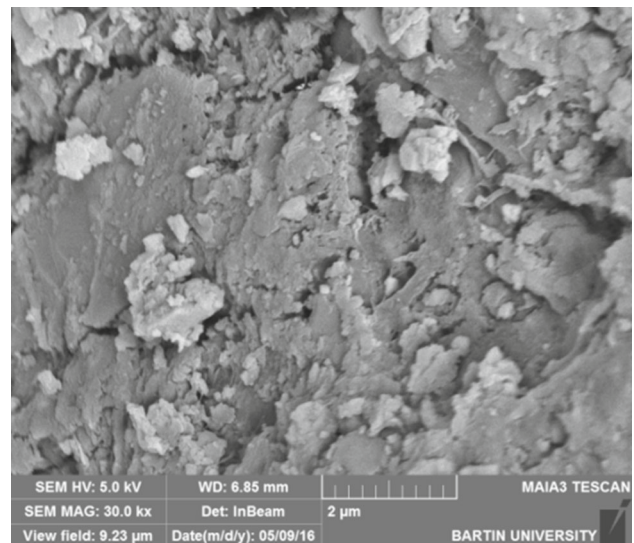
Table 1 Characteristics of used PMS in experiments

Ultimate analysis of PMS	
Component	Value (%)
C	29.3
H	3.20
N	0.70
O	38.85
Proximate analysis of PMS	Value
Preliminary analysis	
Moisture (at 105 °C)	1.35
Ash (%) (at 950 °C)	12.65
Volatile matter (%) (at 550 °C)	22.70
BET surface area (m^2g^{-1})	15.2
Langmuir surface area (m^2g^{-1})	29.5
Cation exchange capacity (CEC)	0.86
Methylen blue sorption capacity (mgg^{-1})	243.3
Iodine number ($mg\,g^{-1}$)	69
Structure analysis of PMS	Value (%)
Cellulose	59.45
Hemicellulose	31.01
Lignin	9.54

$$\ln\left(\frac{1}{b}\right) = \frac{\Delta G^{\mathrm{o}}}{RT} \qquad (11)$$

$$\ln b = \ln b_0 - \frac{\Delta H^{\mathrm{o}}}{RT} \qquad (12)$$

$$\Delta G^{\circ} = \Delta H^{\mathrm{o}} - T\Delta S^{\mathrm{o}} \qquad (13)$$

Changes in the enthalpy (ΔH^{o}) of the process were calculated using the slope of the plotted graph of $\ln b$ versus $1/T$.


**Fig. 2** SEM image of PMS

4 Result and Discussion

This chapter investigated some characteristic properties of PMS used in the adsorption experiments and analyzed, by taking into account isotherm/kinetic and thermodynamic parameters, the results of the experiments carried out under different process conditions.

4.1 Characterization of Adsorbent (PMS)

Table 1 presents the characteristics properties of PMS used in experiments. PMS is composed of cellulose fiber and inorganic components. Table 1 clearly shows that PMS has high

Fig. 1 FT-IR spectrums of paper mill sludge
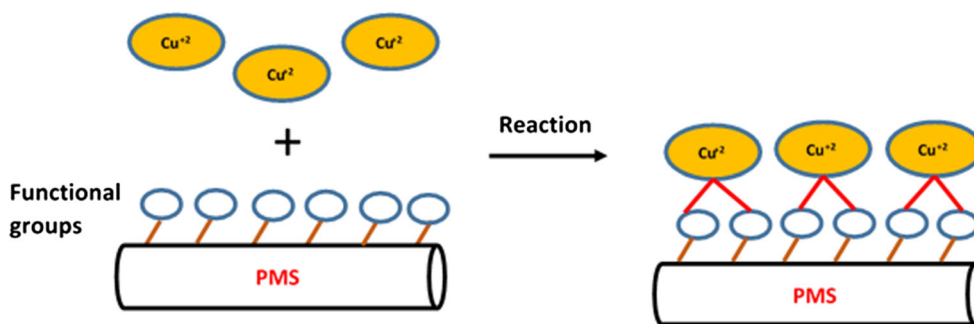
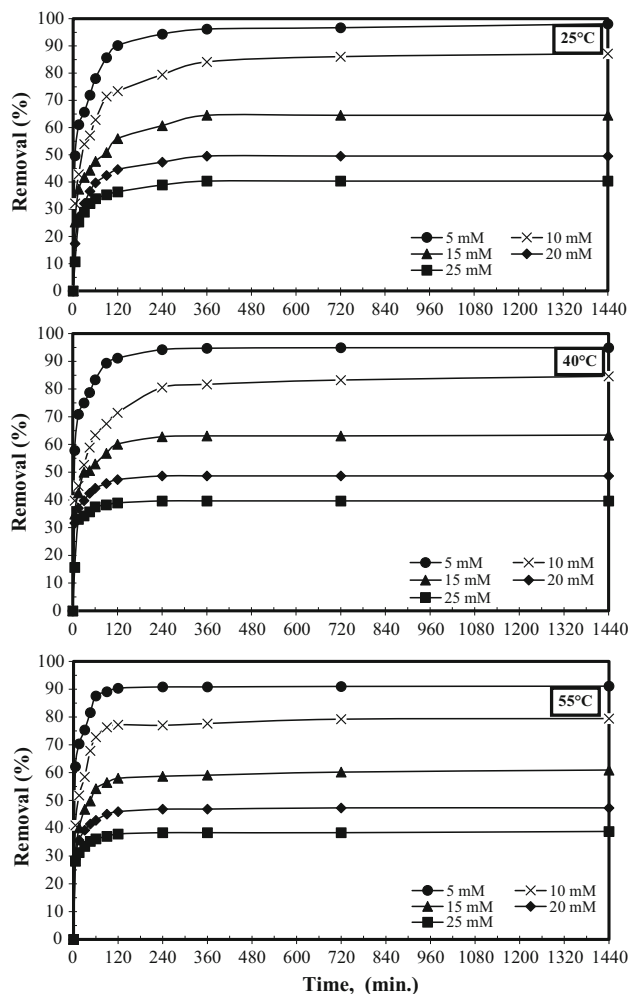**Fig. 3** Adsorption mechanism of Cu (II) ion onto PMS
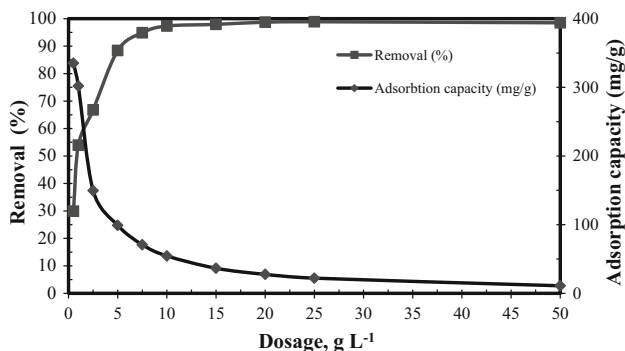
Fig. 4 Effect of adsorbent (PMS) dosage on adsorption of Cu (II) ion. (Experimental conditions: initial concentration: 5 mM; 25 °C; agitation time: 24 h; agitation speed: 200 rpm)

rates of carbon and oxygen elements due to its cellulose structure.

FT-IR spectra in Fig. 1 verified the functional groups of PMS. Broad bands at 3333 and 2920 cm^{-1} pertain to the characteristic stretching –OH of cellulose and C–H of the CH$_2$ groups, respectively. Relevant studies presented all absorption signals of PMS [30]. The weak signals appeared at about 1600 cm^{-1} were associated with the deformation vibration of OH group. The characteristic peak observed at about 1430 cm^{-1} was related to the presence of calcium carbonate (CaCO$_3$), and the corresponding peak was also accounted for by the abundance of calcite in PMS. The presence of peaks at 1149 and 1024 cm^{-1} was attributed to C–O–C bond and to the vibration of glucose stretching of C–O and -OH, respectively. The absorbance peak at 875 cm^{-1} is known as belonging to C–O–C bond.

As can be seen in Fig. 2, SEM was used to examine the surface morphology of PMS. It is evident that PMS has a porous surface with various sizes and forms.

PMS consists substantially of cellulose, hemicellulose and lignin, as well as little amounts of inorganic salts. Some studies in the literature indicated that the heavy metals in aqueous solutions are removed by binding with the functional groups in the waste-based lignocellulosic such as PMS. In other words, the adsorption process is occurred by interac-

Fig. 5 Effect of temperature, contact time and initial concentration of metal solution on removal of Cu (II) ion. (Experimental conditions: dosage of the PMS 10 g L^{-1}; agitation speed: 200 rpm)

tions between the cationic ions in solution and the functional groups as seen from Fig. 3 [31].

4.2 Effect of Adsorbent Dosage

In order to assess the effect of adsorbent dosage on the process of adsorption, the dosage of PMS was altered within the
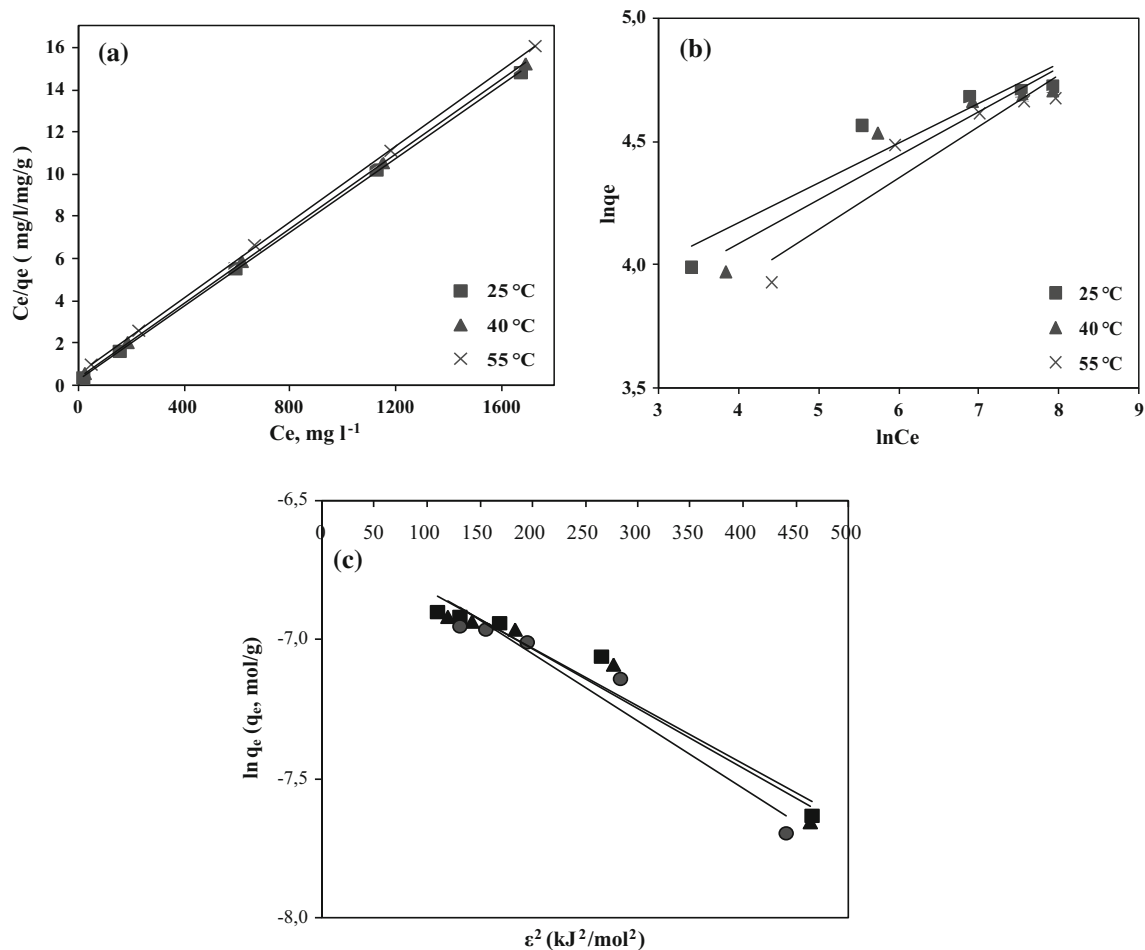
Fig. 6 Langmuir (**a**), Freundlich (**b**) and D–R (**c**) isotherms for adsorption of Cu (II) ion onto PMS (Experimental conditions: Initial metal concentration: 5; 10; 15; 20, 25 mM; adsorbent dosage: $10 \, \mathrm{g \, L^{-1}}$; contact time: 12 h; agitation speed: 200 rpm)

Table 2 Calculated parameters and regression coefficients from Langmuir, Freundlich and D–R isotherm models

Temperature (°C)	Langmuir isotherm			Freundlich isotherm			D–R isotherm		
	b (L mmol^{-1})	q_{max} (mg g^{-1})	R^2	$1/n$	K_f	R^2	q_m (mg g^{-1})	E ($kJ \, mol^{-1}$)	R^2
25	0.03607	114.42	0.9999	0.161	36.70	0.9010	150.54	15.43	0.9989
40	0.02612	113.64	0.9999	0.178	31.75	0.9040	153.04	15.08	0.9995
55	0.01645	111.11	1	0.208	24.66	0.9000	157.51	14.43	0.9987

Table 3 Calculated r values for various initial concentrations at different temperatures

Temperature, °C	r values for various initial concentration at different temperatures				
	5 mM	10 mM	15 mM	20 mM	25 mM
25	0.85	0.73	0.65	0.58	0.53
40	0.88	0.79	0.72	0.66	0.60
55	0.92	0.86	0.80	0.75	0.71

Table 4 Calculated adsorbent dosage to achieve 99% removal yield and experimental results obtained using these dosages for temperatures of 25 °C in different initial concentrations

Temperature, °C	5 mM	10 mM	15 mM	20 mM	25 mM
Calculated m / V values (adsorbent dosage) (g L^{-1})					
25	28.8	33.7	38.5	43.4	48.2
40	38.2	43.1	48.0	52.9	57.7
55	59.2	64.1	69.1	74.1	79.1
Experimental removal yields (%)					
25	98.84	98.77	98.61	98.42	98.19

Table 5 Kinetic parameters for the removal of copper by paper mill sludge

Temperature, °C	C_o (mM)	C_e^a (mM)	$q_{e,exp}$ (mg g^{-1})	Pseudo-first-order model			Pseudo-second-order model			Inter-particle diffusion model		
				k_1, ad (min^{-1})	$q_{e,cal}$ (mg g^{-1})	R^2	k_2, ad (g mmol^{-1} min^{-1})	$q_{e,cal}$ (mg g^{-1})	R^2	k_3, ad (mmol g min$^{-1/2}$)	R^2	$q_{e,cal}$ (mg g^{-1})
25	5	0.09 ± 0.19	54.90	0.0168	28.02	0.9957	0.0015	55.25	0.9997	0.891	0.6788	29.27
	10	1.29 ± 0.11	97.60	0.0127	57.59	0.9714	0.0005	99.01	0.9999	2.223	0.6591	39.61
	15	5.32 ± 2.98	108.40	0.0117	59.11	0.9627	0.0006	109.89	0.9998	2.519	0.6910	47.91
	20	10.09 ± 1.69	111.00	0.0156	64.52	0.9703	0.0007	112.36	0.9999	2.043	0.7148	49.29
	25	14.91 ± 1.98	113.00	0.0157	57.84	0.8746	0.0008	113.64	0.9999	1.556	0.7252	53.27
40	5	0.25 ± 0.02	53.20	0.0196	20.45	0.9864	0.0032	53.48	1	1.131	0.7940	35.59
	10	1.54 ± 0.10	93.30	0.0113	48.43	0.9821	0.0006	96.15	0.9999	2.901	0.9179	43.73
	15	5.49 ± 2.43	106.00	0.0179	46.27	0.9751	0.0012	107.53	0.9998	2.640	0.8188	64.70
	20	10.27 ± 1.71	109.00	0.0212	37.92	0.9946	0.0020	109.89	1	2.093	0.7747	77.17
	25	15.09 ± 1.87	111.00	0.0264	39.41	0.9056	0.0024	111.11	0.9999	2.653	0.4679	73.38
55	5	0.44 ± 1.52	51.00	0.0337	20.21	0.9844	0.0061	51.28	0.9999	1.539	0.8616	37.93
	10	2.05 ± 2.46	88.80	0.0270	45.32	0.9774	0.0016	89.29	0.9999	3.308	0.8748	54.70
	15	5.86 ± 1.46	101.00	0.0222	46.99	0.9805	0.0011	103.09	1	3.567	0.9018	62.01
	20	10.54 ± 0.87	106.00	0.0218	37.49	0.9888	0.0019	106.38	1	3.847	0.8125	74.62
	25	15.29 ± 5.35	107.50	0.0257	30.39	0.9889	0.0022	108.70	0.9998	3.837	0.6790	84.34

[a] Each value represents the mean ± SD of three replicates

range of 1 to $50\,g\,L^{-1}$ while other experimental conditions constant (5 mM initial Cu (II) concentration, 25 °C temperature, 200 rpm agitation speed and 24 h) were kept constant. As can be seen in Fig. 4, while the rate of Cu (II) ion removal increased from 30 to 90% with an increase in the adsorbent dosage, there was no significant change at the adsorbent dosages higher than 10 $(g\,L^{-1})$. Contrary to this, adsorption capacity decreased with an increase in the adsorbent dosage. The results elucidated that adsorbent dosage 10 $(g\,L^{-1})$ may be sufficient for the maximum removal in these experimental conditions. A similar trend on the adsorption process of Cu (II) ion using various adsorbents has also been reported by some researchers in the literature [12,14,32].

4.3 Effect of Initial Concentration

Figure 5 demonstrates that the removal efficiency of Cu (II) ion decreased with an increase in the initial metal concentration. This may be related to the saturation of the surface area and active sites of the adsorbent. The highest adsorption capacity was calculated as 97.6 mg in 10 mM concentration.

4.4 Effect of Temperature and Time

The studies were performed at three different temperatures (25, 40 and 55 °C) to investigate the effect of temperature on the adsorption of Cu (II) ion, and other experimental conditionds were kept constant. The results in Fig. 5 indicate that the rate of Cu (II) ion removal decreased with an increase in temperature. A reduction in the rate of Cu (II) ion removal from 87.1 to 79.5% throughout the experiment was due to an increase in the temperature from 25 to 55 °C. On the other hand, the elevation of time led to an increase in the rate of Cu (II) ion removal. About 98.1% of the highest rates of Cu (II) ion removal occurred at 25 °C in 360 min. However, there was no significant change in the rate of Cu (II) ion removal after 360 min. In the light of the information obtained from the results, it is possible to state that the adsorption process is of exothermic nature [14].

4.5 Determination of Equilibrium Parameters

The experimental and calculated values for the adsorption process are given in Fig. 6 and Table 2 in order to determine the validity of the Langmuir, Freundlich and Dubinin–Radushkevich isotherm models at different temperatures. The results indicate that the Langmuir isotherm model was clearly more successful in yielding the adsorption data than the others. Similar results have also been reported in the literature [14,31,33].

Table 3 shows that all calculated r values are between 0 and 1. It can, therefore, be suggested that the adsorption process is favorable at all temperatures which have been investigated.

As shown in Table 4, PMS dosages were calculated using Langmuir isotherm parameters to obtain the removal yields of 99% at different initial concentrations and at temperatures within the range of 25–55 °C. Table 4 indicates that the value of 99% was within reasonable limits and quite close to the removal yield results achieved using theoretical adsorbent dosages.

4.6 Determination of Kinetic Parameters

Table 5 demonstrates that the calculated values ($q_{cal.}$) of the pseudo-second-order kinetic model are in perfect concordance with the experimental data ($q_{exp.}$) due to the fact that the correlation coefficient is closer to unity. Contrary to this, the pseudo-first-order kinetic model does not fit well the adsorption of Cu (II) ion onto PMS because the calculated values of the correlation coefficient are not closer to unity, and there is a considirable difference between the values of q_{cal} and q_{exp}, as shown in Table 5. Consequently, this indicates that most likely a chemical adsorption mechanism controls the adsorption of Cu (II) ion onto PMS.

4.7 Determination of Thermodynamic Parameters

Changes in the entalphy (ΔH^{o}) and entropy (ΔS^{o}) in the process of adsorption were determined using the slope and intercept of the linear plot of ln b versus $1/T$ as given Fig. 7. Table 6 demonstrates the calculated thermodynamic parameters. Since the calculated values of free energy (ΔG^{o}) for all the temperatures were negative, it can be stated that this adsorption process was of spontaneous nature [33–36]. On the other hand, it would have been suggested that the adsorption process occurred more easily at lower temperatures due
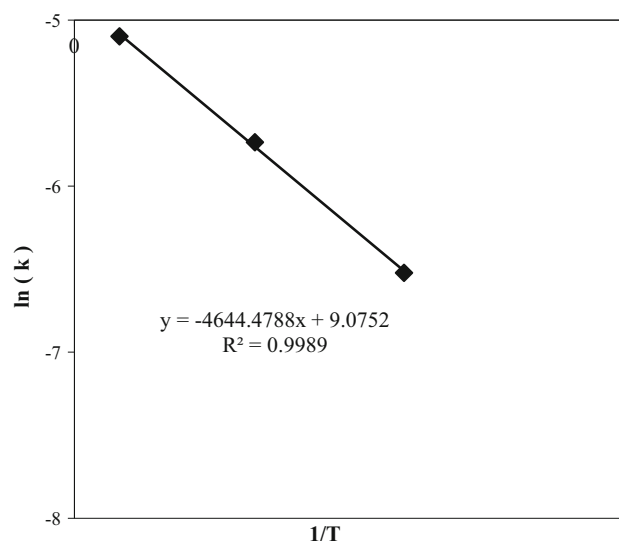
Fig. 7 1/T-lnk plot for adsorption of Cu (II) ion onto PMS

In the figure: $y = -4644.4788x + 9.0752$, $R^2 = 0.9989$

Table 6 Calculated thermodynamic parameters for adsorption of Cu (II) ion onto PMS

Temperature, °C	ΔH^o (kJ mol^{-1})	ΔG^o (kJ mol^{-1})	ΔS^o (kJ mol^{-1} K^{-1})
25	−21.19	−8.883	0.101
40		−8.491	0.095
55		−7.637	0.088

Table 7 Comparison of maximum adsorption capacities of various adsorbents for removal of Cu (II) ion

Adsorbent	Sorption capacity (mg g^{-1})	Reference
Mentha spicata	176.96	[37]
Peanut hulls	14.13	[38]
Chestnut shell	32.6	[39]
Hyacinth roots	22.73	[40]
Arca Shell	38.62	[41]
Meranti sawdust	32.05	[42]
Potato peel	84.74	[43]
Orange peel	106.12	[44]
Banana peel	87.94	[44]
Coconut husk	66.65	[44]
Paper mill sludge	114.42	This study

to an increase in the temperature leading to an increase in free energy (ΔG^o) values. The negative entalphy (ΔH^o) value (−21.19 kJ mol^{-1}) demonstrated that the adsorption of Cu (II) ion onto PMS was of exothermic nature. The positive entropy (ΔS^o) values were an indication of an increase in randomness at the solid/solution interface for this adsorption process.

It is very important to determine the sorption capacity of adsorbent on top of kinetic and equilibrium parameters for adsorption process. In this context, the value of sorption capacity obtained in our study given together with previous studies is relevant to the removal of Cu (II) ion in Table 7.

5 Conclusion

In this paper, the adsorption characteristics of Cu (II) ion onto PMS was assessed at different adsorbent dosages, initial concentrations of metal solution, temperatures and contact times.

The results illustrated that the increase in the rate of Cu (II) ion removal depended on the increase in the adsorbent dosage (10 g L^{-1}) and reaction time (360 min). It is the exact opposite for the temperature and initial concentration of the metal solution.

According to the obtained statistical parameters, the pseudo-second-order kinetic model appeared to be a better fit for the analysis of the adsorption process than the other models. The value of activation energy was determined to be 38.61 kJ mol^{-1} based on the rate constants obtained from the pseudo-second-order kinetic model applied for all temperatures in the metal solution (5 mM).

Three different adsorption isotherm models (Langmuir, Freundlich and Dubinin–Radushkevich) were used to analyze the experimental data, which, in return, turned out to be in excellent agreement with the first one, and the adsorption capacity of Cu (II) ion ranged from 111.1 to 114.4 (mg g^{-1}) for the all temperatures studied.

The magnitude of the calculated r values varying between 0 and 1 showed that this adsorption process is favorable.

The negative values of entalphy (ΔH^o) and free energy (ΔG^o) indicated the spontaneous and exothermic nature of the process. The positive values of entropy (ΔS^o) suggested the increased randomness at the solid/solution interface.

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