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Removal of Copper from Water by Adsorption onto Banana Peel as Bioadsorbent

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ABSTRACT: Banana peel, a fruit waste were used to produce bioadsorbent through environment friendly process. It were cut, washed, dried, grounded into powder and used for copper removal. Copper adsorption onto banana peel was depended upon the controlling parameters such as particle size, doses, pH, contact time, agitation speed and temperature. Slightly acidic water (pH = 6) was found to be suitable for copper removal. Equilibrium data were well fitted ($R^2 = 0.998$) with the Langmuir and Freundlich isotherms. The monolayer adsorption capacity was 27.78 mg/g. The calculated R_L and 'n' values has proved the favorability of copper adsorption onto banana peel. Copper adsorption was followed the second order kinetic properly rather than other models. The equilibrium adsorption capacity was 1.439, 8.849, 18.182, 31.250 and 71.429 mg/g when initial copper concentrations were 10, 50, 100, 200, and 400 mg/l respectively. Solvent 0.1N Sulphuric acid showed higher desorption of copper (94%) and adsorption-desorption process can be continued till seven cycles efficiently.

Keywords: Banana peel, Adsorption, Biosorbents, Isotherm models

1. INTRODUCTION

Eco-toxicity on living organism has become a prime concern from the last few decades. Massive urbanization are continuously releasing waste and wastewater to the ecosystem and, causing pollution to environment and eventually toxicity to living being. The industrial effluents which contain different derivatives of heavy metals such as Cd, Pb, Ni, Cr, As, Cu, Fe etc. are continuously discharging to the ecosystem and producing a significant toxic impact on aquatic environment. Among the heavy metals, copper is the major available type of heavy metal in the aquatic environment. Copper in the blood system may generate reactive free oxygen species and damage the protein, lipids and DNA [1]. The excess copper compound in the body may also affects on aging, schizophrenia, mental illness, Indian childhood cirrhosis, Wilson's and Alzheimer's diseases [2-4]. Copper has damaged the marine ecosystem and damaged the gills, liver, kidneys, the nervous system and changing sexual life of fishes [5-6]. Recent awareness of toxicity originated from water and wastewater are attending the interest for environmental scientist and researcher.

The sustainable removal of heavy metals from water and wastewater has become a major challenge for scientists. Besides the available methods for copper removal, bio-technological removal are shown some advantages as they are cheap, readily available, low cost, simplicity to use and environment friendliness. Huge and abandoned agro-wastes may be the potential sources for producing bioadsorbents besides the high cost adsorbents for heavy metals removal. Different bioadsorbents are developed from agro-wastes and used for heavy metals removal such as rice straw [7], seaweed [8], wood and bark [9], tea-waste [10], maize corn cob, jatropha oil cake, sugarcane bagasse [11], tamarind hull [12], sawdust [13], rice husk [14], saltbush [15], marine algal biomass [16], olive pomace [17], activated sludge [18], sugar beet pulp [19], wool, olive cake, sawdust, pine needles, almond shells, cactus leaves, and charcoal [20], seafood processing waste sludge [21] and pine bark [22]. Bioadsorbents which produced from agro-wastes may act as a significant material for copper adsorption. Banana peel, an agro wastes is discarded all over the world as useless material. It is causing waste management problems though it has some compost, cosmetics and adsorbent potentiality. It is an abandoned, readily available, low cost and cheap, environment friendly bio-material. Considering the above criteria, banana peel was selected to prepare the biosorbent. A step was taken for preparing biosorbent and used for removal of copper from water. The main aim of this research was to determine the potentiality and adsorption capacity of banana peel as bioadsorbent.

2. MATERIALS AND METHODS

2.1 Materials

The stock solution of copper (1000 mg/l) was prepared by dissolving 3.929 g of copper sulphate ($CuSO_4.5H_2O$) in 1L of milli-Q water and used for all experiments with required dilution. The banana peel were collected from kitchen and used for whole experiments.

2.2 Methods

2.2.1 Preparation of adsorbent

The collected banana peel were cut into small pieces (< 5 mm), washed three times with tap water and three times with distilled water to remove external dirt. The wetted banana peel were kept in air for removing the water from the surface and dried in oven at 105°C for 24 hours. The dried banana peel were grounded into powder and kept in an air tied bottle for experimental uses.

2.2.2 Study of adsorbent doses

The effect of adsorbent doses on the equilibrium adsorption of copper was investigated with banana peel of 0.05, 0.1, 0.2, 0.5, 1, 2, 5 and 10 g in five set of 100 ml water which contained 1, 2.5, 5, 10 and 15 mg/l of copper concentration each. The Erlenmeyers were shaken for 24 hours with 120 rpm at room temperature. The water samples were then filtered and analyzed in terms of Cu by AAS.

2.2.3 Study of pH

The effect of pH for copper adsorption onto banana peel was investigated with 0.5g of banana peel in 100 ml water containing 10mg/l of copper and each sample were adjusted to pH between 1.18 to 13.5 using either 1N H_2SO_4 or NaOH solution. The Erlenmeyers were shaken for 24 hours with 120 rpm at room temperature.

2.2.4 Study of particle sizes

The grounded banana peel were graded with standard sieves to six particles sizes of 600, 420, 300, 150, 75 and < 75 μm. Banana peel (0.5g) from each graded sizes were added to six Erlenmeyer with 100 ml water containing 10 mg/l copper concentration and shaken for 24 hrs at 120 rpm.

2.2.5 Study of temperature, contact time and shaking speed

The effect of temperature, contact time and shaking speed (rpm) on adsorption of copper were examined with different temperature (30-70°C), time (3h) and speed (30-200 rpm) for 10 mg/l copper concentration with 0.5 g banana peel in 100 ml water.

2.2.6 Equilibrium study

Equilibrium adsorption experiments (triplicate) were conducted with 16 Erlenmeyer of 100 ml water containing 1 to 500 mg/l of copper concentration. Grounded banana peel of 0.05, 0.1 and 0.5 g were added in each sets of experiments and shaken for 24 hours with 120 rpm at room temperature without pH adjustment. The equilibrium data were fitted with Langmuir, Freundlich and Temkin isotherm models.

2.2.7 Kinetics study

Kinetics experiments were conducted with 10, 50, 100 and 200 mg/l copper concentration in 1L water and with 5 g of banana peel at room temperature (20^oC) without pH adjustment. Water was agitated at 120 rpm for 2 hours. At different intervals 5ml of water samples were withdrawn and filtered for analysis. The kinetics data were evaluated with pseudo-first-order, pseudo-second-order, Elovich and Reichenberg kinetics equation.

2.2.8 Desorption study

Desorption of banana peel was studied using 8 types of solvent medium including tape water, milli-Q water, distilled water, 0.1N H_2SO_4, 0.1N HCl, 0.1N HNO_3, 0.1N NaOH and 0.1 N CH_3COOH. For this purpose, 0.5 g of saturated (with Cu) banana peel was taken in 100 ml of above mentioned medium and shaken at 120 rpm for 24 hr.

2.3 Analysis

The collected water samples from different experiments were filtered with filter paper (Whatmann 5) and prepared for AAS analysis. The samples were analyzed in term of Cu by Atomic Absorption Spectrometer (AAS 932 plus, GBC, Australia). The pH was measured by Hanna HI 9025 (HANNA Instrument, Romania) pH meter.

2.4 Calculation

The amount of copper adsorbed by adsorbent (*q*) in the adsorption systems were calculated by the following mass balance equation:

$$q = \frac{V.(C_i - C_e)}{m} \qquad (1)$$

and the percent removal (%) of copper was calculated using the following equation:

$$\%\text{removal} = \frac{(C_i - C_e)}{C_i} \times 100 \qquad (2)$$

where, V is the volume of solution (l), m is the amount of adsorbent (g), and C_i and C_e (mg/l) are the initial and equilibrium metal concentrations in the water, respectively. The percent deviation was calculated as follows:

$$\%\text{deviation} = \frac{(q_{e.exp} - q_{e.cal})}{q_{e.cal}} \times 100 \qquad (3)$$

where, $q_{e.exp}$ and $q_{e.cal}$ are experimental and calculated values of amount of copper adsorption onto banana peel.

3. RESULTS AND DISCUSSION

3.1 Environment friendly preparation

The preparation methods are the key factor for any type of bioadsorbent, because morphological properties such as particle size and shape, binding surface area, and overall removal capacity depend on it. Simple, easy to prepare and use, hazard free and environment friendly treatments are the requirement for sustainable preparation of bioadsorbent. Considering the above this research is used simple and non-treated preparation methods rather than the expensive and high-tech pyrolysis and non-environment friendly acid/base pre-treatment methods [7-22]. This is the novelty of this study. The SEM micrograph (Fig.1) revealed that microporous structures, heterogeneous, rough surface with crater-like pores were existed in banana peel. The electron micrographs also revealed that the particles are of irregular shape and its surface exhibits a micro-rough texture, which can promote the adherence of copper.

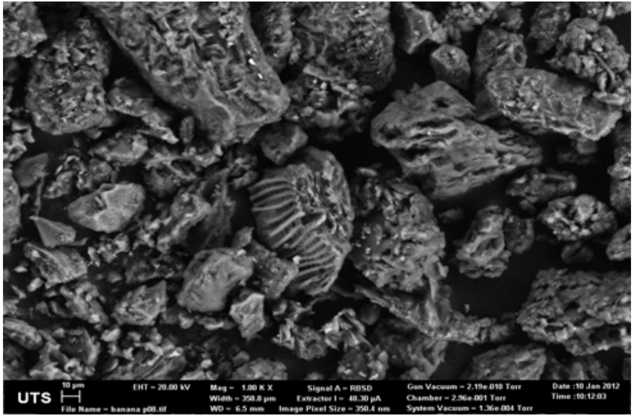

Fig.1 SEM micrograph (×1k) of banana peel

3.2 Effect of doses

The effect of doses was investigated with five copper concentration-sets (1-15 mg/l) in 100 ml water by adding eight doses for each set (Fig.2). The percent removal of copper was found to increase with an increase in the mass of adsorbent. Highest copper removals were 85 and 88 % for the initial copper concentration of 5 and 10 mg/l, respectively at the adsorbent dose of 5 g/l. Thereafter, the removal of copper started to decline with increasing in mass of adsorbent for all five sets and then remained leveled. The partial aggregation among the available active binding sites may acts for less removal of copper at high doses [23]. Also, due to lack of active binding site, the lower removals were obtained at low adsorbent doses [24]. Thus, 5g (0.5

g/100ml) of banana peel and 10 mg/l of copper concentration were chosen to use for other experiments.

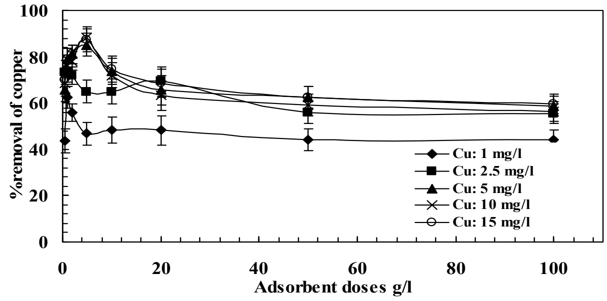

Fig.2 Effect of adsorbent doses on removal of copper (t: 24h; rpm: 120; pH: 6-6.5; T: 20°C)

3.3 Effect of pH

pH is a controlling factor for any kind of metal adsorption process from aqueous solution. The surface properties of adsorbents, ionic state of functional groups and species of metals are dependent on pH condition. pH dependent experiments were conducted and the result are shown in Fig.3. The copper adsorption was found to increase with an increase in pH from 2 to 6 and attained a maximum value (1.76 mg/g) at pH 6 (which was slightly acidic). Latter the copper adsorption capacity was declined. The speciation diagram [25] has confirmed that Cu^{2+} is the dominant free species below pH 6 which involved in true adsorption. The H_3O^+ ions compete with Cu^{2+} for binding on adsorbent sites and it may be responsible for lower adsorption capacity at low pH [24, 26]. At higher pH, the removal was also low compared to the optimum condition. This can be explained as the binding site may not activate in basic condition [27]. Above pH 6, the copper started precipitating as $Cu(OH)^{2+}$, therefore the removal was not completely by adsorption [25, 26].

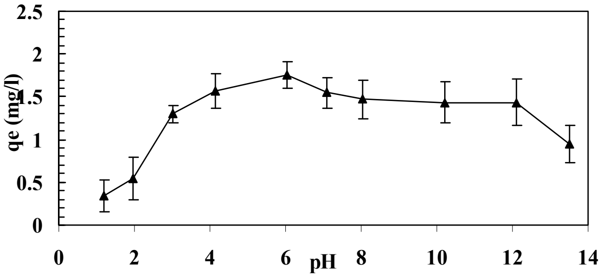

Fig.3 Effect of pH of copper adsorption (t: 24h; C_o: 10 mg/l; d: 5 g/l; rpm: 120; T: 20°C)

3.4 Effect of particles sizes of adsorbent

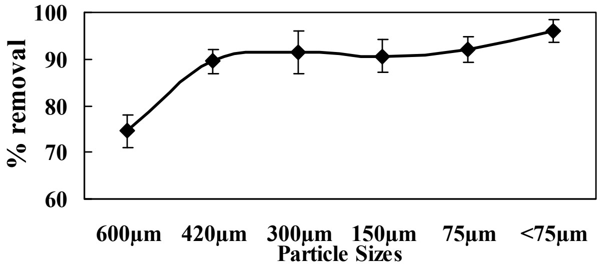

Fig.4 Effect of particle size on removal of copper (t: 24h; C_o: 10 mg/l; d: 5 g/l; rpm: 120; T: 20°C; pH: 6-6.5)

Batch experiments for the effects of particles on adsorption were conducted for six particle sizes (600μm to <75 μm) at room temperature and pH of 6-6.5 (without adjustment). Fig.4 indicates that the removal of copper was increased by decreasing the particle sizes. The percent removal of copper increased from 74 to 96% when decreasing particle sizes from 600μm to <75μm. This behavior can be attributed to the effective surface area increased as the particle size decreased and as a consequence, the copper adsorption increased [28].

3.5 Effect of contact time

Experiments for contact time were conducted with five initial copper concentrations (C_o:10, 20, 50, 100 and 200 mg/l) with a dose of 5 g/l banana peel at 120 rpm and room temperature for 2 hours. Fig.5 shows the effect of contact time on adsorption of copper ions by banana peel. Adsorption rate of copper on banana peel was found to be relatively much faster than those reported for some other bio-adsorbents [24]. The rate of copper removal was very rapid during the first 30 min, and thereafter, the rate of copper removal remained constant. There was no significant increase in adsorption after about 60 min. The experiment with high C_o showed the higher amount of copper removal. The copper ion adsorption on banana peel was reached at equilibrium after 1h. Initially, there were large number of vacant active binding sites in banana peel and consequently large amount of copper ions were bound rapidly onto banana peel. The binding site was shortly become limited and the remaining vacant surface sites are difficult to be occupied by copper ions due to the formation of repulsive forces between the copper on the solid surface and the liquid phase [29-30]. Besides, the meso-pores become saturated at the initial stage of adsorption where the metal ions are adsorbed. As a result, the driving force of mass transfer between liquid and solid phase in an aqueous adsorption system decreases with time elapse. Further, the metal ions have to pass through the deeper surface of the pores for binding and encounter much larger resistance which slowing down the adsorption during the later phase of adsorption [29].

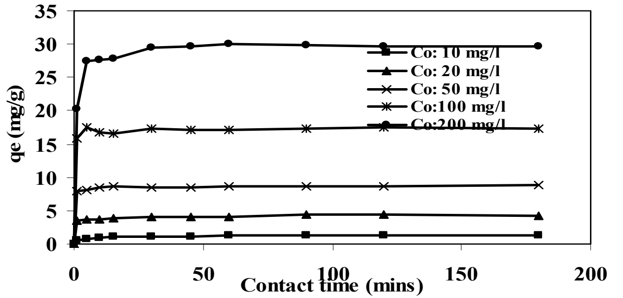

Fig.5 Effect of contact time on removal of copper (C_o: 10 mg/l; d: 5 g/l; rpm: 120; T: 20°C; pH: 6-6.5)

3.6 Effect of shaking speed

The effect of shaking speed on adsorption of copper was studied over the range of 30-200 rpm for 2h with 100 ml water containing 10 mg/l copper and 0.5 g of banana peel. Fig.6 indicates that the percent adsorption increased with an increased of shaking speed and obtained a maximum 88% adsorption at near 120 rpm. This shaking speed was employed for other experiment. At low and high speeds, the copper removal was lower than optimum. Low speed could not spread the particles properly in the water for providing active binding sites for adsorption of copper. It is resulted an accumulation of banana peel in the bottom of water and buried the active binding sites. On the other hand, the high speed vigorously spreading the particles of banana peel in the water and did not allow sufficient time to bind with copper ions [23].

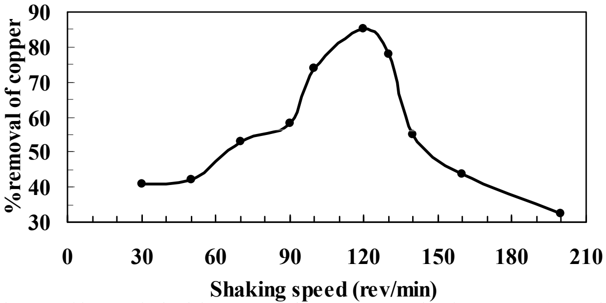

Fig.6 Effect of shaking speed on removal of copper (t: 24h; C_o: 10 mg/l; d: 5 g/l; T: 20°C; pH: 6-6.5)

3.7 Thermodynamics properties

To determine the thermodynamic properties and thermal effects on the adsorption, the temperature variation experiments were conducted at 30, 40, 50 and 70°C, with an initial copper concentration between 1-200 mg/l and 0.5g banana peel. The experimental data show that the equilibrium adsorptions were decreased with an increase of temperature (Table1). It seems to be that higher temperature has negative impact on copper adsorption. The thermodynamic parameters such as Gibbs free energy (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) were calculated to evaluate the nature of the adsorption process. For a given temperature, a phenomenon is considered to be spontaneous if the ΔG° has a negative value. Moreover, if ΔH° is positive, the process is endothermic and if it is negative, the process is exothermic. The magnitude of ΔG° (kJ/mol) was calculated using the following equation:

$$\Delta G^\circ = -RT\ln K_a \qquad (4)$$

where, R is universal gas constant, 0.008314 kJ/mol K; T is absolute temperature (°K) and K_a the adsorption equilibrium constant from Langmuir and Temkin isotherm and ΔH° (kJ/mol) was calculated by the following equation:

$$\Delta H^\circ = \Delta G^\circ + T\Delta S^\circ \qquad (5)$$

A plot of ΔG° versus T was found to be linear (Fig.7) and the values of ΔH° and ΔS°, were calculated from the slope and intercept of the plots. The thermodynamic parameters calculated from both Langmuir and Temkin isotherm are shown in Table 1. The negative values of ΔG° for Langmuir isotherm have confirmed the feasibility of process and the spontaneous nature of adsorption. However, the positive values from Temkin isotherm showed the opposite of nature of adsorption. The values of ΔG° were decreased from -6.95 to -4.63kJ/mol for Langmuir isotherm and increased from 1.95 to 2.43 kJ/mol for Temkin isotherm as the temperature increases from 30 to 70°C. The values of ΔH° and ΔS° calculated from Fig.6, using Langmuir constant, K_a and Temkin constant K_T are given as 0.057 kJ/mol and -24.4 kJ/mol K and 0.011kJ/mol and -1.32 J/mol K, respectively. The positive value of ΔH° indicates that the adsorption reaction was endothermic and strong affinity of the banana peel for copper ions and suggests some structural changes in copper ions and banana peel fiber [31]. In addition, the negative value of ΔS° (for both isotherms) also suggests that the adsorption was enthalpy driven and spontaneous in nature [27].

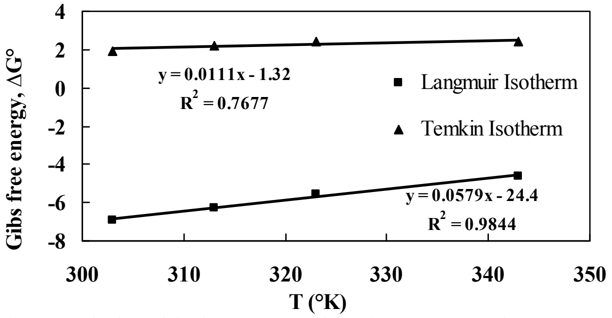

Fig.7. Relationship between Gibbs free energy change, ΔG° and temperature, T (°K) of adsorption reaction

Table 1 Calculated values of thermodynamic parameters for the equilibrium adsorption of copper onto banana peel

T (°C)	q_m (mg/g)	ΔG° (kJ/mol)		ΔH° (kJ/mol)		ΔS° (kJ/mol K)	
		Lang	Tem	Lang	Tem	Lang	Tem
30	4.082	-6.945	1.950	0.057	0.011	-24.4	-1.32
40	2.203	-6.268	2.224				
50	0.710	-5.521	2.391				
70	0.884	-4.626	2.425				

* Lang : Langmuir ; Tem : Temkin

3.8 Adsorption isotherms

Adsorption isotherms describe the equilibrium relationships between adsorbent and adsorbate. Three adsorption isotherms (6)-(8) were used to fit the equilibrium data namely, Langmuir [32], Freundlich [33] and Temkin [34]. Its applicability was judged with the correlation coefficients (R^2). Langmuir equation can be linearized by the following form:

$$\frac{1}{q_e} = \frac{1}{bq_mC_e} + \frac{1}{q_m} \qquad (6)$$

where, C_e is the equilibrium concentration in liquid phase (mg/l), q_m is the monolayer adsorption capacity (mg/l) and *b* is the Langmuir constant related to the free adsorption energy (l/mg).

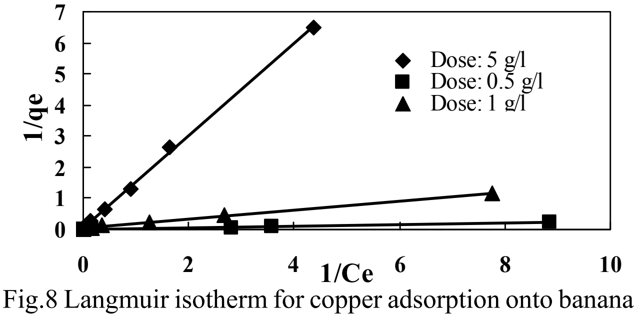

Fig.8 Langmuir isotherm for copper adsorption onto banana peel (C_o: 1-500 mg/l; t: 24h; rpm: 120; pH: 6-6.5; T: 20°C).

Freundlich equation can be linearized by the following form:

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e \qquad (7)$$

where, K_F is a constant indicative of the adsorption capacity of the adsorbent (mg/ g) and the constant 1/*n* indicates the intensity of the adsorption. The linearized form of Temkin isotherm is as follows:

$$q_e = B_1 \ln K_T + B_1 \ln C_e \qquad (8)$$

where, $B_1 = RT/b_T$, K_T (l/g) and b_T (kJ/mol) are the Temkin constants.

The linear plot of Langmuir isotherm for copper adsorption and the calculated parameters along with regression coefficients are shown in Fig.8 and Table 2, respectively. Maximum adsorption capacity, q_m, for complete monolayer coverage are found 125, 35.714 and 28.571 mg/g for 0.5, 1 and 5 g/l doses, respectively. R^2 values approaching to one, clearly suggest that Langmuir isotherm follows a good relation of copper adsorption with banana peel. The adsorption capacity for banana peel was found higher than the previously reported methods of metal adsorption [27]. 'b' is the adsorption constant related to the affinity of binding sites(l/g) and lower value of 'b' (0.364, 0.191 and 0.024 l/g for three doses) indicate that the particles radius of banana peel were small toward adsorption [23]. Separation factor (R_L), an essential characteristic of Langmuir isotherm model was calculated as the following equation:

$$R_L = 1/(1 + bC_i) \qquad (9)$$

where, C_i is the initial concentration of metal ions. The values of R_L (0.9-0.07) revealed that copper adsorption on banana peel is favourable as the values lies between 0 and 1 [32]

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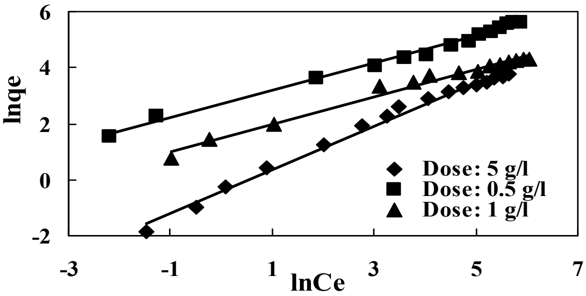

Fig.9 Freundlich isotherm for copper adsorption onto banana peel (C_o: 1-500 mg/l; t: 24h; rpm: 120; pH: 6-6.5; T: 20°C)

The linear plot of Freundlich equation for copper adsorption and the calculated parameters are shown in Fig.9 and Table 2, respectively. The Freundlich isotherm model was found best fitted with experimental data as its poses higher R^2 value (0.992, 0.982 and 0.989). K_F is a Freundlich constant that shows adsorption capacity on heterogeneous sites with non-uniform distribution of energy level and n shows the intensity between adsorbate and adsorbent. The calculated values of 'n' (Table 2) prove that the adsorption of copper onto banana peel is favourable as the magnitude lies between 1 and 3 [30].

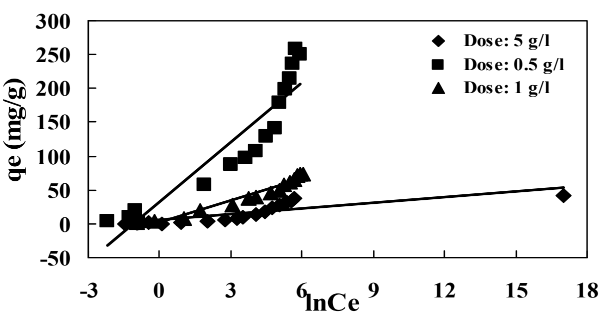

Fig.10 Temkin isotherm for copper adsorption onto banana peel (C_o: 1-500 mg/l; t: 24h; rpm: 120; pH: 6-6.5; T: 20°C)

Fig.10 and Table 2 shows Temkin isotherm and calculated constant related to heat of adsorption (b_T). Its' were 0.083, 0.228 and 0.474 kJ/ mol for copper adsorption on banana peel for the doses of 0.5, 1 and 5 g/l respectively. The lower values of b_T (<8) indicate that the interaction between metal and banana peel was weak. The adsorption process of copper onto banana peel can be expressed as physiosorption as indicated by the value of b_T.

Table 2 Langmuir, Freundlich and Temkin isotherm parameters and correlation coefficients for the adsorption of copper onto banana peel at different adsorbent doses.

Doses	Langmuir			Freundlich			Temkin		
	q_m	b	R^2	K_F	n	R^2	b_T	K_T	R^2
(g/l)	(mg/g)	(l/mg)		(mg/g)			(kJ/mol)	(l/mg)	
0.5	125	0.36	0.975	14.60	2.05	0.992	0.08	3.07	0.858
1	35.71	0.19	0.993	4.44	2.05	0.983	0.23	1.21	0.942
5	28.57	0.03	0.998	1.51	1.29	0.989	0.47	1.22	0.806

3.9 Adsorption kinetics

Kinetic studies are significant for any kind of biosorption processes. Adsorption kinetics not only describes the adsorption mechanism of metals on adsorbents but also describe the metal adsorption rate which controls the contact time of metals at the solid-liquid interface [35]. The adsorption mechanism depends on the physical and chemical characteristics of adsorbent and adsorbate, pH of medium, temperature, contact time and aids and mass transport process [30]. Kinetics studies were conducted at non adjusted pH condition with four initial copper concentrations. The data were fitted with different kinetics equation namely First Order, Second Order, Elovich and Reichenberg kinetics models.

3.9.1 The pseudo-first-order and pseudo-second-order kinetics equation

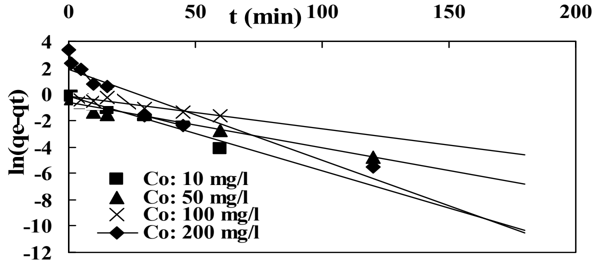

Fig.11 Linear plot of pseudo-first-order equations for copper adsorption onto banana peel

The linear form of pseudo first-order kinetic model [44] is as follows:

$$\ln(q_e - q_t) = \ln q_e - k_{ad} t \qquad (10)$$

The adsorption rate (k_{ad}) are calculated from linear regression analysis from the slope of linear plot of experimental data (*ln(q_e - q_t)* vs *t*). The linear plot of the experimental data and the calculated parameters are shown in Fig.11 and Table 3, respectively. The experimental data is not well fitted for pseudo-first-order kinetic equation as the R^2 were low. The kinetics data were also analyzed by pseudo-second order equation and the linear form as [37]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (11)$$

where, k_2 is the constant of pseudo-second-order rate; q_e is the biosorption capacity at equilibrium; and q_t is the biosorption capacity at time t. If the initial adsorption rate, as h = q_t/t when t approach to 0, h, (mg/g min) [35], is:

$$h = kq_e^2 \qquad (12)$$

Table 3 Calculated parameters of pseudo-first-order and pseudo-second-order kinetics

Kinetics models	Parameters	10 mg/l	50 mg/l	100 mg/l	200 mg/l
Pseudo-first-order					
	$q_{e.exp}$ (mg/g)	1.288	8.692	17.732	29.752
	$q_{e.cal}$ (mg/g)	1.148	1.811	1.198	6.488
	k_{ad} (min^{-1})	0.056	0.034	0.024	0.068
	R^2	0.903	0.951	0.915	0.881
Pseudo-2nd-order					
	$q_{e.cal}$ (mg/g)	1.439	8.849	18.182	31.250
	k_2 (g/mg.min)	0.097	0.156	0.078	0.027
	h (mg/g.min)	0.200	12.195	25.641	26.316
	R^2	0.997	0.999	0.999	0.999

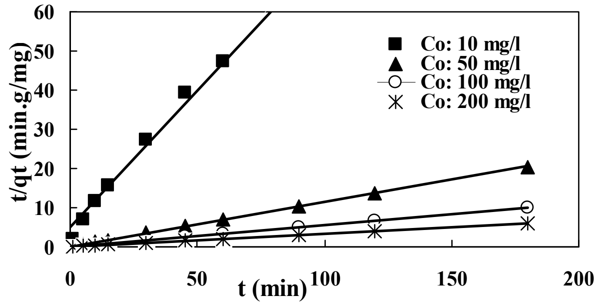

Fig.12 Linear plot of pseudo-2nd-order equation for copper adsorption onto banana peel at various C_o

The equilibrium adsorption capacity and the second-order rate constant were calculated from the slope and the intercept of the plot t/q_t against t. The graphical interpretation of the data for second-order-kinetic model and calculated parameters are shown in Fig.12 and Table 4, respectively. A good fitted (R^2>0.999) linear plots are obtained from experimental data (Table 3) while the calculated values of q_e also agreed with the experimental values. This finding revealed that the copper adsorption onto banana peel follows the pseudo-second-order mechanism and the chemical adsorption process controls the adsorption rate. It was found that equilibrium adsorption capacity (q_e) increased with an increase in initial copper ion concentration (C_o). The adsorption capacity increased from 1.288 to 70.304 mg/g when C_o was increased from 10 to 400 mg/l. The calculated values of equilibrium adsorption capacities ($q_{e.cal}$) were well agreed with the experimental values ($q_{e.exp}$) for the second-order kinetic model and the lower '% deviation' confirmed the process (Table 4). The q_e increased with increasing C_o, while the k decreases and the h increases with increasing C_o.

3.9.2 The Elovich kinetics

The simplified and linearized form of Elovich kinetics model [38] can be expressed as:

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t) \qquad (13)$$

where, α is the initial adsorption rate (mg/g.min) and β is the desorption constant (g/mg). A plot of q_t versus $ln(t)$ yielded a linear relationship with a slope of (1/β) and an intercept of (1/β) ln(αβ).

Table 4 Calculated kinetic parameters of Elovich equation for copper adsorption onto banana peel at different C_o

Parameter			Elovich kinetics model			
C_o (mg/l)	$q_{e.exp}$ (mg/g)	$q_{e.cal}$ (mg/g)	α (mg/g.min)	β (g/mg)	R^2	%deviation
10	1.288	1.217	1.863	5.236	0.991	5.8
50	8.692	8.582	$1.45x10^{+22}$	6.623	0.951	1.28
100	17.732	17.526	$7.69x10^{+18}$	2.762	0.914	1.17
200	29.752	29.140	36796.5	0.469	0.866	2.10

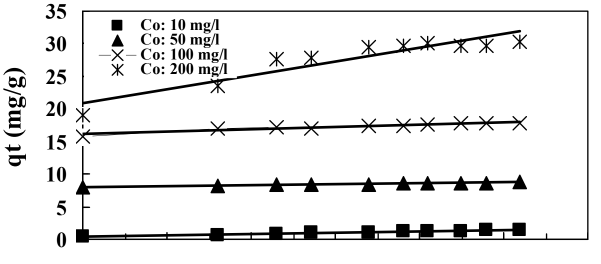

Fig.13 Linear plot of Elovich model for copper adsorption onto banana peel at various C_o

The Elovich model is used to explain the copper adsorption mechanism onto banana peel. The two parameters (α and β) were calculated from the slope and intercept of the linear plot of q_t vs $ln(t)$ (Fig.13) and tabulated in Table 4. A good range of R^2 values (0.914 to 0.991) were found except when initial copper concentration was 200 mg/l. The calculated values of α and β (Table 4) showed a general trend of changes with an increase in the initial copper concentration. The values of α increased from 1.863 to 36796.5 with increased C_o (10 to 200 mg/l), suggesting that the process was chemisorptions corresponding to the heterogeneity in nature of active sites [39]. On the other hand, with increased of C_o, the β-values showed a reduction trend (45.236 to 2.762 g/mg). Thus, 1/β (which is apparently indicative of the number of sites available for adsorption, as per the second assumption) showed a distinct increase with an increase in concentration, again reinforcing the occurrence of chemisorptions [40].

3.9.3 Reichenberg equation

Reichenberg [41] stated that the radius of adsorbent's particles (r) controls the effective diffusion of exchanging ions and film diffusion in adsorption may be reduced from the linear fit:

$$Q = 1 - \frac{6e^{-Bt}}{\pi^2} \qquad (14)$$

where, Q is the ratio of adsorbed concentration at time 't' and the maximum adsorption capacity of the adsorbent (=q_t/q_m), $Bt = \pi^2 Di/r^2$ and Di is the coefficient of effective diffusion of ions exchanging inside the adsorbent particles. The value of Bt can be calculated mathematically for each value of Q, using the following equation:

$$Bt = -0.4977 - \ln(1-Q) \qquad (15)$$

The linear plot of 'Bt' versus contact time't' is shown in Fig.14. The linear plot revealed that the data was not quite fitted with model for 2 h time period as produce low R^2 values (0.962, 0.855, 0.931 and 0.900) for the initial copper concentration of 10, 50, 100 and 200 mg/l, respectively.

However, it was linear between 0 to 60 min with a higher R^2 values (>0.98). The regression lines did not pass through the origin which indicated that a thin film of copper was formed on the surface of banana peel.

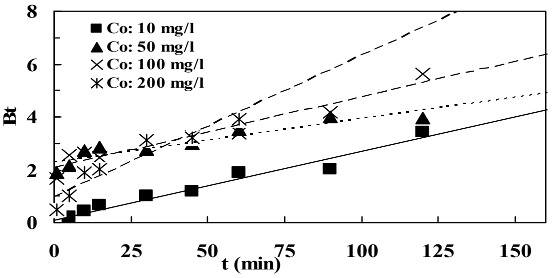

Fig.14 Linear plot of Reichenberg kinetics equation for copper adsorption onto banana peel

3.10 Desorption performance

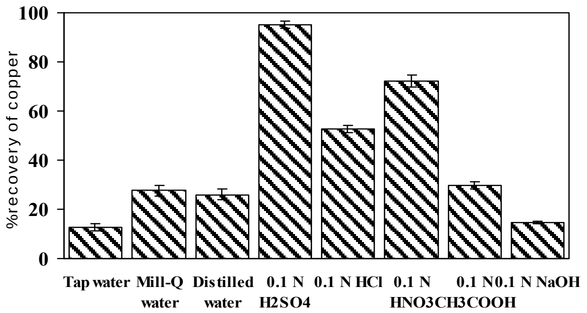

Fig.15 Desorption of copper from banana peel (Co: 10 mg/l; desorption time: 24h; rpm: 120; T: 20°C)

Desorption of metals or regeneration of adsorbents from used-adsorbents are crucial to repeat the use of adsorbents, recover of precious metals and reduce the cost of operation in any water treatment system. The adsorbed metals on adsorbents can not be completely reversible as reported by several observations on literature [42-44]. Eight solvent were used for desorption/regeneration experiment and the results are presented in Fig.15. Among the solvents the tap water, milli-Q water, distilled water, CH_3COOH and NaOH were resulted a limited amount of copper ion recovery (<30%). The highest (94%) recovery was found with the use of 0.1N H_2SO_4. The other two acids 0.1 N HCl and 0.1 N HNO_3 were shown lower efficiencies (54 and 72%). In the desorption system H^+ released from the acids which replaced metal cation (Cu^{2+}) on the surface of the banana peel [24]. The recovery and reuse processes for banana peel can be continued upto 7 times with minor deviation in removal efficiency.

3 CONCLUSION

Banana peel is a high capacitate, economically viable and low cost adsorbent for copper removal. Copper adsorption onto banana peel follows a pseudo second order kinetics. Adsorption of copper on banana peel shows high association with Langmuir and Freundlich isotherm model. The 1g of banana peel can adsorb 28 mg of copper in a favourable condition. This study can conclude that banana peel is the favourable alternative of copper removal from water.

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