Biosorption of Cu(II) From Water by Banana Peel Based Biosorbent: Experiments and Models of Adsorption and Desorption

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ABSTRACT
Banana peel, a discarded agricultural waste was used to produce bioadsorbent through easy and environmental friendly processes. This banana peel based biosorbent was evaluated for adsorptive removal of copper from water and its desorption capability. The characterisation results showed this biosorbent had very high specific surface area, potential binding sites and functional groups. The optimal conditions for biosorption were found at pH 6.5, biosorbent size of less than 75µ, dose of 0.5g/100ml and 1-hour contact time. Thermodynamic analysis also indicated that its adsorption was spontaneous. Significant desorption of copper (94%) was obtained when using 0.1N H₂SO₄. Both adsorption and desorption equilibrium data were well described by Langmuir, SIPS and Koble-Corrigan models whilst kinetics data by pseudo-first order, Elovich and Intraparticle diffusion models. Models’ parameters were optimised by MATLAB’s non-linear modelling. All models had good fitness with the experimental data from high R² (0.970-1.00), low non-linear errors - RMSE (0.004-10.00) and low χ² (0.0004-10.00). The maximum adsorption and desorption capacities were 20.37 and 32.40 mg/g, respectively. The adsorption processes were controlled by chemisorption. Both adsorption and desorption processes could be described by the pseudo-first order kinetic. The potential applicability of banana peel based bioadsorbent could be further examined in a large-scale.

Keywords: Banana peel; Adsorption isotherm; Desorption isotherm; Copper removal; Regeneration

1. INTRODUCTION
It is well known that the consumption of copper contained water causes various health problems to living organism and transmits to the food, especially shellfish, liver, mushrooms and nuts (Antunes et al., 2003). Intake of over dosed copper by humans may cause to severe mucosal irritation, hepatic and renal damage, widespread capillary damage, gastrointestinal irritation and central nervous problems (Larous et al., 2005; Madhava Rao et al., 2006). Presence of high copper compound in the body may also effect on aging, schizophrenia, mental illness, Indian childhood cirhosis, Wilson’s and Alzheimer’s diseases (Brewer, 2007; Faller, 2009; Hureau and Faller, 2009). Copper in the blood system may generate reactive free oxygen species and damage the protein, lipids and DNA (George J, 2010). Excessive copper in the marine system has been found to damage marine life (Van Genderen et al., 2005) and damage the gills, liver, kidneys, the nervous system and changing sexual life of fishes (Flemming and Trevors, 1989). Therefore, the copper concentration must be reduced to acceptable level by treating the effluent from industrial wastewater before entering receiving water bodies.

Adsorption technology has the potentiality to remove, recover and recycle of metals from
wastewaters (Bhattacharyya and Gupta, 2006). Activated carbon is a widely used adsorbent for metals removal due to its high specific surface area and affinity to metals. However, its high cost and technical preparation lead to a development of new adsorbents with similar characteristics (Özcan et al., 2005). Thus, there is a scope to discover an alternative adsorbent which has low cost and high efficiency. Many researchers have investigated low-cost adsorbents originated from agro-wastes for heavy metals removal (Gao et al., 2008; Sari et al., 2008; Yang and Chen, 2008). In this aspect, an agricultural waste such as banana peel has been used as bioadsorbents for the copper adsorption. Banana peels are readily available, low cost and cheap, environment friendly bio-materials. A step was taken for preparing bioadsorbents from banana peels for removal of copper from water.

The main aims of this study were: (i) to prepare adsorbent and characterization, and (ii) to evaluate the effectiveness of banana peel for copper removal by determining the maximum adsorption capacities. The regeneration of exhausted banana peel and recovery of copper were examined by desorption capacities. Langmuir, SIPS and Koble-Corrigan isotherm models were used to fit the equilibrium data from adsorption. At first time by this research, the models fitness was examined with the data from desorption equilibrium of copper from banana peel based biosorbent. The adsorption and desorption kinetic characteristics were determined using pseudo-first-order, Elovich and Intra-particle diffusion models. Thermodynamic of copper adsorption were also evaluated.

2. MATERIALS AND METHODS

2.1 Materials

Copper sulphate (CuSO₄·5H₂O) was dissolved in 1L of milli-Q water for preparing stock solution of copper (1000 mg/l Cu²⁺) and used for all experiments with required dilution with distilled water. The banana peels (Cavendish bananas) were collected from kitchen and used for whole experiments.

2.2 Methods

2.2.1 Preparation and Characterization of Adsorbent

Collected banana peels were cut it into small pieces (< 5 mm), washed three times with tap water and three times with distilled water to remove external dirt. Wetted banana peels were kept in air for removing the free water from the surface and dried in oven for 24 hours at 105°C. The dried banana peels were grounded into powder and kept in an air tied bottle prior to the experiments. Grounded banana peel was characterised by FT-IR, SEM and BET test.

2.2.2 Effects of Experiment Conditions

The effects of experiment conditions such as pH, particle sizes, doses, contact time and temperature were investigated for copper adsorption onto banana peel. The pH dependent experiments were conducted in 100 ml water with 10 mg/l copper and 0.5g banana peel between 1.18 to 13.5 pH. The grounded banana peels were graded to six particles sizes i.e., 600, 420, 300, 150, 75 and < 75 µm with standard sieves. The effect of particle sizes on removal of copper were evaluated with 0.5g banana peels from each particle sizes after adding to six Erlenmeyers with 100 ml water contained 10 mg/l copper. The effect of bioadsorbent doses on equilibrium uptake of copper was investigated with adsorbent masses of 0.05, 0.1, 0.2, 0.5 and 1 g per 100 ml of water contained 1, 2, 5, 10 and 15 mg/l of copper. The Erlenmeyers were shaken for 24 hours with 120 rpm at room temperature.
The effect of temperature and contact time on adsorption of copper were examined with different temperature (30-70°C) and time (3h) for 10 mg/l copper concentration with 0.5 g banana peels in 100 ml water.

2.2.3 Desorption Study

Desorption of copper from banana peels were studied using 8 types of eluents including tape water, milli-Q water, distilled water, 0.1N H$_2$SO$_4$, 0.1N HCl, 0.1N HNO$_3$, 0.1N NaOH and 0.1 N CH$_3$COOH. Pre-adsorbed banana peel (0.5g) was taken in 100 ml of above mentioned medium and shaken at 120 rpm for 24 hr. The eluents were filtered and tested for desorbed copper. The filtrated banana peels were washed with distilled water and again used for second time adsorption of copper. These adsorption-desorption cycles of banana peel were conducted till nine times with the best eluent.

2.2.4 Study of Adsorption and Desorption Equilibrium

Three set of equilibrium adsorption experiments were conducted in 100 ml water with copper concentration ranges from 1 to 500 mg/l. Grounded banana peel (0.05, 0.5 and 1g) were added in each sets of experiments. The Erlenmeyers were shaken for 24 hours with 120 rpm at room temperature with pH between 6-6.5. The water samples were then filtered and analysed in terms of Cu. The filtered banana peel were used for desorption equilibrium after washing. Three doses (0.05, 0.5 and 1g) were added in 100ml of best eluent found from desorption study and shaken at 120 rpm for 24 hours.

2.2.5 Study of Adsorption and Desorption Kinetics

Kinetic experiments were conducted by agitating a 1L of water with 10, 50 and 100 mg/l copper concentration and 5 g of banana peels at room temperature (20°C) with pH of 6-6.5. The water was agitated at a constant speed of 120 rpm for 3 hours. 5 ml samples were withdrawn at different time intervals and, filtered and analysed in terms of copper. Desorption kinetics experiments were performed with same banana peel (after filtered and washing) in 1L of best eluents found from desorption study.

2.2.6 Analysis, Calculation and Models’ Fitness

The water samples were filtered with Whatmann® filter GF/C (1.2µm) and copper concentration in water were analysed by Atomic Absorption Spectrometer (Contra®AA 300, Analytikjena, Germany). The equilibrium adsorptions/desorption of copper by/from adsorbent were calculated as follows:

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

where, $q_e$, the equilibrium adsorption capacity (mg/g); $C_o$ and $C_e$, the initial and equilibrium copper concentrations in the water (mg/l), respectively; $V$, volume of used water (L); and $m$, the mass of dried (grounded powder) bioadsorbent (g). The equilibrium data for adsorption and desorption were fitted with Langmuir, SIPS and Koble-Corrigan isotherm models. All equilibrium model parameters were evaluated and optimised by non-linear regression using MATLAB® (R2010b). The evaluation of fitness of the model equations with experimental data requires an error function with optimization (Ho et al., 2002). The models fitness was signified by the coefficient of determination ($R^2$), non-linear error functions: the residual root mean square error (RMSE) and the chi-square test ($\chi^2$). The standard equations are as follows:
\[ R^2 = \frac{1 - \sum_{n=1}^{n} (q_{en} - q_{mn})^2}{\sum_{n=1}^{n} (q_{en} - q_{mn})^2} \]  
\[ \text{RMSE} = \sqrt{\frac{1}{n-1} \sum_{n=1}^{n} (q_{en} - q_{mn})^2} \]  
\[ \chi^2 = \sum_{n=1}^{n} \frac{(q_{en} - q_{mn})^2}{q_{en}} \]

where, \( q_e \) is the equilibrium adsorption capacity found from the batch experiment, \( q_m \) is the prediction from the isotherm model for corresponding to \( C_e \) and \( n \) is the number of observations. The small values of RMSE and \( \chi^2 \) indicate the better model fitting and the similarity of model with the experimental data respectively (Ho et al., 2002).

In the kinetics tests, the copper retained in the biosorbent phase (\( q_t, \text{mg/g} \)) was calculated by the following equation:

\[ q_{t} = \frac{(C_0 - C_t)V}{m} \]  

where: \( C_0 \) and \( C_t \) are the initial and concentrations of the copper at \( t \) time in the water (mg/l), \( V \) is the water volume (l) and \( m \) is the mass of dried (grounded powder) biosorbent (g). The kinetics data for adsorption and desorption were fitted to the Pseudo-First-order, Elovich and Intra-particle diffusion models. The parameters of the models were optimised by non-linear analyses. Along with the coefficient of determination \( (R^2) \), the degree of fitness of kinetics models were judged by two non-linear errors: the normalized standard deviation (NSD) and average relative error (ARE). The equations are defined as:

\[ NSD = 100 \times \sqrt{\frac{1}{N-1} \sum_{i=1}^{N} \left[ \frac{q_{e} - q_{m}}{q_{e}} \right]_i^2} \]  
\[ ARE = \frac{100}{N} \sum_{i=1}^{N} \left[ \frac{q_{e} - q_{m}}{q_{e}} \right]_i \]  

where, \( q_e \) and \( q_m \) (mg/g) are experimental ('e') and model ('m') predicted amount of copper adsorbed onto banana peel at time 't' and 'N' is the number of observations made. The smaller values of NSD and ARE will indicate the better fitted model.

3. RESULTS AND DISCUSSION

3.1 Environment Friendly Preparation

Formations of particles’ size and shape, surface morphology as well as specific surface area of bioadsorbent fully depend on the preparation method. In addition, easy to prepare, easy to use, hazard free and environment friendly treatments are the requirement for sustainable preparation of bioadsorbents. In this circumstances, this research adopted a simple and non-treated preparation method rather than the expensive and high-tech pyrolysis and non-environment friendly acid/base treated methods (Al-Asheh et al., 2000; Al-Rub, 2006; Özcan et al., 2005). The novelty of this research is that simply banana peels were cut, wash, dry and ground to powder and used for experiments.

3.2 Characterisation of Banana Peel

3.2.1 FT-IR

To understand the nature of the functional groups present in banana peel, the FT-IR spectra were obtained by SHIMADZU FTIR 8400S (Kyoto, Japan). FT-IR spectra (Figure 1) displayed a number of peaks and indicated a complex nature of the adsorbent. Bands appearing at 3620.54, between 3537.60-3348.57, 3147.96-3102.63, 2957.97-2850.91, 2360.97-2347.47, 1654.03, 1560.48, 1459.21-
1411.95 and 996.28-936.48 cm\(^{-1}\) were assigned to OH stretch, free hydroxyl (Alcohols, phenols), OH stretch, H-bonded (Alcohols, phenols), OH stretch (carboxylic acids), \(\equiv\)C-H stretch (alkanes), \(\equiv\)N stretch (Nitriles), -C≡C- stretch (alkanes), N-H bend (primary amines), C-H bend (alkanes) and O-H bend (carboxylic acid or ester) respectively. Among the active groups carboxylic acid and hydroxyl groups could play major role for copper adsorption (Annadurai et al., 2002; Memon et al., 2008).

3.2.2 Scanning Electronic Microscopy (SEM)

Zeiss (JEOL-JSM-35CF, UK) Scanning Electronic Microscope (SEM), operating in variable pressure (VP) mode at 0.3 Tor and 20kV accelerating voltage was used for studying the surface morphology of the banana peel (Figure 2). Figure 2(a) shows the original banana peel which revealed the combination of small and large particles size, heterogeneous rough and porous surfaces with crater-like pores (Memon et al., 2008). Its surface also exhibited a micro-rough texture, which could promote the adherence of copper (Annadurai et al., 2002). Figure 2(b) shows the BSE image of banana peel after adsorption of copper and it was changed to homogeneous surface from heterogeneous rough and porous surfaces after adsorption of copper (Albarelli et al., 2011).

3.2.3 Pore Structure and Pore Size Distribution

The BET surface areas of banana peel were determined from \(\text{N}_2\) adsorption isotherm by Nano Porosity System (Micrometrics ASAP 2020, Mirae SI, Korea). The BET surface area, Langmuir surface area and average pore diameter of banana peel were 22.59 m\(^2\)/g, 4.82 m\(^2\)/g and 8.71 Å, respectively. This BET area (specific surface area) was higher than chitosan flakes and pine bark (Ngah and Fatinathan, 2006; Vázquez et al., 2007) but lower than palm oil fruit shell (Hossain et al., 2012). On the contrary, the surface area was low compared to pyrolysis produced activated carbon (Table 4), but it could be considered as it was produced from the non-treated, low cost and simple processes. According to International Union of Pure and Applied Chemistry (IUPAC) classification, the majority of pores were mesopore (83%).

![Figure 1 FTIR spectra of banana peel](image-url)
3.3 Effect of Experimental Conditions

The experimental conditions such as pH, particle sizes, doses and contact time, thermal effect on copper adsorption were investigated for banana peel and the results are shown in Figure 3.

3.3.1 pH

pH is one of the most important parameter which controls the surface properties of adsorbents, functional groups and ionic state of metal’s species. The adsorption capacities of copper from water onto banana peel were strongly affected by the pH (Figure 3(a)). The adsorption capacities were increased from 0.7 mg/g to 1.76 mg/g with the increase in pH from pH 2 to pH 6. Copper adsorption was significantly increased between pH 4 and 6. This can explained as Cu$^{2+}$, Cu(OH)$^+$ and Cu(OH)$_2$ species are available for adsorption at below pH 6 (Wang and Qin, 2005). The adsorption capacity decreased after pH 6 and continued to decreases till pH 12. Low adsorption capacities were observed at both low and high pH. At low pH, H$_3$O$^+$ ion competes with Cu$^{2+}$ for binding and surrounded hydronium ions (H$^+$) preventing the copper ions from approaching the binding sites and it could be responsible for low adsorption capacities (Karthikeyan et al., 2007). At higher pH, the binding site may not be activated in basic condition (Demirbas, 2009). Above pH 6, the copper started precipitating as Cu(OH)$_2$+, so the removal was not completely by adsorption (Memon et al., 2008).

3.3.2 Particle Sizes

The exposure and availability of binding sites depend on particle shapes and sizes of adsorbent. Figure 3(b) indicates that the removal of copper was increased from 74 to 96% by decreasing the particle sizes from 600µm to <75µm. This behaviour can be attributed to the effective surface area increased as the particle size decreased (Sengil and Özacar, 2008).

3.3.3 Doses

Dose dependent experiments show that copper removal was low at lower doses and gradually increased with increasing in doses (Figure 3(c)). Latter at higher doses, the copper removal again decreased. The highest copper removal (88%) was obtained by the initial copper concentration of 10 mg/l and dose of 5g/l. The partial aggregation among the available active binding sites at higher doses and lack of active binding site at lower doses retards the copper adsorption onto banana peel (Anwar et al., 2010; Karthikeyan et al., 2007).
9.3.4 Contact Time

The effect of contact time on copper adsorption is shown in Figure 3(d). Figure 3(d) indicates that the rate of copper adsorption was very rapid during first 30 min, and thereafter, the rate of copper removal remained stable. There were no significant increases found after 60 minutes of experiment and eventually it was the equilibrium time (Karthikeyan et al., 2007). Initially, there were large number of vacant active binding sites available at the first phase of experiment and large amount of copper ions were bound rapidly on banana peel at a faster adsorption rate. The binding site was shortly become limited and the remaining vacant surface sites were 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 (Anwar et al., 2010).

3.3.5 Thermodynamic Parameters

Normally temperature stimulates the molecules, functional groups and surface mor-
phology of the adsorbent and metals during adsorptions processes. To determine the thermal effects of copper adsorption onto banana peel, temperature variation experiments were conducted at 30, 40, 50 and 70°C, with an initial copper concentration between 1-200 mg/l. The experimental data show that the equilibrium adsorptions (q_m) were decreased with an increase in temperature (Table 1), suggesting that higher temperature helped to desorb the copper or retard the copper adsorption onto banana peel. From the data the thermodynamic parameters such as Gibbs free energy (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) were calculated. The magnitude of ΔG° (kJ/mol) was calculated using the following equation:

\[ ΔG° = -RT\ln K_a \]  

(8)

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

\[ ΔH° = ΔG° + TΔS° \]  

(9)

A plot of ΔG° versus T was found to be linear and both values of ΔH° and ΔS° were calculated from the slope and intercept. The thermodynamic parameters calculated for both Langmuir isotherm and Temkin isotherm are shown in Table 1. The ΔG° values were opposite in nature (-ve and +ve) calculated from Langmuir and Temkin isotherm. The negative nature of ΔG° has confirmed that the adsorption process was spontaneous in nature (Memon et al., 2008). The values of ΔG° were decreased from -6.95 to -4.63 kJ/mol for Langmuir isotherm and increased from 1.95 to 2.43 kJ/mol for Temkin isotherm at the temperature increases from 30 to 70°C. The positive value of ΔH° indicated that the adsorption reaction was endothermic and has strong affinity of banana peels towards copper ions. It was also suggested some structural changes in copper ions and banana peel (Gupta, 1998). In addition, the negative value of ΔS° (for both isotherms) also suggested that the adsorption was enthalpy driven and spontaneous in nature (Memon et al., 2008).

3.4 Regeneration of Banana Peel

The regeneration of exhausted banana peel is crucial to reuse and recovery of valuable metals and to reduce the operating cost for any type of water treatment. Regeneration experiments were done with eight eluents. The batch desorption results with eight eluents and adsorption-desorption cycle with 0.1N H_2SO_4 is presented in Figure 4. Among the solvents, the highest (94%) recovery was found when using 0.1N H_2SO_4. In desorption system, H⁺ released from acids which replaced Cu^{2+} on the surface of the banana peel (Wang and Qin, 2005). The adsorption and desorption cycles were continued till nine times with 0.1N H_2SO_4 (Figure 4(b)). Figure 4(b) showed that the banana peel could be reused till seven cycles without any significant change of efficiency. After first phase of desorption process the both adsorption and desorption efficiency were significantly increased. The acid solution might dissolve the organic portion of banana peel and activate the binding site, and consequently help to increase the efficiency.

3.5 Adsorption and Desorption Equilibriums

Adsorption as well as desorption process can be quantified by isotherm equation. Isotherm helps to understand the adsorption and desorption behaviour of bioadsorbents. The parameters used to derive the mathematical equation in isotherm are related to the surface properties and affinity of the adsorbent (Montazer-Rahmati et al., 2011). Three
isotherm models namely Langmuir, SIPS and Koble-Corrigan were employed to describe the adsorption as well as desorption of copper onto banana peel. The model predictions are plotted in Figure 5 and tabulated in Table 2.

![Figure 4](image4.png)

**Figure 4** Regeneration of banana peel and adsorption and desorption cycles

![Figure 5](image5.png)

**Figure 5** Isotherm modelling of adsorption and desorption of copper onto banana peel with different doses (Co: 1-500 mg/l; d: 0.05-1 g; t: 24h; pH: 6-6.5; rpm: 120; T: 20°C)
Generally both two-parameter (Langmuir) and three-parameter models (SIPS and Koble-Corrigan) were shown good fitness with experimental data obtained at doses of 0.05, 0.5 and 1 g for both adsorption and desorption processes. It can be due to the presence of both heterogeneous and homogeneous surface on the banana peel (Febrianto et al., 2009). Among the three doses, data from 1g dose was shown better association with all three models for both adsorption and desorption equilibrium ($R^2$: 0.998 to 1). Low RMSE and small $\chi^2$ values were also found from that dose. Monolayer adsorption capacities ($q_m$) were 20.37 and 32.40 mg/g from adsorption and desorption processes, respectively. This adsorption and desorption capacities ($q_m$) of copper were higher than other bioadsorbent reported in literature (Montazer-Rahmati et al., 2011). Lower values of $K_L$ (< 1) were noticed from both adsorption and desorption process (Table 2) which indicated the higher affinity of banana peel to copper (Davis et al., 2003; Febrianto et al., 2009). In comparison with RMSE values of three models, the lowest RMSE values (0.0003, 1.914 and 0.323) were predicted by Langmuir model for the used three doses. Similarly the lowest $\chi^2$ values (7.85, 0.240 and 0.036) were also predicted from Langmuir model. The calculated values of exponent ($\beta_S$) from SIPS model were close to unity for both adsorption and desorption of copper. It was signified that copper adsorption and desorption processes in this study was more of Langmuir form rather than that of Freundlich (Foo and Hameed, 2010). From the analysis of three isotherm models and the knowledge of the most important parameters ($q_m$, $R^2$, RMSE and $\chi^2$), the isotherms can be arranged according to their capacity to predict their efficiency in forecasting the experimental behaviour of the banana peel-copper system. Therefore, the best fit of adsorption isotherm models were in the order of: Langmuir > Koble-Corrigan>Sips.

Table 2 Predicted parameters of isotherm models for adsorption and desorption of copper onto banana peel

<table>
<thead>
<tr>
<th>Isotherm models</th>
<th>Parameters</th>
<th>Adsorption (Doses)</th>
<th>Desorption (Doses)</th>
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<tr>
<td></td>
<td></td>
<td>0.05g</td>
<td>0.5g</td>
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<tr>
<td>1. Langmuir</td>
<td>$q_m$</td>
<td>298.30</td>
<td>58.90</td>
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<td></td>
<td>$K_L$</td>
<td>0.020</td>
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<td></td>
<td>$R^2$</td>
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<td>0.989</td>
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<tr>
<td></td>
<td>$\chi^2$</td>
<td>7.86</td>
<td>0.240</td>
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<tr>
<td></td>
<td>RMSE</td>
<td>0.0003</td>
<td>1.914</td>
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<td>2. SIPS</td>
<td>$K_s$</td>
<td>1.839</td>
<td>0.318</td>
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<td></td>
<td>$\alpha_S$</td>
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<tr>
<td></td>
<td>$\beta_S$</td>
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<td>1.251</td>
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<tr>
<td></td>
<td>$R^2$</td>
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<td>0.991</td>
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<tr>
<td></td>
<td>$\chi^2$</td>
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<td></td>
<td>RMSE</td>
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<td>3. Koble-Corrigan</td>
<td>$A_{KC}$</td>
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<tr>
<td></td>
<td>$B_{KC}$</td>
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<tr>
<td></td>
<td>$p$</td>
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<tr>
<td></td>
<td>$R^2$</td>
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<td></td>
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<td></td>
<td>RMSE</td>
<td>9.942</td>
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Table 3  Predicted parameters of kinetics models for copper adsorption and desorption onto banana peel

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<thead>
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<th>Kinetic models</th>
<th>Parameters</th>
<th>Adsorption Copper concentration</th>
<th>Desorption Copper concentration</th>
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<td></td>
<td></td>
<td>10mg</td>
<td>50mg</td>
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<tr>
<td>Experiments qₑ (mg/g)</td>
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<td>8.520</td>
<td>17.476</td>
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<td>R²</td>
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<td>NSD</td>
<td>23.559</td>
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<td>ARE</td>
<td>7.031</td>
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<td>2. Elovich</td>
<td>α (mg/g.h)</td>
<td>2.193</td>
<td>26.3x10¹²</td>
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<td></td>
<td>β (g/mg)</td>
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<td>R²</td>
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<td>0.970</td>
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<td>NSD</td>
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<td>ARE</td>
<td>-0.415</td>
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<td>3. Intra particle diffusion</td>
<td>kₚ (g/mg.√min)</td>
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</tbody>
</table>

On the other hand, desorption data were followed the similar tendencies of fitness like adsorption models. It was surprisingly noticed that all used models posed good fitness (R² =0.991 to 1.000) with the desorption data found from all three doses. Among the three models, Langmuir and Koble-Corrigan models were shown better fitness than SIPS. The nonlinear errors such as RMSE and χ² were remained near unity (<1) for Langmuir and Koble-Corrigan models and it is testified the suitability of the model to describe the desorption processes (Tseng et al., 2009; Uchimiya et al., 2011). From the comparison of models prediction, the following remarks could be taken:

- The form of the isotherm equations were unique for best description of both adsorption and desorption data. For example, all isotherm models had good fitness with the experimental data obtained from adsorption and desorption equilibrium of copper onto banana peel. Thus, the models used were appropriate for describing adsorption process as well as desorption process.
- The Langmuir and Koble-Corrigan models were best for both adsorption and desorption data though other model posed good association (Uchimiya et al., 2011).
- Comparison of models’ parameters predicted from adsorption and desorption system (Tables 2) revealed that the magnitude were not same, indicating a significant hysteresis effect (Tseng et al., 2009).

3.6 Adsorption and Desorption Kinetics

Kinetic data were analysed using three kinetic models namely pseudo-first order, Elovich and Intra particle diffusion equation. Nonlinear regression analysis method was used to fit the kinetic data by MS Excel Spread-sheet and optimised the parameter with Solver tool. The
association between the experimental data and the model-predicted values was examined by R², the normalized standard deviation (NSD) and average relative error (ARE). The non-linear fitting curves of the pseudo-first-order, Elovich and Intra particle diffusion equations for adsorption and desorption of copper onto banana peel are presented in Figure 6 and parameters are summarised in Table 3.

### 3.6.1 Pseudo-First Order Model

The pseudo-first-order kinetic model (Tseng et al., 2009) can be represented by Eq. (10):

$$q_t = q_e - q_e e^{-k_1 t}$$

where $k_1$ (1/min) is the pseudo-first-order kinetic rate constant and $t$ (min) the contact time. Adsorption and desorption kinetics were very fast at the beginning of processes. The adsorption processes reached equilibrium after 60, 30 and 20 min for the initial copper concentration of 10, 50 and 100 mg/l, respectively. The initial faster rate of copper adsorption onto banana peel may be due to the availability of the non-used binding sites (Renaud et al., 2011). Desorption process reached equilibrium after 100, 100 and 50 min for the same doses. The equilibrium adsorption and desorption capacities increased with increasing in initial copper concentration and close to experimental values (Table 3). This strongly suggests that the adsorption and desorption could be represented by a pseudo-first order kinetic model (Bueno et al., 2008; Kambhaty et al., 2009). The values of pseudo-first order kinetics constant ($K_1$) for adsorption were 0.130, 2.720 and 2.376 Lh⁻¹ for the initial copper concentration of 10, 50 and 100 mg/l while being 0.031, 0.152 and 1.00 l/h for desorption processes. The value of $K_1$ increases with increasing of initial copper concentration for both adsorption and desorption kinetics. The $K_1$ values were near unity which revealed that the processes were controlled by chemisorption and suitability of the model (Ho and Ofomaja, 2006; Ho et al., 2000; Kambhaty et al., 2009). The significantly small values of NSD and ARE were also testified the statement.

### 3.6.2 The Elovich Equation

The Elovich kinetic equation (Behnamfard and Salarirad, 2009) is given by Eq. (11).

$$q_t = \beta \ln(\alpha t)$$

where $\alpha$ (mg/g.min) is the initial biosorption rate and $\beta$ (g/mg) the desorption constant related to the extent of surface coverage and activation energy for chemisorption. The adsorption and desorption processes were also tried to describes by Elovich kinetic model. In fact, this model was shown a moderate fitness ($R^2$: 0.914 to 0.970) with the experimental data for adsorption but not with desorption data ($R^2$: 0.869 to 0.970). The low correlation coefficients indicating that this model was not applicable in the present case. Parameters $\alpha$ and $\beta$, were used to interpret and understand the initial rate of the process as well as the nature of sites involved in the adsorption processes. An opposite trend was noticed from the calculated values of $\alpha$ and $\beta$. The $\alpha$ increased from 2.193 to $8.8 \times 10^{13}$ mg/g.h for adsorption and from 1.106 to 7.944 mg/g.h for desorption while copper concentrations lied between 10 to 100 mg/l. On the other hand, $\beta$ decreased from 5.353 to 0.160 g/mg for adsorption and increased from 0.043 to 0.172 g/mg for desorption while copper concentrations were same. This is the general trend of variation for $\alpha$ and $\beta$ with increase in initial copper concentration in case of adsorption and proved that activation energies required for chemisorptions corresponding to the heterogeneity in the nature of the active sites of banana peel (Behnamfard and Salarirad, 2009; Viswanathan, 2004). However, desorption process did not follow the trend of $\alpha$ and $\beta$. It
can be assumed that desorption process does not follow the Elovich kinetics though low NSD and ARE values were observed.

3.6.3 Intra-Particle Diffusion Model

Adsorption and desorption kinetic data were further used to define whether the intra-particle diffusion was rate limiting and also to find the diffusion rate constant, $k_p$, (mg/g min$^{0.5}$). Intra-particle diffusion model (Srihari and Das, 2008) is presented by the relationship between specific adsorption ($k_p$) and the square root of time ($t$), according to the following equation (Eq.12):

$$q_t = k_p t^{0.5} + C$$  \hspace{1cm} (12)

Intraparticle diffusion model is characterized by the relationship between specific adsorption and the square root of time (Rudzinski and Plazinski, 2006). This relation also keep same for desorption kinetics. The experimental data were not properly fitted with model prediction as the $R^2$ values were low. The rate parameter ($k_p$) was increased with increased copper concentration for both adsorption and desorption processes. The adsorption rate constant ($k_p$) was increased from 0.540 to 16.135 mg/g.min$^{0.5}$ with increasing in the initial copper concentration (10 to 100 mg/l). The similar trends were also followed by desorption processes and values were increased 1.127 to 7.958 mg/g.min$^{0.5}$ for the same initial copper concentration.

Figure 6  Modelling of adsorption and desorption kinetics of copper onto banana peel (Co: 10, 50, 100 mg/l; d: 5 g/l; t: 3 h; pH: 6-6.5; rpm: 120; T: 20°C)
Table 4  Comparison of performance of copper adsorption by biosorbent produces from agricultural wastes

<table>
<thead>
<tr>
<th>Name</th>
<th>Temp. (°C)</th>
<th>pH</th>
<th>RPM</th>
<th>C₀   (mg/l)</th>
<th>qₘ   (mg/g)</th>
<th>BET area(m²/g)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Activated carbon form</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rubber wood dust</td>
<td>30</td>
<td>6.0</td>
<td>180</td>
<td>10-40</td>
<td>5.73</td>
<td>1674</td>
<td>(Kalavathy et al., 2005)</td>
</tr>
<tr>
<td>Hazelnut shells</td>
<td>25</td>
<td>5.0</td>
<td>90</td>
<td>8500</td>
<td>200</td>
<td>1651</td>
<td>(Milenković et al., 2009)</td>
</tr>
<tr>
<td>Peanut shells</td>
<td>NA</td>
<td>4.8</td>
<td>300</td>
<td>818-3177</td>
<td>50.4</td>
<td>725</td>
<td>(Wilson et al., 2006)</td>
</tr>
<tr>
<td><em>Ceiba pentandra</em></td>
<td>30</td>
<td>6.0</td>
<td></td>
<td>40-100</td>
<td>20.8</td>
<td>521</td>
<td>(Madhava Rao et al., 2006)</td>
</tr>
<tr>
<td>Peanut hulls</td>
<td>30</td>
<td>5.0</td>
<td>180</td>
<td>10-20</td>
<td>65.57</td>
<td>208.0</td>
<td>(Goswami et al., 2005)</td>
</tr>
<tr>
<td>Hazelnut shells</td>
<td>18</td>
<td></td>
<td>170</td>
<td></td>
<td>39.54</td>
<td>10.1</td>
<td>(Şayan, 2006)</td>
</tr>
<tr>
<td>Hazelnut husk</td>
<td>18</td>
<td>5.7</td>
<td>200</td>
<td>200</td>
<td>6.645</td>
<td>4.31</td>
<td>(Imamoglu and Tekir, 2008)</td>
</tr>
<tr>
<td><strong>Normal grounded form</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Macroalgae (<em>Fucus vesiculosus</em>)</td>
<td>20</td>
<td>4.2</td>
<td>350</td>
<td>100</td>
<td>114.9</td>
<td>0.22</td>
<td>(Cochrane et al., 2006)</td>
</tr>
<tr>
<td>Crab carapace</td>
<td>20</td>
<td>5</td>
<td>350</td>
<td>100</td>
<td>79.4</td>
<td>33.4</td>
<td>(Cochrane et al., 2006)</td>
</tr>
<tr>
<td><em>Cancer pagurus</em></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(Özer et al., 2004)</td>
</tr>
<tr>
<td>Wheat bran</td>
<td>20</td>
<td>5</td>
<td>150</td>
<td>0-100</td>
<td>51.5</td>
<td>7.72</td>
<td>(Hossain et al., 2012)</td>
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<tr>
<td>Palm oil fruit shell</td>
<td>20</td>
<td>NA</td>
<td>120</td>
<td>1-35</td>
<td>20-60</td>
<td>39.76</td>
<td>(Ho, 2003)</td>
</tr>
<tr>
<td>Tree fern</td>
<td>30</td>
<td>NA</td>
<td>100</td>
<td>30-150</td>
<td>11.7</td>
<td>2.39</td>
<td>(Sen Gupta et al., 2009)</td>
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<tr>
<td>Irish peat moss</td>
<td>25</td>
<td>2.8</td>
<td>NA</td>
<td>5-100</td>
<td>17.6</td>
<td>203.41</td>
<td>(Ulmanu et al., 2003)</td>
</tr>
<tr>
<td>Cellulose pulp waste</td>
<td>22</td>
<td>&lt;6.0</td>
<td>NA</td>
<td>65-200</td>
<td>4.98</td>
<td>2.64</td>
<td>(Ulmanu et al., 2003)</td>
</tr>
<tr>
<td>Compost</td>
<td>22</td>
<td>7.3</td>
<td>NA</td>
<td>0-100</td>
<td>12.77</td>
<td>1.36</td>
<td>(Ulmanu et al., 2003)</td>
</tr>
<tr>
<td>Aquatic plant</td>
<td>25</td>
<td>5-6</td>
<td>NA</td>
<td>2-70</td>
<td>10.37</td>
<td>1.56</td>
<td>(Keskinkan et al., 2004)</td>
</tr>
<tr>
<td>Banana peel</td>
<td>Room temp.</td>
<td>NA</td>
<td>120</td>
<td>1-500</td>
<td>20.37</td>
<td>22.59</td>
<td>Present study</td>
</tr>
</tbody>
</table>

*NA = Not adjusted / Not Available  
* AC = Activated Carbon

### 3.7 Comparison of Performances

The acceptability of bioadsorbent depends on the metal adsorption capacity, specific surface area, consumer friendly, availability and environment friendly applications. In this context, the adsorption capacities (calculated from the Langmuir isotherm model) of copper with other parameters obtained from banana peel and other adsorbents and activated carbon produced from agricultural wastes were compared in Table 4. Table 4 indicates...
that the banana peel based biosorbent adsorbs more copper ions from water than others.

CONCLUSIONS

Banana peels is a low cost and readily available materials for preparing biosorbent. This study has explored the economically viable biosorbents for copper removal from water. The banana peel could be regenerated and reused till seven times without reducing efficiency. The data from adsorption and desorption equilibrium were well fitted with three models used showing the variation for degrees of fitness. Langmuir model were predicted the maximum equilibrium adsorption and desorption capacities from a 1g dose and the values found were higher than some biosorbent and activated carbon. The kinetics of adsorption of copper onto banana peels could follow a pseudo-first-order equation and chemisorption controls of the adsorption process. Desorption processes were also well fitted with kinetics models. The reuse of banana peel was viable as the desorption study revealed. Hence, the banana peel based biosorbent can be a favourable alternative for copper removal from water and wastewater.

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