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Removal of Cu(II) from aqueous phase using tailor made sulfur-impregnated activated carbon inspired by Claus process

Krishnan Anoop Krishnan[a,*], Kumaran Girija Sreejalekshmi[b], Vinu V. Dev[a], Sibin Antony[a], Harsha Mahadevan[a]

[a]*NREM, National Centre for Earth Science Studies (NCESS), Ministry of Earth Sciences (MoES), Akkulam, Trivandrum 695011, India, Tel. +91 9447402468; emails: sreeanoop@rediffmail.com (K. Anoop Krishnan), vinuvdev.dev@gmail.com (V.V. Dev), santony41@gmail.com (S. Antony), harshmahadevan@gmail.com (H. Mahadevan)*
[b]*Department of Chemistry, Indian Institute of Space Science and Technology (IIST), Department of Space, Near LPSC, Valiamala Post, Trivandrum 695547, India, sreejalekshmi@gmail.com (K.G. Sreejalekshmi)*

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ABSTRACT

The study assesses the effectiveness of sugarcane biomass based sulfur-impregnated activated carbon (SIAC) in removing Cu(II) from aqueous phase in conditions. The sulfurization of activated carbon was effected by an adapted Claus process to leverage on the affinity of Cu(II) for sulfur. The optimum pH for the adsorption of Cu(II) onto SIAC was found to be at 6.0. It was observed that an amount of 11.84 mg/g (94.7%) and 22.83 mg/g (91.3%) of Cu(II) was removed from an initial Cu(II) concentration of 25 and 50 mg/L, respectively. The adsorption kinetic data were modeled using pseudo-second-order kinetics. The equilibrium data exhibit a Langmuir type isotherm and a quite higher adsorption capacity value of 73.53 mg/g was obtained. The reusability of the spent adsorbent was determined and found that about 77.4% of the initial desorption capacity was retained after the fourth cycle. This establishes the technical feasibility of the adsorption process. Moreover, the adsorption studies were conducted for a series of simulated and wastewaters containing Cu(II) and the results obtained were of promising ones for water treatment strategies.

Keywords: Adsorption; Claus process; Cu(II); Removal; Sulfur impregnation

1. Introduction

Copper is a micronutrient and at the same time, it acts as a toxicant to phytoplankton and microorganism [1,2]. Copper is a persistent and toxic metal having bioaccumulative nature and is not easily metabolized [3]. Copper toxicity known as copperiedus occurs due to the excess of copper in the body, either by eating foods cooked in uncoated copper pan or by using drinking water with excess copper [4]. Acute copper poisoning may cause hematemesis, coma, low blood pressure and gastrointestinal distress. The maximum permissible level of copper in drinking water is 2.0 mg/L. The higher concentrations of copper in drinking water may cause kidney failure, anemia, damaging the central nervous systems, stomach cramp, vomiting and nausea [5]. Industries such as metal plating, electrical, copper plumbing and ceramic material processing cause copper pollution in receiving water bodies. Thus, the removal of copper from aqueous phase is highly warranted to maintain the health of the watersheds.

Adsorption is one of the best methods in removing heavy metals from aqueous solutions [6–9]. The rest of the methods including biological treatment, osmosis and precipitation are found to be less effective due to various reasons [10]. In the case of Cu(II), adsorptive removal technique is found to be best enough to reduce the trace amount of Cu(II) from water and wastewaters compared with precipitation and biological treatments. Moreover, the local availability of effective precursors for developing adsorbent materials that include plant wastes,

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* Corresponding author.

clays and fly ash may bring the cost effective and eco-friendly concept in adsorptive treatment strategies. A wide spectra of natural resources such as pomegranate peel [11], sawdust [12], plant leaves [13], shells of lentil, wheat and rice [14] and cashew nut shell [15] were used as adsorbent materials for the removal of Cu(II) from aqueous solutions. Perusal of literature also showed a variety of materials that include tea industry waste [16], waste fungal biomass [17] as well as activated carbons (ACs) [18–20] were used for the adsorptive removal of Cu(II) from aqueous phase. Surface functionalization on nanofibers [21], chitosan microspheres [22] and copolymer [23] were also reported with effective Cu(II) removal capacity.

The concept of sulfurization for enhancing the adsorption capacity of AC for the removal of Cu(II) from aqueous solution is unexplored. Some of the researchers reported the use of surface-modified ACs for the effective removal of Cu(II) from water and wastewaters [24,25]. The purpose of our research program is to develop an active sulfurized carbon from sugarcane bagasse for removing Cu(II) from aqueous phase to capitalize on the affinity of Cu(II) toward sulfur. Bagasse has the advantage of being easily available and eco-friendly precursor whereas the source for sulfur was a customized Claus process. Our choice of Claus process for generating elemental sulfur for sulfurization was based on the idea that once successful, the strategy will also enable scavenging of hydrogen sulfide and sulfur dioxide gases which are toxic and corrosive gaseous discharges from many industries and sour water stripping water treatment plants. Series of batch adsorption studies were conducted to optimize various conditions such as solution pH, contact time, initial Cu(II) concentration and temperature to establish the effectiveness of sulfur-impregnated activated carbon (SIAC) in removing Cu(II) from aqueous solutions. Both kinetic and equilibrium studies were performed to evaluate the rate of reaction and capacity of adsorption, respectively. Regeneration of spent adsorbent for further adsorption process was effectively done by conducting adsorption–desorption studies.

2. Experimental procedure

2.1. Chemicals and reagents

The GR grade chemicals and reagents of E-Merck, India Ltd., were incorporated in the study without any further treatment/purification. The precursor material, bagasse pith, for the synthesis of SIAC was collected from the premises of famous temples (Sree Bhadrakali Devi temple and Kottiyal Sree Mahadeva temple located at Ooruttukala, Neyyattinkara, Trivandrum, India) during annual festival seasons. During these days, many sugarcane juice shops serve beverages to the pilgrims and dump bagasse pith as a waste material leading to disposal as well as leaching problems severed by the onset of southwest monsoon immediately following the festive seasons in Kerala. Therefore, the utilization of bagasse pith biomass offers dual advantage – availability of the material free of cost and the conversion of a potential solid waste to a value-added product.

2.2. Adsorbents

The sugarcane bagasse pith was washed well with water repeatedly (×10) and dried in sunlight for 3 d. The crispy chunk-like biomass was cut into small pieces, powdered using plant mill (Retsch, Germany, model ZM 200) and again dried in sunlight for one more day to obtain raw sugarcane bagasse pith (R-SBP). The R-SBP was then placed in a muffle furnace (Labline, India) set at a heating rate of 5°C min^{-1} for 2 h when the carbonization was found to be completed within 35 min when the temperature inside the furnace reached 200°C. The carbonized material was further heated at 400°C for 45 min to ensure completion of the carbonization process and was then subjected to steam activation with a view to enhance the surface area. In a muffle furnace maintained at 600°C, the carbon was purged with steam intermittently (10 mL min^{-1} for 5 min with an interval of 15 min) for 2 h. This was followed by sulfurization where the elemental sulfur was sourced from the reaction of H_2S and SO_2 as in Claus process. Briefly, the steam-activated carbon was heated in the muffle furnace at 600°C in the presence of H_2S (5 mL min^{-1}) and SO_2 (5 mL min^{-1}) from their respective gas generators along with intermittent flow of steam (10 mL min^{-1}) for 2 h after which the product was subjected to rapid cooling, then was washed with distilled water and dried at 100°C for 1 h [26]. Thus, obtained SIAC was then ground and sieved to particles of −80 + 230 mesh size and stored in moisture-free polypropylene bottles.

2.3. Analytical methods

The detailed characterization of SIAC was carried out using the methods described in literature. The properties such as cation exchange capacity, surface area, porosity and pH at zero point charge (pH_{zpc}) have influence on the process of adsorption in the solution phase. The impregnated sulfur groups also have great influence on the Cu(II) adsorption process. The cation exchange capacity was determined using the methods described elsewhere [27] and sulfur content was determined using CHNS-O Analyser (Elementar, Vario EL Cube). The surface area and porosity were determined by methods described in the literature [28,29]. The difference in surface charge density, s_o as a function of solution pH at different ionic strengths of 0.1, 0.05, 0.01, 0.005 and 0.001 M KNO_3 was calculated using potentiometric titration method [30] using the following equation:

$$\sigma_o = \frac{F(C_A - C_B + [OH]^- - [H]^+)}{A} \tag{1}$$

where σ_o is expressed in coulomb/cm^2, F is the Faraday constant (coulomb eq^{-1}), C_A and C_B are the concentrations of acid and alkali after each addition during titration (eq/L), $[H]^+$ and $[OH]^-$ are the equilibrium concentrations of H^+ and OH^- bound to the suspension surface (eq/cm) and A is the surface area of suspension (cm^2/L). The pH_{zpc} is the pH of the suspension at which surface charge density becomes zero. In the case of $pH > pH_{zpc}$, the surface is negatively charged and if $pH < pH_{zpc}$, the charge on the surface is positive.

2.4. Batch adsorption experiments

The $Cu(NO_3)_2$ was accurately weighed and made to a stock solution of initial concentration 1,000 mg/L in milli Q water (Type 1 water) from which experimental solutions of preset concentrations were prepared using Type 2 water. The desired solution pH was attained using different concentrations of HNO_3 or NaOH (0.001, 0.005, 0.01, 0.05, 0.1, 0.5, 1.0, 1.5 and 2.0 M). Adsorption experiments were carried out by diluting the Cu(II) stock solution to 50 mL followed by equilibration with 100 mg of SIAC in a temperature-controlled water bath shaker (200 spm) after adjusting the solution pH to desired levels. The solution, after attainment of equilibrium, was filtered using 0.45 μm cellulose nitrate filter paper and the filtrate was analyzed for Cu(II) content using atomic absorption spectrophotometer (GBC Avanta, model A4001, Australia). The amount of Cu(II) adsorbed onto SIAC was estimated using the following equation:

$$q = \left[\left(C_o - C_A\right)V\right] / m \tag{2}$$

where q is the amount of Cu(II) adsorbed onto unit mass of adsorbent (mg/g); C_o and C_A are the initial and equilibrium solution concentrations (mg/L), respectively; V is the volume of aqueous phase (mL) and m is the adsorbent dosage (g).

The optimum pH for Cu(II) adsorption was determined by varying solution pH from 2.0 to 12.0 for different initial concentrations ranging from 25 to 100 mg/L. Studies were conducted to evaluate the effect of agitation time (to determine the equilibrium time for maximum adsorption), initial concentration (50, 75, 100 and 150 mg/L) and temperature (30°C, 40°C, 50°C and 60°C). The adsorption kinetics using SIAC was determined at predetermined time intervals of 5, 10, 15, 30, 45, 60, 90, 120, 150, 180, 210 and 240 min for different initial Cu(II) concentrations (50, 75, 100 and 150 mg/L) and isotherm profile was modeled using equilibrium data for different initial concentrations (50, 75, 100, 150, 200, 250, 300, 400 and 500 mg/L) over a wide range of temperature (30°C–60°C).

2.5. Composition of simulated and industrial wastewaters

We next planned for evaluating the optimized experimental conditions for Cu(II) removal using SIAC on simulated as well as industrial wastewater. To this end, simulated wastewater containing an initial concentration of 50 mg/L of Cu(II) in presence of co-ions having the following composition (mg/L) was prepared: Cu(II), 50; Na, 40; K, 35; Mg, 15; Ca, 15; NH_4, 15; NO_2, 15; SO_4, 35; NO_3, 25; CH_3–COO, 25; Cl, 55–95. The industrial wastewater was collected from the copper processing industry located at Ernakulum, Kerala, South India (composition [mg/L]: Cu, 3.4; Zn, 0.5; Cr, 0.3; Mg, 35.0; Ca, 68.2; Na, 305.1.2; PO_4, 9.6; NO_3, 17.1; NH_4, 18.3; Cl, 561.4; biochemical oxygen demand, 68.3; chemical oxygen demand, 194.2; suspended solids, 545.7). The physicochemical parameters of the simulated and industrial waters were determined using the standard methods [31]. Batch adsorption experiments using wide range of adsorbent dosage (0.5–12.0 g/L) were performed using the SIAC both in simulated and industrial wastewaters containing 50 mg/L of Cu(II) at pH 6.0. The amount of Cu(II) in industrial water being very low (0.5–5.0 mg/L), it was spiked with known concentration of Cu(II) so as to attain the concentration of 50 mg/L. The amount of Cu(II) was determined using atomic absorption spectrometer (GBC Avanta, model A4001, Australia) after attaining the equilibrium condition for each of the experiments.

3. Results and discussion

3.1. Adsorbent characterization

It is well known that the adsorption process relies heavily on surface functionalities of the adsorbent and $pH_{zpc,}$ density, sulfur content, cation exchange capacity, porosity and total active acidic sites and hence, the adsorbents in this study viz; AC and SIAC were thoroughly characterized by various instrumental techniques. The plot of surface charge density against the solution pH gave the pH_{zpc} (figure not shown) and ash content and loss on combustion were determined using muffle furnace and weighing methods. The density measurements were carried out by the displacement of water (ρ_{water}) and nitrobenzene ($\rho_{nitrobenzene}$) using the pycnometric method. Surface characteristics of AC and SIAC are presented in Table 1.

The fourier transform infrared (FTIR) spectra (Fig. 1) of AC and SIAC were recorded and analyzed. The strong asymmetric absorption band at 3,762 cm^{-1} indicated the presence of OH groups in both the adsorbents. As suggested by Hallum and Drushell [32], the peak at 1,606 cm^{-1} indicated the presence of conjugated hydrogen bonded carboxyl group in both the adsorbents. The incorporation of S in the adsorbent was unambiguously proven by the presence of C=S, S=O and S–S stretching vibrations in SIAC indicated by peaks at 1,167, 1,111 and 460 cm^{-1}, respectively. The stretching vibration of C–S and sulfonate groups, respectively, at 690 and 608 cm^{-1} also clearly indicated the presence of sulfur groups bonded to the surface of SIAC [33].

3.2. Influence of solution pH

The extent of Cu(II) adsorption mainly depends on the Cu(II) speciation which is steered by solution pH and pH_{zpc} also plays an important role in determining the amount of Cu(II) adsorption onto SIAC from water and wastewaters. A series of batch adsorption studies were conducted using different initial Cu(II) concentrations of 25, 50, 75 and 100 mg/L over a wide range of pH (2.0–10.0) to identify the optimum value for the effective removal of Cu(II) from aqueous phase. From Fig. 2(A), it was observed that the pH ranging

Table 1
Surface characteristics of SIAC and AC

Parameters	Value	
	SIAC	AC
Sulfur content (%)	9.1	0.0
pH_{zpc}	4.3	5.8
Surface area (m^2/g)	500.5	536.5
Cation exchange capacity (meq/g)	5.02	3.96
Apparent density (g/mL)	1.02	0.92
ρ_{water} (g/mL)	1.06	0.94
$\rho_{benzene}$ (g/mL)	1.22	0.87
Porosity (mL/g)	0.43	0.52
Total acidic sites (meq/g)	2.9	2.0
Ash content (%)	5.2	9.4
Particle size (mesh size)	−80 + 230	−80 + 230

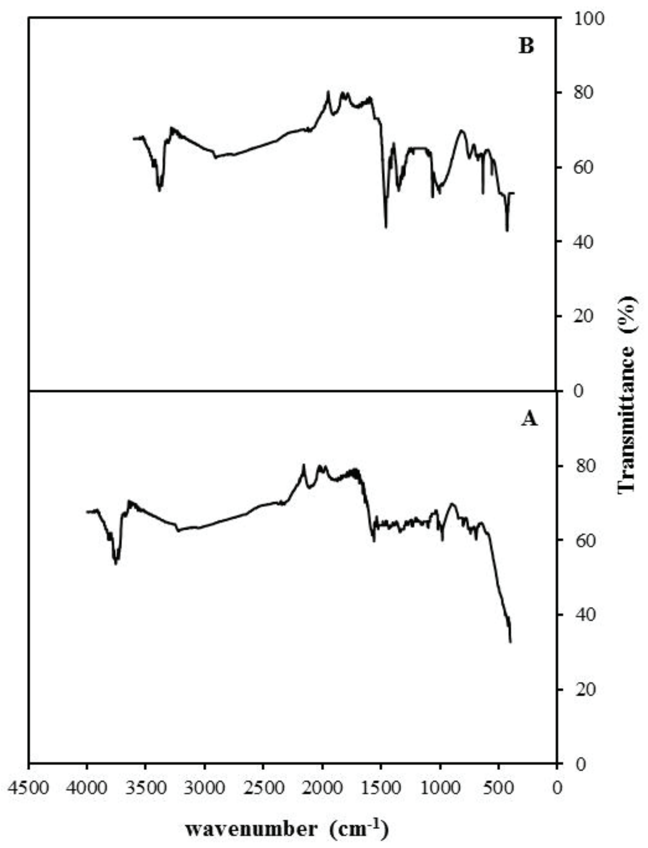

Fig. 1. FTIR spectra of (A) AC and (B) SIAC.

from 5.0 to 8.0 highly favored the adsorption of Cu(II) onto SIAC which peaked at pH 6.0. A maximum amount of 11.84 mg/g (94.7%), 22.83 mg/g (91.3%), 32.81 mg/g (87.5%) and 41.25 mg/g was observed for the adsorption of Cu(II) for initial concentrations of 25, 50, 75 and 100 mg/L, respectively, at 30°C. The pH influence adsorption curve had a steep climb indicating a sharp increase in amount of adsorption up to pH 5.0 and the trend further continued until suspension attained pH 6.0 and then steadily declined till pH 10.0 was reached, thus confirming pH 6.0 as the optimum for the process under study.

The process of Cu(II) adsorption onto SIAC is highly influenced by speciation of Cu(II) as a function of solution pH. The pH_{zpc} of SIAC which also influences the adsorption phenomenon was found to be 4.3, whereas the maximum adsorption was observed at 6.0, which is well above the pH_{zpc}. Thus, surface of SIAC carries negative charge above the pH_{zpc} and therefore at pH 6.0, the positively charged Cu(II) species will have more affinity toward the SIAC surface providing a conducive environment for metal adsorption. However, at the same time, decrease in amount of adsorption was observed below the pH_{zpc}, which may be due to the repulsion between positively charged solid surface and Cu(II) species in aqueous phase. At very high pH, the precipitation tendency of Cu(II) may contribute to a decrease in adsorption process.

It is obvious that the extent of adsorption process is governed by the pH_{zpc} of the adsorbent material and metal speciation in aqueous phase. The pH_{zpc} of SIAC being 4.3 clearly suggested that the surface carries positive charge below pH 4.3 and negative charge above pH 4.3. Batch adsorption experiments clearly indicated low amount of adsorption below pH 4.3 which can be attributed to the repulsion of Cu(II) species by positively charged SIAC surface, whereas the considerable increase in the amount of adsorption above pH 4.3 was suggestive of inter ionic attraction assisted adsorption onto negatively charged SIAC surface. The Cu(II) speciation also favors the adsorption process at pH > 4.3 due to the presence of Cu^{2+} species. However, after the pH 8.0, the amount of Cu(II) adsorption is progressively decreasing due to the formation of $Cu(OH)_2$, which precipitate at higher pH.

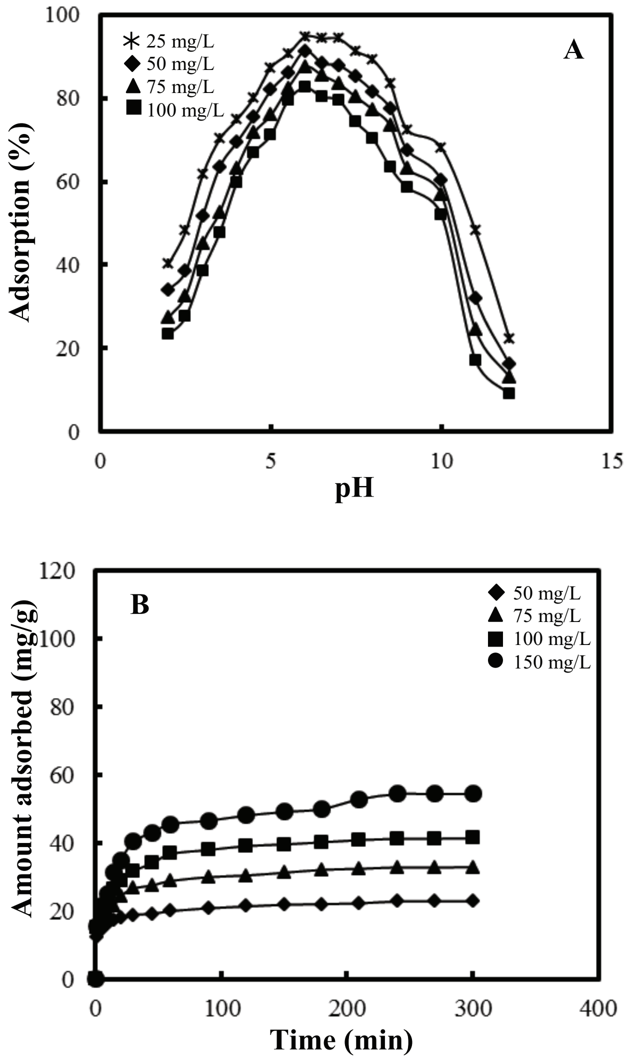

Fig. 2. (A) Effect of pH and (B) effect of agitation speed on the adsorption of Cu(II) onto SIAC.

The SIAC–OH and SIAC–O surface functionalities are common in active carbons [34]. Sulfonic acid (SO_3H) surface entities are present in SIAC due to the sulfurization process. These surface entities are responsible for the higher adsorption of Cu(II) onto the surface of SIAC. Thus, the adsorptive mechanism behind the retention of Cu(II) onto SIAC can be described as below:

$$\begin{aligned} 2(\underline{C}\mathrm{OH}) + \mathrm{Cu}^{2+} &\rightleftharpoons (\underline{C}\mathrm{O}^-)_2\mathrm{Cu}^{2+} + 2\mathrm{H}^+ \\ 2\underline{C}\mathrm{O}^- + \mathrm{Cu}^{2+} &\rightleftharpoons (\underline{C}\mathrm{O}^-)_2\mathrm{Cu}^{2+} \end{aligned}$$

$$\begin{aligned} \underline{C}\mathrm{OH} + \mathrm{Cu(OH)}^+ &\rightleftharpoons (\underline{C}\mathrm{O}^-)\mathrm{Cu(OH)}^+ + \mathrm{H}^+ \\ \underline{C}\mathrm{O}^- + \mathrm{Cu(OH)}^+ &\rightleftharpoons (\underline{C}\mathrm{O}^-)\mathrm{Cu(OH)}^+ \end{aligned}$$

$$\begin{aligned} 2\underline{C} - \mathrm{SO_3H} + \mathrm{Cu}^{2+} &\rightleftharpoons (\underline{C} - \mathrm{SO_3}^-)_2\mathrm{Cu}^{2+} + 2\mathrm{H}^+ \\ 2\underline{C} - \mathrm{SO_3}^- + \mathrm{Cu}^{2+} &\rightleftharpoons (\underline{C} - \mathrm{SO_3}^-)_2\mathrm{Cu}^{2+} \end{aligned}$$

$$\begin{aligned} \underline{C} - \mathrm{SO_3H} + \mathrm{Cu(OH)}^+ &\rightleftharpoons (\underline{C} - \mathrm{SO_3}^-)\mathrm{Cu(OH)}^+ + \mathrm{H}^+ \\ \underline{C} - \mathrm{SO_3}^- + \mathrm{Cu(OH)}^+ &\rightleftharpoons (\underline{C} - \mathrm{SO_3}^-)\mathrm{Cu(OH)}^+ \end{aligned}$$

where $\underline{C}$ is carbon surface.

The speciation of Cu(II) as a function of solution pH clearly indicated the presence of Cu^{2+} species over a wide range of pH from 2.0 to 10.0. The optimum pH for the adsorption of Cu(II) onto SIAC was found to be 6.0 and thereby the adsorption mechanism may be explained as an exchange between H^+ on the surface of SIAC and the Cu^{2+} in the aqueous phase leading to the formation of an ion exchange complex due to which there occurred lowering of pH after the Cu(II) adsorption.

3.3. *Effect of initial concentration and agitation time*

The influence of various initial concentrations of Cu(II) and the equilibrium time for maximum Cu(II) adsorption onto SIAC were determined using series of batch adsorption studies at optimum pH of 6.0. The temperature was retained at room temperature (30°C) throughout the study. A wide range of Cu(II) initial concentrations of 50–150 mg/L were selected for the study by keeping the shaking speed of 200 rpm. The results clearly showed that the amount of adsorption increased along with increase in initial Cu(II) concentration and was found to be 22.83, 32.81, 41.25 and 54.38 mg/g for different initial concentrations of 50, 75, 100 and 150 mg/L, respectively. This increase in amount of Cu(II) adsorption as a function of initial concentration may be due to the ratio of the initial number of moles of Cu(II) to the available adsorption sites being high at higher initial concentrations. However, the time for attaining the equilibrium remained the same for entire range of initial concentrations.

The effect of agitation time on the adsorption of Cu(II) on SIAC (Fig. 2(B)) indicated a sharp increase in the amount of Cu(II) adsorbed onto SIAC up to 1 h, gradually approached a maximum value and finally attained equilibrium at 4 h. The curves in Fig. 2(B) present a double nature, consisting of a linear curve followed by leveling of the curve at 4 h of contact time beyond which there was no further increase in amount of adsorption. The linear portion of the adsorption curve reflects surface layer diffusion and its plateau region represents pore diffusion [35].

3.4. *Adsorption kinetics*

Adsorption kinetic data of Cu(II) onto SIAC for different Cu(II) initial concentrations (50, 75, 100 and 150 mg/L) over a wide range of predetermined time intervals between 1 and 300 min (figure not shown) were determined. The plots represent the amount of Cu(II) adsorption onto SIAC vs. time that increased with agitation time and reached equilibrium at 4 h for all the initial Cu(II) concentrations under study. It is obvious that the kinetic outline in all cases showed a relatively rapid initial rate of adsorption followed by a slow approach to equilibrium. A reaction time of 4 h was employed for all the subsequent equilibrium studies and this time was sufficient to ensure adsorption process to attain equilibrium.

The process of Cu(II) adsorption onto SIAC and its kinetics at the solid–solution interface may be discussed in the light of the interaction of the Cu(II) species with the functional groups on SIAC when an equilibrium is established in the heterogeneous system. We employed two adsorption kinetic models in this study – pseudo-first-order and pseudo-second-order equations developed by Lagergren [36] and Ho and McKay [37], respectively. The Lagergren pseudo-first-order equation is represented in the form:

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

where k_1 is the rate constant of pseudo-first-order adsorption and q_e and q_t denote the amount of adsorption at equilibrium and at time '*t*', respectively. The pseudo-second-order equation is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

where q_e and q_t are the amounts of Cu(II) adsorbed (mg/g) at equilibrium and at time '*t*', respectively. The product $k_2 q_e^2$ is the initial adsorption rate given by $h = k_2 q_e^2$. Kinetic data were evaluated by plotting $\log(q_e - q_t)$ and t/q_t vs. t for pseudo-first-order and pseudo-second-order kinetic expressions, respectively (Fig. 3). The kinetic parameters calculated using Eqs. (3) and (4) are given in Table 2. The k_1 and k_2 values for the adsorption of Cu(II) on SIAC were found to decrease as the initial Cu(II) concentration increased from 50 to 150 mg/L at 30°C.

To compare the validity of each model, a normalized standard deviation $\Delta q(\%)$ is calculated using the following equation:

$$\Delta q(\%) = 100x\sqrt{\frac{\sum\left[\left(q_t^{\mathrm{exp}} - q_t^{\mathrm{cal}}\right)/q_t^{\mathrm{exp}}\right]^2}{N-1}} \tag{5}$$

where q_t^{exp} and q_t^{cal} are experimental and calculated amount, respectively, of Cu(II) adsorbed onto SIAC at time '*t*' and *N* is the number of measurements made during the batch adsorption process. The values of $\Delta q(\%)$ and correlation coefficients (r^2) are presented in Table 2. The value of $\Delta q(\%)$ for pseudo-second-order kinetic model is considerably low compared with that for pseudo-first-order kinetic model. The correlation coefficient values for the adsorption of Cu(II) onto

SIAC were found to be 0.99 for pseudo-second-order kinetic model and 0.91–0.97 for pseudo-first-order kinetic model which suggested that the adsorption of Cu(II) onto SIAC can be best described by the pseudo-second-order kinetic model. Fig. 4 represents the comparison between the calculated and observed values of q_t vs. t for the adsorption of Cu(II) onto SIAC.

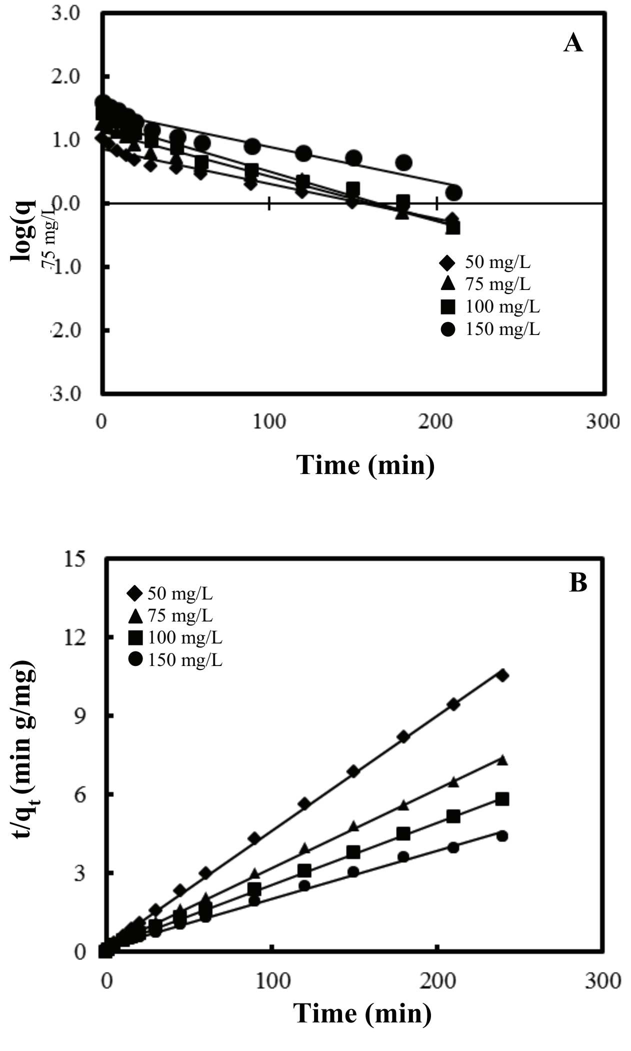

Fig. 3. (A) Pseudo-first-order and (B) pseudo-second-order kinetic plots for adsorption of Cu(II) onto SIAC.

3.5. Equilibrium studies

The isotherm experiments were carried out over a wide range of initial Cu(II) concentration varying from 50 to 500 mg/L at pH 6.0. The amount of Cu(II) adsorbed onto SIAC was determined at equilibrium after 4 h of constant agitation. The exact equilibrium isotherm model to explain the adsorption of Cu(II) onto SIAC from aqueous solutions were confirmed by the values of regression coefficient (r^2) and normalized standard deviation [Δq(%)]. The equilibrium data were analyzed by Langmuir [38] and Freundlich [39] isotherm models and represented as (Eqs. (6) and (7), respectively):

$$\frac{C_e}{q_e} = \frac{1}{Q^o b} + \frac{C_e}{Q^o} \tag{6}$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{7}$$

where q_e is the amount of Cu(II) adsorbed per unit mass of SIAC in mg/g, C_e is the solution concentration at equilibrium in mg/L, Q^o and b are the Langmuir constants related to the capacity (mg/g) and energy (L/mg) of adsorption, respectively. The K_F and $1/n$ are Freundlich constants related to adsorption capacity and intensity of adsorption, respectively. The constants of Langmuir and Freundlich were obtained

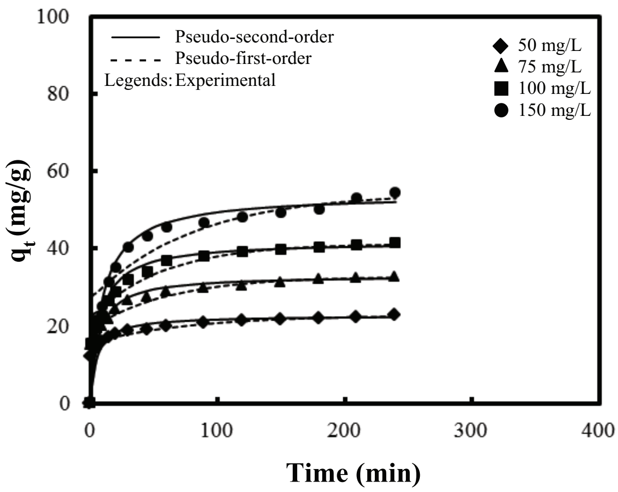

Fig. 4. Plots of q_t vs. t on the adsorption of Cu(II) onto SIAC.

Table 2
Kinetic parameters for the adsorption of Cu(II) onto SIAC

C_o (mg/L)	Pseudo-first-order			Pseudo-second-order			
	k_1 (min^{-1})	r^2	Δq (%)	k_2 (g/mg min)	h (mg/g min)	r^2	Δq (%)
50	1.13×10^{-2}	0.957	8.93	9.07×10^{-3}	4.69	0.998	6.38
75	1.44×10^{-2}	0.965	9.77	4.88×10^{-3}	5.35	0.998	5.71
100	1.83×10^{-2}	0.964	7.18	3.37×10^{-3}	5.91	0.998	5.75
150	2.07×10^{-2}	0.914	24.21	1.96×10^{-3}	5.72	0.995	6.11

Table 3
Langmuir, Freundlich and Dubinin–Radushkevich isotherm constants for the adsorption of Cu(II) on SAC

Isotherm constants	Values	95% Confidence limit
Langmuir isotherm		
Q^o	73.53 ± 3.21	70.73–76.33
b	0.08 ± 0.0012	0.0789–0.0811
r^2	0.999	–
Δq (%)	5.73	–
Freundlich isotherm		
K_F	18.57 ± 1.28	17.47–19.67
$1/n$	3.92 ± 0.26	3.69–4.11
r^2	0.922	–
Δq (%)	11.64	–

from the linear plots of C_e/q_e vs. C_e and logq_e vs. logC_e (data presented in Table 3, figures not shown).

The applicability of the Langmuir isotherm can be articulated by the equilibrium parameter, R_L [40]

$$R_L = \frac{1}{\left(1 + bC_o\right)} \tag{8}$$

where b and C_o are same as in the Langmuir isotherm model and represent the Langmuir constant and initial concentration of Cu(II) solution, respectively. R_L values in the order $0 < R_L < 1$ indicated the feasibility of adsorption process when experiments were conducted for all initial concentrations of Cu(II) varying from 50 to 500 mg/L and thereby obeying the Langmuir isotherm model. The experimental results were compared with theoretically calculated amounts of Cu(II) adsorbed onto SIAC using Langmuir and Freundlich isotherm models and are depicted in Fig. 5. From the figure, Langmuir isotherm was confirmed as the suitable model for explaining the equilibrium data for adsorption process rather than Freundlich isotherm model. Table 4 presents the comparison of adsorption capacity of SIAC with that of other reported materials which attests to our goal of developing sulfurized AC for effective removal of Cu(II) from aqueous phase. The results of the study gains significance in its approach of leveraging Claus process for the conversion of waste biomass into a value-added adsorbent material in the removal of heavy metals from aqueous solutions, and hence contributing to a sustainable remediation.

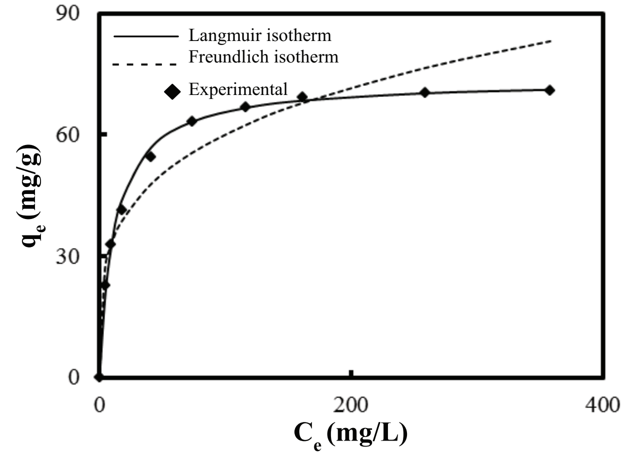

Fig. 5. Plots of q_e vs. C_e on the adsorption of Cu(II) onto SIAC.

Table 4
Comparison of adsorption capacity of various adsorbents for the removal of Cu(II) from aqueous phase

Adsorbent	Solution pH	Range of C_o (mg/L)	Q^o (mg/g)	Reference
Areca waste	5.6	4–12	2.84	[41]
P-mod bentonite	–	0–300	27.62	[42]
Fired coal fly ash	–	20–80	20.92	[43]
Kaolin-modified	5.9	0–80	39.80	[44]
SIAC	6.6	50–500	73.53	Present work

3.6. Desorption and regeneration studies

In order to test the applicability of SIAC in water purification systems, we have studied the reusability of SIAC by means Cu(II) adsorption–desorption–adsorption experiments. This was done by desorbing the adsorbed Cu(II) from the spent SIAC using various extractants among which 0.01 M HCl was found to be more effective. The SIAC preloaded with the maximum amount of Cu(II) at pH 6.0 was placed in the desorption medium containing 0.01 M HCl and the amount of Cu(II) desorbed in 4 h was estimated. Table 5 shows the results of the adsorption and desorption of Cu(II) onto SIAC for an initial concentration of 100 mg/L. It was noted that adhered Cu(II) quantitatively desorbed from SIAC to the suspending medium with a desorbing efficiency of 93.2% in the first cycle with a loss of less than 1% in the adsorbent mass. The successive regeneration cycles also revealed that SIAC can be reused with very small loss in efficiency. Approximately, 77.4% of the initial desorption capacity was retained after the fourth cycle.

3.7. Test with simulated and industrial wastewaters

The simulated and industrial wastewaters containing Cu(II) species (composition provided in section 2.) were used for testing the applicability of SIAC in removing Cu(II) from systems. The effect of adsorbent dosage on Cu(II) removal in the presence of various ions by SIAC from simulated and industrial wastewaters is presented in Fig. 6. The study revealed that the Cu(II) removal percentage increased with increase in adsorbent dosage and complete removal happened at particular dosage, after which the process attains steady state without any decrease in removal percentage. In all cases, the percent removal increased with increasing adsorbent dose which was quite expected due to the greater availability of adsorption sites or surface area at higher concentrations of the adsorbent. The results showed that a minimum adsorbent dosage of 50 mg in 50 mL of wastewater (1.0 g/L) is sufficient for the removal of 56.2% and 48.6% of

Table 5
Desorption and regeneration data for Cu(II) onto SIAC[a]

Cycle	Adsorption for each cycle (mg/g)	Total adsorbed amount (mg/g)	Desorption at 0.01 M HCl (mg/g)	Remaining amount of Cu(II) after desorption (mg/g)
1	41.25 (82.5)	41.25	38.45	2.80
2	38.70 (77.4)	41.50	37.68	3.82
3	35.65 (71.3)	39.47	34.77	4.70
4	32.40 (64.8)	37.10	31.94	5.16

[a] Values shown in the parentheses are in percentage.

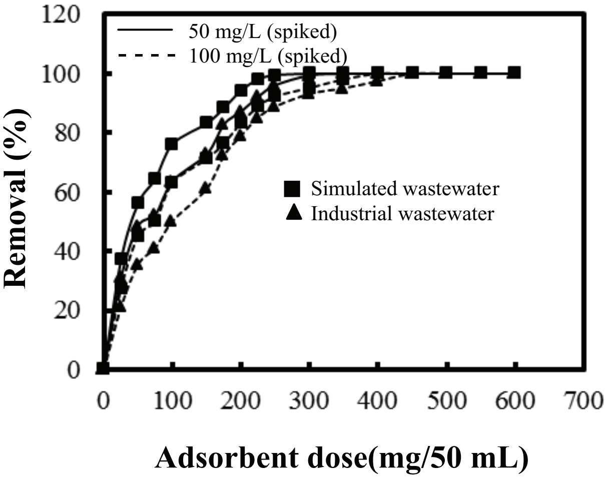

Fig. 6. Effect of SIAC dose on the removal of Cu(II) from simulated and industrial wastewaters.

Cu(II) from simulated and industrial wastewaters, respectively, at pH 6.0 for an initial Cu(II) concentration of 50 mg/L. However, for 100 mg/L of initial Cu(II) concentration, under same conditions, 45.2% and 35.6% of Cu(II) was removed from simulated and industrial wastewaters, respectively. At the same time, the complete removal of Cu(II) of initial concentration 50 mg/L from 50 mL of simulated and industrial wastewater samples was attained using 300 and 350 mg of adsorbent doses, respectively. Whereas for an initial Cu(II) concentration of 100 mg/L from 50 mL of simulated and industrial wastewater required 400 and 450 mg of SIAC for complete removal of Cu(II), respectively.

4. Conclusion

The SIAC prepared from the bagasse pith precursor finds effective application in removing Cu(II) from water and wastewaters. Sulfurization of the biomass was effected using a modified Claus process for the generation of elemental sulfur, whereby the probable use of H_2S and SO_2 generated as wastes from industries as reagents for the process was explored. The SIAC showed enhanced adsorption in removing Cu(II) from aqueous solution compared with the existing surface impregnated adsorbents. The optimum pH for the maximum adsorption of Cu(II) from aqueous phase is 6.0 and a maximum of 11.84 mg/g (94.7%), 22.83 mg/g (91.3%), 32.81 mg/g (87.5%) and 41.25 mg/g (82.5%) of Cu(II) was adsorbed onto SIAC for different initial concentrations of 25, 50, 75 and 100 mg/L. The kinetic data were well in agreement with pseudo-second-order kinetic model for the entire initial concentration range (50–150 mg/L). The isotherm data were in agreement with Langmuir isotherm model. The Cu(II) adsorption capacity of SIAC was high and found to be 73.53 mg/g. The reusability of spent SIAC was confirmed by conducting repeated desorption studies and found to be effective even after four cycles. The optimized experimental conditions for the adsorption of Cu(II) onto SIAC may act as a platform for developing an economically and environmentally friendly system for adsorptive removal of Cu(II) from wastewater in the near future.

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References

[1] S.E. Manahan, M.J. Smith, Copper micronutrient requirement of algae, Environ. Sci. Technol., 7 (1973) 829–833.

[2] L.E. Brand, W.G. Sunda, R.R.L. Guillard, Reduction of marine phytoplankton reproduction rates by copper and cadmium, J. Exp. Mar. Bio. Ecol., 96 (1986) 225–250.

[3] T.A. Davis, B. Volesky, R.H.S.F. Vieira, Sargassum seaweed as biosorbent for heavy metals, Water Res., 34 (2000) 4270–4278.

[4] L.J. Casarett, J. Doull, Toxicology in the Basic Science of Poisons, 5th ed., D.K. Curtis, Ed., McGraw-Hill, New York, 2005, p. 715.

[5] D.W. Cho, B.H. Jeon, C.M. Chon, Y. Kim, Y.W. Schwartz, E.S. Lee, H. Song, A novel chitosan/clay/magnetite composite for adsorption of Cu(II) and As(V), Chem. Eng. J., 200–202 (2012) 654–662.

[6] C.W. Cheung, J.F. Porter, G. McKay, Sorption kinetic analysis for the removal of cadmium ions from effluents using bone char, Water Res., 35 (2001) 605–612.

[7] M.A.P. Cechinel, S.M.A.G.U. Souza, A.A.U. Souza, Study of lead (II) adsorption onto activated carbon originating from cow bone, J. Cleaner Prod., 65 (2014) 342–349.

[8] P. Xu, G.M. Zeng, D.L. Huang, C.L. Feng, S. Hu, M.H. Zhao, C. Lai, Z. Wei, C. Huang, G.X. Xie, Z.F. Liu, Use of iron oxide nanomaterials in wastewater treatment: a review, Sci. Total Environ., 424 (2012) 1–10.

[9] J.L. Gong, B. Wang, G.M. Zeng, C.P. Yang, C.G. Niu, Q.Y. Niu, W.J. Zhou, Y. Liang, Removal of cationic dyes from aqueous solution using magnetic multi-wall carbon nanotube nanocomposite as adsorbent, J. Hazard. Mater., 164 (2009) 1517–1522.

[10] D.A. Clifford, Water Quality and Treatment, A Handbook of Community Water Supplies, American Water Works Association, 4th ed., McGraw Hill, New York, 1990.

[11] E.-S.Z. El-Ashtoukhy, N.K. Amin, O. Abdelwahab, Removal of lead (II) and copper (II) from aqueous solution using pomegranate peel as a new adsorbent, Desalination, 223 (2008) 162–173.

[12] D. Bozic, V. Stankovic, M. Gorgievski, G. Bogdanovic, R. Kovacevic, Adsorption of heavy metal ions by sawdust of deciduous trees, J. Hazard. Mater., 171 (2009) 684–692.

[13] R. Salim, R.A. El-Halawa, Efficiency of dry plant leaves (mulch) for removal of lead, cadmium and copper from aqueous solutions, Process Saf. Environ. Prot., 80 (2002) 270–276.

[14] H. Aydin, Y. Bulut, C. Yerlikaya, Removal of copper (II) from aqueous solution by adsorption onto low-cost adsorbents, J. Environ. Manage., 87 (2008) 37–45.

[15] P. SenthilKumar, S. Ramalingam, V. Sathyaselvabala, S.D. Kirupha, S. Sivanesan, Removal of copper(II) ions from aqueous solution by adsorption using cashew nut shell, Desalination, 266 (2011) 63–71.

[16] S. Cay, A. Uyanık, A. Ozasık, Single and binary component adsorption of copper(II) and cadmium(II) from aqueous solutions using tea-industry waste, Sep. Purif. Technol., 38 (2004) 273–280.

[17] R. Razmovski, M. Sciban, Biosorption of Cr(VI) and Cu(II) by waste tea fungal biomass, Ecol. Eng., 34 (2008) 179–186.

[18] H. Demiral, C. Gungor, Adsorption of copper(II) from aqueous solutions on activated carbon prepared from grape bagasse, J. Cleaner Prod., 124 (2016) 103–113.

[19] T.Y. Kim, H.J. Jin, S.S. Park, S.J. Kim, S.Y. Cho, Adsorption equilibrium of copper ion and phenol by powdered activated carbon, alginate bead and alginate-activated carbon bead, J. Ind. Eng. Chem., 14 (2008) 714–719.

[20] M. Imamoglu, O. Tekir, Removal of copper (II) and lead (II) ions from aqueous solutions by adsorption on activated carbon from a new precursor hazelnut husks, Desalination, 228 (2008) 108–113.

[21] J.H. Doh, J.H. Kim, H.J. Kim, R.F. Ali, K. Shin, Y.J. Hong, Enhanced adsorption of aqueous copper(II) ions using dedoped poly-N-phenylglycine nanofibers, Chem. Eng. J., 277 (2015) 352–359.

[22] E. Zheng, Q. Dang, C. Liu, B. Fan, J. Yan, Z. Yu, H. Zhang, Preparation and evaluation of adipic acid dihydrazide cross-linked carboxymethyl chitosan microspheres for copper ion adsorption, Colloids Surf., A, 502 (2016) 34–43.

[23] E.A. Ali, S.S. Elkholy, R.E. Morsi, M.Z. Elsabee, Studies on adsorption behavior of Cu(II) and Cd(II) onto aminothiophene derivatives of Styrene Maleic anhydride copolymer, J. Taiwan Inst. Chem. Eng., 64 (2016) 325–335.

[24] J.P. Chen, S. Wu, K.-H. Chong, Surface modification of a granular activated carbon by citric acid for enhancement of copper adsorption, Carbon, 41 (2003) 1979–1986.

[25] H. Hamad, Z. Ezzeddine, F. Lakis, H. Rammal, M. Srour, A. Hijazi, An insight into the removal of Cu (II) and Pb (II) by aminopropyl-modified mesoporous carbon CMK-3: adsorption capacity and mechanism, Mater. Chem. Phys., 178 (2016) 57–64.

[26] K.A. Krishnan, K.G. Sreejalekshmi, V. Vimexen, V.V. Dev, Evaluation of adsorption properties of sulphurised activated carbon for the effective and economically viable removal of Zn(II) from aqueous solutions, Ecotoxicol. Environ. Saf., 124 (2016) 418–425.

[27] K.A. Krishnan, A. Sheela, T.S. Anirudhan, Kinetic and equilibrium modeling of liquid-phase adsorption of lead and lead chelates on activated carbons, J. Chem. Technol. Biotechnol., 78 (2003) 642–653.

[28] S. Viladkar, R. Agarwal, B. Kamaludhin, Adsorption of adenine, adenosine, and adenosine nucleotides on nickel(II) hexacyanoferrate(II), Bull. Chem. Soc. Jpn., 69 (1996) 95–100.

[29] K.A. Krishnan, T.S. Anirudhan, Removal of mercury(II) from aqueous solutions and chlor-alkali industry effluent by steam activated and sulphurised activated carbons prepared from bagasse pith: kinetics and equilibrium studies, J. Hazard. Mater., B92 (2002) 161–183.

[30] J.A. Schwarz, C.T. Driscoll, A.K. Bhanot, The zero point of charge of silica-alumina oxide suspensions, J. Colloid Interface Sci., 97 (1984) 55–61.

[31] APHA, Standard Methods for the Examination of Water and Wastewater, 20th ed., APHA, AWWA, WEF, Washington, D.C., USA, 1998.

[32] J.V. Hallum, H.V. Drushell, The organic nature of carbon surfaces, J. Phys. Chem., 62 (1958) 110–117.

[33] K. Nakanishi, P.H. Solamon, Infrared Absorption Spectroscopy, Holden Day, Inc., USA, 1977.

[34] M.O. Corapcioglu, C.P. Huang, The adsorption of heavy metals onto hydrous activated carbon, Water Res., 21 (1987) 1031–1044.

[35] H.M. Asfour, M.M. Nazar, O.A. Fadoli, M.S.E. Geundi, Color removal from textile effluents using hard wood saw dust as an adsorbent, J. Chem. Technol. Biotechnol., 35 (1985) 28–35.

[36] S.K. Lagergren, About the theory of so-called adsorption of soluble substances, Kungl. Vet. akad. Handl., 24 (1898) 1–39.

[37] Y.S. Ho, G. McKay, The kinetics of sorption of divalent metal ions onto sphagnum moss peat, Water Res., 34 (2000) 735–742.

[38] I. Langmuir, The adsorption of gases on plane surface of glass, mica and platinum, J. Am. Chem. Soc., 40 (1918) 1361–1403.

[39] H.M.F. Freundlich, Over the adsorption in solution, J. Phys. Chem., 57 (1906) 385–470.

[40] G. McKay, H.S. Blair, J.R. Gardner, Two resistance mass transport model for the adsorption of acid dye onto chitin in fixed beds, J. Appl. Polym. Sci., 33 (1987) 1249–1257.

[41] W. Zheng, X. Li, F. Wang, Q. Yang, P. Deng, G. Zeng, Adsorption removal of cadmium and copper from aqueous solution by areca – a food waste, J. Hazard. Mater., 157 (2008) 490–495.

[42] B.I. Olu-Owolabi, E.I. Unuabonah, Kinetic and thermodynamics of the removal of Zn2+ and Cu2+ from aqueous solution by sulphate and phosphate-modified Bentonite clay, J. Hazard. Mater., 184 (2010) 731–738.

[43] A. Papandreou, C.J. Stournaras, D. Panias, Copper and cadmium adsorption on pellets made from fired coal fly ash, J. Hazard. Mater., 148 (2007) 538–547.

[44] Z. Dankova, A. Bekenyiova, I. Styriakova, E. Fedorova, Study of Cu(II) adsorption by siderite and kaolin, Procedia Earth Planet. Sci., 15 (2015) 821–826.