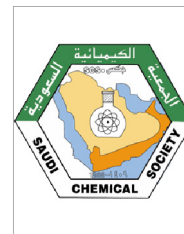




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## ORIGINAL ARTICLE

# Removal of copper (II) from wastewater using green vegetable waste derived activated carbon: An approach to equilibrium and kinetic study



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## KEYWORDS

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Flame Atomic Absorption  
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Wastewater

**Abstract** The present paper reports on the use of modified activated carbon as an environmental friendly adsorbent, obtained from a green vegetable waste, for the removal of copper (II) from wastewaters. The activated carbon was prepared from green vegetable waste by KOH treatment for 24 h at 60 °C and thereafter evaluated by studying the effects of pH, contact time, dosage and initial concentration and optimized in the batch processing mode. The morphological and chemical changes in activated carbon were fully characterized by SEM, TGA, DSC, FTIR techniques. The Langmuir isotherm, yielded adsorption capacity of 75.0 mg g<sup>-1</sup> for a pseudo-second-order model. Overall, these results suggest that green vegetable waste derived activated carbon as a low-cost adsorbent for the removal of copper (II) will be useful for future scale-up for the tertiary treatment of wastewater.

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*Abbreviations:* GVW-AC, green vegetable waste activated carbon; TGA, thermogravimetric analysis; TBA, Thermogravimetry Before Adsorption; TAA, Thermogravimetry After Adsorption; DSC, differential scanning calorimetry; DBA, DSC-before adsorption; DAA, DSC-After Adsorption; FAAS, Flame Atomic Absorption Spectrometer

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## 1. Introduction

In recent years, there has been a tremendous interest in the bio-sorption approaches which are efficient in removing heavy metals from aqueous solutions. The level of water contamination is one of the key topics that have attracted much attention globally. The focus of environmental research has been centered on municipal or industrial wastewater because of their potential impact on human. The challenge of trace metals is escalated by the fact that they are non-biodegradable, hence very resolute in both the environment and biological systems. They can slowly accumulate in the body of human being thereby exceeding the expectable levels, and causing various diseases such as nervous system damage and cancer (Leone et al., 2006). For this

reason, several materials are being evaluated either as living or non-living adsorbents for removal of heavy metals by adsorption. The mechanisms of surface sorption are based upon physico-chemical interactions between metal and activated carbon surface and they are much more dynamic than assumed in the equilibrium models (Flouty and Estephane, 2012). Indeed, there are several reports on the removal of metals at lower levels by bio-sorption processes and are best described by the Langmuir, Freundlich, first and second order kinetics which shows dependence of the rate of adsorption on the coverage fraction of the surface (Runtti et al., 2014; Shen et al., 2009). Ultimately bio-sorption approaches which are efficient in removing heavy metals from aqueous solutions have been on the focus for preparation of cheap and effective novel sorbents. Some of the adsorbents reported include peanut husks carbon (Ricordel et al., 2001), *Sargassum* sp. (Kalyani et al., 2004), modified orange peel (Feng et al., 2009; Sha et al., 2009), and *Padina* sp., *Ulva* sp. and *Gracilaria* sp. (Sheng et al., 2004), *Pleurotus pulmonarius* and *Schizophyllum commune* (Veit et al., 2005), sawdust (Larous and Meniai, 2012), green energy waste (Kanchi et al., 2014), and bio-hydrogen fermented waste (Kanchi et al., 2017).

The activated carbon adsorption is also vastly used sequentially with ultrafiltration, in the purification of leachate with mostly organic load. Activated carbons have been identified as potential adsorbents for the removal of different heavy metals from industrial wastewaters because of their high surface area, microporous structure and chemical nature of their surface which longs for modification (Wang et al., 2011). However, the studies on the derived activated carbon from green vegetable waste are very much limited in the literature. Therefore, in this paper, we discussed the development and evaluation of green vegetable waste activated carbon (GVW-AC) for the removal of copper (II) ions from wastewaters. The experimental parameters affecting adsorption included pH, contact time, adsorbent dose, and the initial concentration of metal ions were investigated in this work. The kinetic studies were also performed, based on their isothermal data. The results clearly demonstrate that the GVW-AC is an economical adsorbent for the removal of copper (II) ions from wastewaters.

## 2. Experimental

### 2.1. Chemicals and reagents

Hydrochloric acid and sodium hydroxide were used to adjust the pH and KOH was used as a chemical activation agent (Merck Laboratory Suppliers Pty Ltd, SA). Deionized water used throughout the experiment was generated from an aqua MAX™ – Basic 360 series water purification system from the TRILAB SUPPORT (Durban, SA). Stock solutions of copper (II) were prepared by dissolving appropriate amounts of 3.929 g of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (Capital Lab suppliers, Durban, South Africa) in deionized water. All the experiments were performed at room temperature of  $\pm 25^\circ\text{C}$  using freshly prepared solutions. The chemicals used were of analytical reagent grade. Wastewater samples were collected from Umlazi River and Rossburg drain, Durban, South Africa, and stored in polypropylene bottles previously washed with 1.0 M nitric acid and deionized water and kept in the refrigerator at  $6 \pm 2^\circ\text{C}$ .

### 2.2. Instrumentation

An oven muffle furnace (NOVEL, CNW, model SXL) that can go up to  $1200^\circ\text{C}$  for drying and calcination purposes to produce activated carbon from green vegetable waste was employed in this study. All the pH optimization measurements were carried out with Crison micro pH model 2000 pH meter.

A shaker platform (FSIM-SPO16, Labcon) was used to agitate the adsorbate-adsorbent mixtures during batch adsorption experiments. The copper (II) ion concentration was measured using the Flame Atomic Absorption Spectrometer (SpectrAA 55 B, Varian) equipped with a 4 mA hollow cathode lamp and 0.5 nm slit width monochromator positioned at 324.8 nm. The surface morphology of the adsorbents was visualized via Scanning Electron Microscope (SEM) model EVO HD15, equipped with a LaB6 emitter and coupled with energy dispersive X-ray (EDX, OXFORD instruments). The thermal profile in the temperature range 10 to  $1000^\circ\text{C}$  was recorded with the STARE system of TGA/DSC 1 SF/1346 model supplied with a STARE software version 9.20 by METTLER TOLEDO (Johannesburg, South Africa). In addition, the Fourier Transform Infrared (FTIR) spectrum of % transmittance was recorded in the range  $500\text{--}4000\text{ cm}^{-1}$  on a Varian 800 FT-IR Scimitar Series (SMM Instruments, Durban, South Africa (SA)) system to explore the functional groups available on the surface of the GVW-AC for the binding of copper (II). Infrared (IR) spectroscopy is known to require well prepared samples to obtain optimum absorption spectra; however, it is very challenging for highly opaque samples such as activated carbon. The sintered and dried activated carbon was physically pulverized to very fine powder in a mortar before homogenization to 0.05% (w/w) with spectroscopic grade KBr. The process yielded after vacuum pressure approximately 25 mm diameter and 1 mm thickness. The transmission FTIR spectra were recorded within  $4000\text{--}500\text{ cm}^{-1}$  for four scans at a fixed resolution to 4 units.

### 2.3. Collection of green vegetable waste

Food waste is a global and a local challenge, which costs South Africa about R61.5 billion a year (Oliveira, 2013). Subsequently, South Africa based scientific and technology research, development and implementation organization, the Council for Scientific and Industrial Research (CSIR) is undertaking research on food waste, its causes and impact on the South African economy. As the researchers acknowledge that there will be a dramatic increase in the quantity of green vegetable residues produced, recycling green vegetable wastes for various aspects could lead to the development of cost effective technologies. The green vegetable wastes were collected from various food stores situated within Durban University of Technology, Durban, South Africa.

### 2.4. Adsorbent: Preparation and treatment

GVW-AC was prepared by thermal and chemical process of green vegetable waste from solid waste material. The collected GVW material was treated following a literature reported protocol with slight modification (Wafwoyo et al., 1999). The GVW material was first washed with deionized water to remove impurities adsorbed on the surface of the waste material. Thereafter, the material was dried at  $60^\circ\text{C}$  for 24 h before crushing with a mill to obtain average particle size of  $\sim 1\text{ mm}$ . The dry material was soaked with 10% KOH solution for 24 h after which, the excess KOH solution was decanted off and the solid material was air-dried before calcination for 30 min at  $400^\circ\text{C}$  in a muffle furnace. The resultant carbon powder was activated in the same muffle furnace at  $800^\circ\text{C}$  for a period

of 10 min followed by sufficient sequential washing with 1.0 M HCl and deionized water to remove the residual KOH. Finally, the obtained GVW-AC was dried at 110 °C for 2 h and then stored in the desiccator for subsequent uses.

### 2.5. Batch experiments

The copper (II) stock solution of 1.0, 1.5, 2.5, 3.0, and 5.0 mg L<sup>-1</sup> was prepared by serial dilution and then used for linear calibration. Adequate mass equivalent to 0.6 g L<sup>-1</sup> of dried powder GVW-AC fractions was added into 30 mL of 1.5 ppm copper (II) solution and the resultant mixtures were subjected to a shaker at 150 rpm for 90 min at controlled 25 °C. Subsequently, the adsorbents were collected at different time intervals by filtering the solution through a 0.5 mm Whatman filter paper prior to FAAS analyses. By using a six data point standard calibration curve which excludes deionized water at zero absorbance, the concentration of copper (II) is based on proportionality as per Beer Lambert's Law. Henceforth, to maximize copper (II) removal by the adsorbent, batch experiments were conducted at constant temperature of 25 °C using the best conditions of all variable parameters such as pH, dose, initial concentration and contact time. The overall sorption of the metal ion ( $q_e$ ) in the GVW-AC system was calculated using the mass balance:

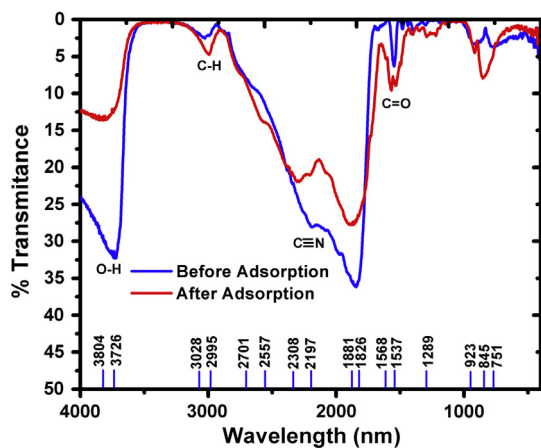
$$q_e = (C_i - C_0) \frac{V}{W} \quad (1)$$

where  $V$  is the volume of the solution (mL),  $C_i$  and  $C_0$  are the initial (before) and final (after) metal ion concentrations (mg L<sup>-1</sup>), and  $W$  is the weight of activated carbon (g).

## 3. Results and discussion

### 3.1. Characterization of GVW-AC

The adsorption of copper (II) on the GVW-AC was depicted by changes in vibration peaks in the FTIR spectra due to chemical changes as shown in Fig. 1. The broad band at about 3400 cm<sup>-1</sup> was observed for both samples (before and after adsorption), and it was assigned to the O—H stretching vibra-



**Figure 1** FTIR spectrum of GVW-AC recorded before and after adsorption of copper (II).

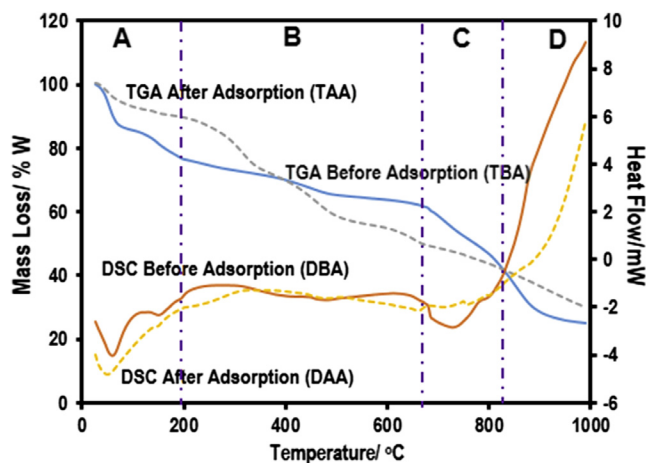
tion of the hydroxyl functional group; this peak shows the presence of alcohols, phenol or carboxylic acids. The O—H band demonstrated that the sintered adsorbent was hygroscopic which was further confirmed by the presence of the TGA mass loss at ~100 °C on both the thermograms recorded before and after adsorption studies. These major shifts in bands suggest the involvement of alcohols/phenols and carboxylic acid groups in metal binding during the adsorption process.

The peak at 2995 cm<sup>-1</sup> is attributed to asymmetric and symmetric aliphatic methyl group in GVW-AC. The absorption peaks at 2205 cm<sup>-1</sup> appeared for the GVW-AC are possibly attributed to C≡N stretching. The FTIR spectrum of the GVW-AC contains absorbance peak at 1550 cm<sup>-1</sup> which is the characteristics of C=O in quinone (Tsai et al., 2001) structure. Absorption peak at 855 cm<sup>-1</sup> is ascribed to out-of-plane deformation mode of C—H in variously substituted. This is also a clear indication that the sintered GVW-AC has a potential to participate in chemisorption process if the energetics of the process is more favorable than that of physisorption.

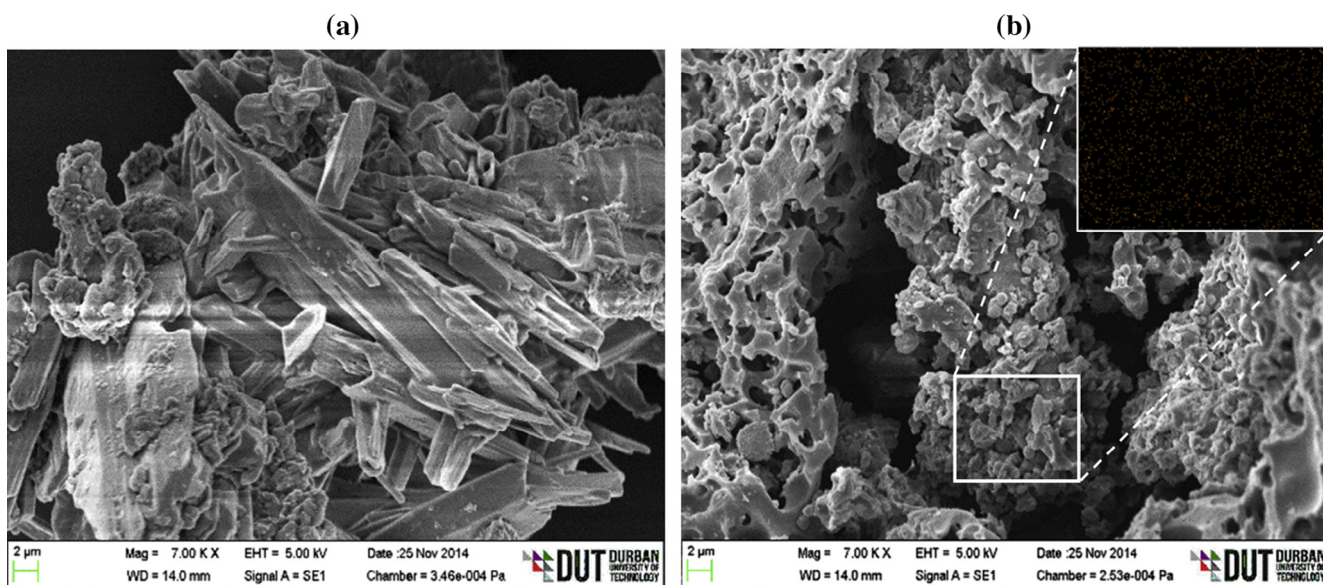
Thermogravimetric and heat flow profiles shown in Fig. 2 were recorded at the heating rate of 10 °C min<sup>-1</sup> from 10 to 1000 °C. Interesting observations were made between 200 and 680 °C (part B), where both DSC scan almost levels off and TGA scan continue to descend. In this range, there are three significant steps observed for Thermogravimetry Before Adsorption (TBA) with a total mass loss of 16.08%, while Thermogravimetry After Adsorption (TAA) shows only steps with a marginable mass loss of 40.38%.

At lower temperature range, 10–325 °C (part A), there is an exothermic heat flow which favors DSC After Adsorption (DAA) probably due to the presence of water as an adsorption medium. In contrary to highest temperature range of 840–1000 °C (part D), DSC Before Adsorption (DBA) is the favored exothermic system, probably due to the formation of CuO on the surface of GVW-AC.

The morphology of GVW-AC before and after adsorption was taken at 7.00 KX magnification operating at an accelerating voltage of 15 kV. It can be observed in Fig. 3a that the sintered pure AC has a porous surface and well-arranged structure, that were responsible for maximum adsorption of copper (II) ions.



**Figure 2** Simultaneous DSC/TGA thermogram recorded at 10 °C min<sup>-1</sup> from 10 to 1000 °C.



**Figure 3** SEM morphology of GVW-AC taken at 5.0 kV with a 7.00 KX magnification: (a) before and (b) after adsorption of copper (II).

The definite shape of the GVW-AC could not be established; however, SEM enables us to see that the surface of AC was wood-like shape, while the maximum size possible was  $\sim 1$  mm based on the efficiency of the miller. After adsorption, a carpet like surface suggesting agglomeration or clustering is observed. Therefore, further confirmation of copper (II) ions adsorption was done by EDS mapping as shown in Fig. 3b (inset).

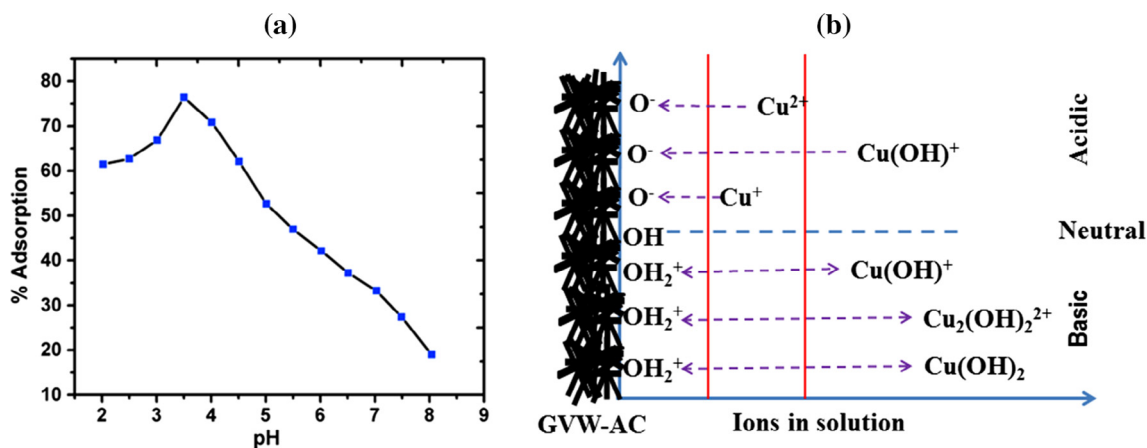
### 3.2. Method optimization

#### 3.2.1. Effect of pH

The effect of pH on adsorption of copper (II) ions as shown in Fig. 4 was studied at ambient temperature with the World Health Organization (WHO) maximum acceptable concentration in drinking water of  $1.5 \text{ mg L}^{-1}$  for a  $0.6 \text{ g L}^{-1}$  of adsorbent dose and metal solution of pH ranging from 2.0 to 8.0

(Madhava Rao et al., 2006). It was observed that the percentage adsorption increases with the pH at lower range as depicted in Fig. 4a.

The minimum adsorption observed at low pH is probably due to the presence of higher concentration and higher mobility of  $\text{H}^+$  ions favored adsorption as compared to copper (II) ions. In the acidic medium, there is high solubility and ionization of metal ions; however, there is a build-up of negatively charged surface area with increase in pH, thus facilitating greater copper (II) ions removal. The maximum adsorption was observed within the pH ranging from 2.0 to 4.5 which might be due to partial hydrolysis of copper (II) ions. In contrary to lower pH, the surface of the adsorbent becomes more positively charged at high  $\text{H}^+$  concentration such that the attraction between adsorbents and metal cations is reduced. In this system, the hydronium ions from the R-OH and R-COOH groups on GVW-AC can be exchanged for cations in solution, improving the adsorption for a narrow lower pH



**Figure 4** (a) Effect of pH on the removal of copper (II), (b) Schematic representation of the layer-by-layer model for the adsorption of copper (II) onto the GVW-AC with pH.

range as illustrated in Fig. 4b. Further increase in pH beyond 4.0 gradually caused precipitation or rather sedimentation of copper (II) ions on the surface of the adsorbent by nucleation. The trend observed in this study was in agreement with that of the reported studies (Runtti et al., 2014; Schiewer and Wong, 2000; Sheng et al., 2004) and, ultimately the optimum pH was noted to be 3.5 with the highest adsorption of 76.36% as shown in Fig. 4a.

### 3.2.2. Effect of adsorbent dosage

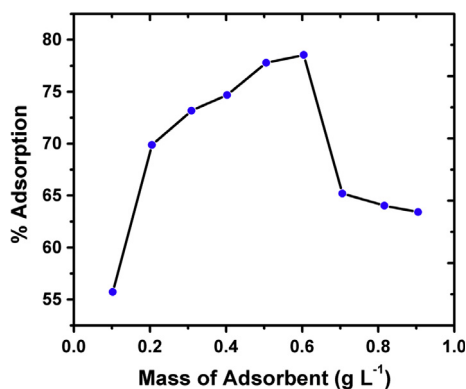
The effect of GVW-AC dose on copper (II) adsorption was studied at 298 K, with a  $1.5 \text{ mg L}^{-1}$  copper (II) solution and continuous addition of either KOH or HCl to avoid any change of the optimum pH of 3.5. The results of adsorbent dose on the percentage removal of copper (II) ions on GVW-AC reflected in Fig. 5 show a steady increase within  $0.1\text{--}0.6 \text{ g L}^{-1}$  before descending continuously.

It is due to increased adsorbent surface area and availability of more adsorption sites that gradual improvement of adsorption was observed. But after  $0.6 \text{ g L}^{-1}$  adsorbent dose, the copper (II) ions adsorbed per unit weight of adsorbent decreased which is due to the fact that at higher adsorbent dose the solution ion concentration drops to a lower value of  $q_e$  (amount adsorbed) indicating that adsorption sites become unsaturated. Based on these results,  $0.6 \text{ g L}^{-1}$  was noted as optimum adsorbent dose for the further studies.

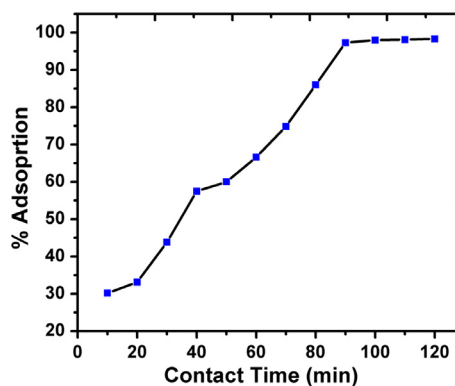
### 3.2.3. Effect of contact time

The removal of copper (II) from aqueous solution is a dynamic process and therefore the adsorption is studied as a function of contact time in the range of 0–120 min using copper (II) ion concentration of  $1.5 \text{ mg L}^{-1}$  and pH 3.5 for a  $0.60 \text{ g L}^{-1}$  GVW-AC. The effect of contact time on the removal of copper (II) is shown in Fig. 6.

From Fig. 6, it was observed that the rate of copper (II) removal was higher until reaching equilibrium in 90 min. The difference in the degree of adsorption is probably due to the fact that in the beginning, all the adsorption sites on the surface of the GVW-AC were vacant; hence, solute concentration gradient was relatively high. Subsequently, the extent of copper (II) ions removal decreased with increase in contact time, which is dependent on the number of vacant sites on the sur-



**Figure 5** Effect of adsorbent dose on  $1.5 \text{ mg L}^{-1}$  copper (II) removal at pH 3.5. Dose usage with increment from  $0.1$  to  $0.9 \text{ g L}^{-1}$  (each data point with a 5% standard error).



**Figure 6** Effect of contact time in the range of 0–120 min on  $1.5 \text{ mg L}^{-1}$  copper (II) removal at pH 3.5 by a  $0.60 \text{ g L}^{-1}$  GVW-AC (each data point with a 5% standard error).

face of GVW-AC. Based on these results 90 min was considered as the optimum time for the further experiments.

### 3.3. Adsorption isotherm

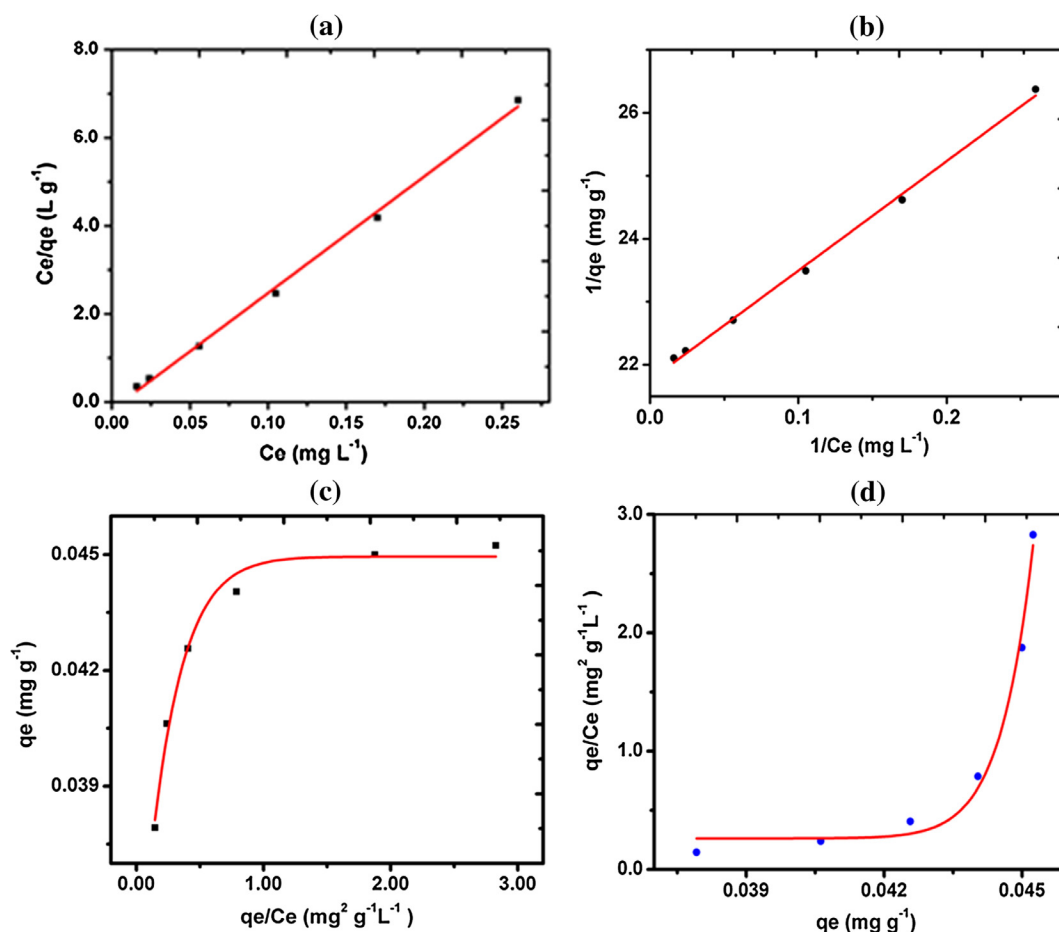
The equilibrium data are important for the evaluation of adsorption mechanism where understanding and improving the efficiency is the priori. Therefore, the evaluation of adsorption capacity of GVW-AC with different models enables us to design a process and optimize operating protocol adequately. For this reason, both the Langmuir and Freundlich isotherms were adopted to best describe the adsorption data for copper (II) adsorption on the GVW-AC. The study of the adsorption equilibrium was carried out varying copper (II) concentration from  $1.5$  to  $5.0 \text{ mg L}^{-1}$  and fitted well with the linearized form of Langmuir as shown in Fig. 7. Clearly, in adsorption, amount of activated carbon versus the equilibrium concentration of copper (II) ions in solution, the adsorption is highly dependent on particle size distribution and on adsorbent/adsorbate ratio (Ricordel et al., 2001).

The Langmuir isotherm describing adsorption in linear form is represented by

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L C_e} \quad (2)$$

where  $q_e$  is the amount of copper (II) adsorbed per unit weight of the GVW-AC ( $\text{mg g}^{-1}$ ),  $q_m$  ( $\text{mg g}^{-1}$ ) is the maximum amount of metal ion per unit weight of adsorbent to form a complete monolayer on the surface,  $C_e$  is the equilibrium concentration of copper (II) in solution ( $\text{mg L}^{-1}$ ), and  $K_L$  is the Langmuir isotherm constant that relates to the energy of adsorption ( $\text{L mg}^{-1}$ ) (Kargi and Cikla, 2006). Therefore, the Langmuir theory is based on the assumptions that adsorption takes place at specific homogenous sites of the GVW-AC and no further adsorption occurs once the copper (II) molecule occupies a site. Ultimately, the  $K_L$  ( $\text{L mg}^{-1}$ ), and  $q_m$  ( $\text{mg g}^{-1}$ ) were determined from the intercept and slope of the linear plots of the experimental data as per the plot of  $C_e/q_e$  versus  $C_e$ , respectively.

The Freundlich isotherm was also applied for the adsorption studies, specifically to model the multilayer adsorption and for the adsorption on heterogeneous surfaces, which was very much likely to be favored considering the source of adsor-



**Figure 7** Different plots of Langmuir isotherm for adsorption of copper (II) on to the GVW-AC: (a)  $C_e$  vs  $C_e/q_e$ , (b)  $1/C_e$  vs  $1/q_e$ , (c)  $q_e/C_e$  vs  $q_e$  and (d)  $q_e$  vs  $q_e/C_e$ .

bent (GVW-AC). The Freundlich equation in linear form is given by

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (3)$$

where  $K_f$  ( $\text{mg g}^{-1}$ ) is the Freundlich equilibrium constant and  $n$  ( $\text{g L}^{-1}$ ) is the adsorption intensity determined from the intercept and slope respectively (Bouhamed et al., 2012; Dinçer et al., 2007; Flouty and Estephane, 2012; Sha et al., 2009). When comparing Langmuir with the Freundlich isotherm, it can be seen from the Langmuir Eq. (2) ( $R^2 = 0.9975$ ,  $q_m = 75.0 \text{ mg g}^{-1}$  and  $K_L = 152 \text{ L mg}^{-1}$ ) model yielded a slightly better fit than Freundlich Eq. (3) ( $R^2 = 0.8655$ ,  $n = 17.24$  and  $K_F = 1.226$ ). The Langmuir sorption isotherms in Fig. 7a and b present the linear plot with increasing concentration of copper (II) ion in the solution phase with maximum adsorption capacities ( $q_m$ ) of  $75.0 \text{ mg g}^{-1}$ .

### 3.4. Kinetic studies

Adsorption is mainly dependent on the ability of the synthesized materials to accumulate heavy metals from aqueous solutions by physico-chemical pathways; therefore, explicit evaluation of the entailed mechanism such as mass transfer, physical and chemical reactions is necessary for kinetic studies (Milenković et al., 2009; Ricordel et al., 2001). Ultimately, the

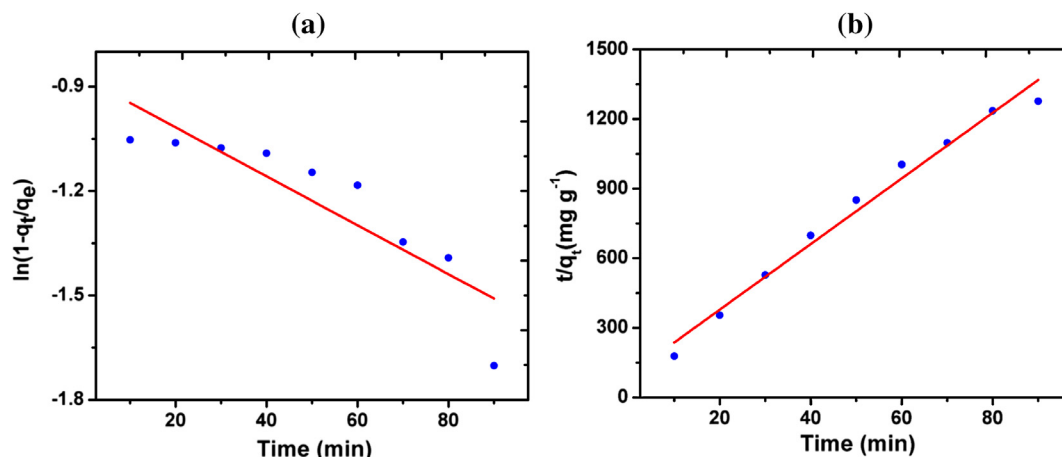
mechanism has to be validated by comparing the likely kinetic models. Herein, both pseudo first-order and second-order kinetic models were optimized further to understand experimental data for adsorption mechanism. The model of the first order kinetics based on the following linear classic equation is as follows:

$$\ln \left( 1 - \frac{q_t}{q_e} \right) = -k_1 t \quad (4)$$

where  $k_1$  ( $\text{min}^{-1}$ ) is the rate constant of the first-order adsorption,  $q_t$  ( $\text{mg g}^{-1}$ ) denotes the amount of adsorption at  $t$  (min) and  $q_e$  ( $\text{mg g}^{-1}$ ) is the amount of adsorption at equilibrium. The adsorption rate constant,  $k_1$ , can be calculated by plotting  $\ln(1 - (q_t/q_e))$  versus  $t$  (Dinçer et al., 2007). The second order model which is based on the assumption that the rate-limiting step involves chemi-sorption can be written in linear form as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

where  $k_2$  ( $\text{g (mg min)}^{-1}$ ) is the rate constant second-order adsorption, and  $k_2$  and  $q_e$  can be obtained from the intercept and slope by plotting  $t/q_t$  versus  $t$ . Fig. 8a and b shows the plots of the first-order and second-order models for adsorption of copper (II) ions, respectively (Kargi and Cikla, 2006).

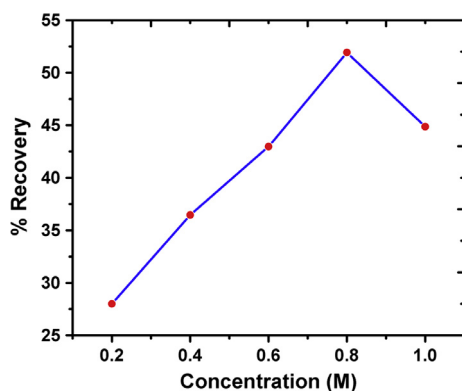


**Figure 8** (a) Pseudo first-order and (b) Pseudo second-order kinetics for adsorption of  $1.5 \text{ mg L}^{-1}$  copper (II) on  $0.6 \text{ g L}^{-1}$  of GVW-AC.

The correlation coefficient ( $R^2$ ) and  $k_1$  ( $\text{min}^{-1}$ ) values for pseudo first-order were found to be 0.7931 and 0.07 respectively. On the one hand, the pseudo first-order model was not in agreement with the corresponding experimental values as demonstrated in Fig. 8a suggesting that copper (II) adsorption did not fit the pseudo-first-order model. The second order model shown in Fig. 8b demonstrated much linearity agreement recording  $R^2$  and  $k_2$  values of 0.9837 and  $2.09$  ( $\text{mg g}^{-1}$ ) $^{-1} \text{ min}^{-1}$ , respectively. The higher correlation coefficients and predicted  $q_e$  values of pseudo second-order model indicated that, it was suitable to describe the kinetic adsorption process of copper (II) onto GVW-AC, which is consistent with the reported studies (Demirbas et al., 2009). Furthermore, the  $q_e$  values were important as they could be affected with surface area modification of the adsorbents. Consequently, it can be concluded that the mechanism of copper (II) adsorption included both chemical adsorption and physical adsorption. This kinetic model appears to be realistic due to the observed chemical modifications as confirmed by the FTIR and TGA results.

### 3.5. Desorption study

Desorption of copper (II) shown in Fig. 9 was studied by adsorbing copper (II)  $1.5 \text{ mg L}^{-1}$  onto the GVW-AC as described in the experimental procedure, then removed by



**Figure 9** Desorption of copper (II) from GVW-AC using hydrochloric acid from 0.2 to  $1.0 \text{ mol L}^{-1}$ .

washing the adsorbate with HCl ranging from 0.2 to  $1.0 \text{ mol L}^{-1}$ . The recovery rate of copper (II) increases with the increase in eluent concentration until it levels off or reaches to 0.8 mM where desorption process starts to be reversible as demonstrated by the effect of pH studies.

The high level of desorption attained in this study showed that the surface adsorption predominates on GVW-AC and the adsorption mechanism may be followed. The process of desorption is much dependent on the volume and concentration used for washing; hence, optimum value reported has to be noted with caution.

To evaluate the efficiency of GVW-AC reusability, the adsorption/desorption steps were carried out for five cycles. The obtained results from five cycles reveal that % recovery of copper (II) ions from adsorption/desorption was 76.36%, 76.0%, 75.5%, 75.0%, 74.0% and 68.5%, 67.3%, 66.2%, 65.8%, 64.7% respectively. There was a slight decrease in both the percentage of copper (II) ion adsorbed and the percentage of copper (II) ion desorbed from the first to the fifth cycle. This showed that the carbon was restored close to the original condition without damage to the nature of the adsorption characteristics of the carbon.

### 3.6. Removal of copper (II) ions from wastewaters with GVW-AC

Two wastewater samples were collected from the Umlazi River, Rossburg Drain, Durban, South Africa, and analyzed as per optimized procedure with optimum parameters: pH 3.5,  $0.6 \text{ g L}^{-1}$  GVW-AC dose, and contact time of 90 min. Due to low concentration of copper (II) in the samples, spiked samples were prepared with known concentrations of 1.5, 2.0 and 3.0 ppm. Overall, the samples demonstrated that, there was no significant influence of the matrix. Once again these results have to be noted with caution as they included matrix which may differ with the source of water as shown in Table 1.

### 3.7. Evaluation of developed activated carbon

Table 2 shows the comparison of copper (II) ions adsorption studied in this work in relation to other relevant literature studies. The value of the adsorption capacity in this study is larger than that reported in the literature. This suggests that

**Table 1** Removal of copper (II) from wastewaters using GVW-AC.

Sample	Concentration copper (II) in real samples (ppm)	Concentration copper (II) in spiked samples (ppm)					
		1.50		2.0		3.0	
		$C_0$ (ppm)	% Adsorption	$C_0$ (ppm)	% Adsorption	$C_0$ (ppm)	% Adsorption
Umlazi river <sup>a</sup> water	ND	1.38	92.12	1.88	94.0	2.58	86.0
Rosburg drain water <sup>a</sup>	ND	1.49	99.33	1.92	96.0	2.91	97.0

<sup>a</sup> Collected from Durban, KZN, South Africa, ND: Not detectable.

**Table 2** Comparison of GVW-AC with the reported activated carbons for removal of copper (II).

Source of adsorbent	Parameters pH (Temp. K)	$q_m$ (mg g <sup>-1</sup> )	Cost factor		Citation
			Less economical	Highly economical	
Green Vegetable waste		75.00		XX	This work
Hazelnut shell	6.0 (323)	58.27		XX	Demirbas et al. (2009)
SP-Sewage sludge and	5.0 (298)	7.73			Wang et al. (2011)
SZ-Sewage sludge	5.0 (298)	10.56	X		
Filtrisorb 300-granular	5.97 (293)	2.667	X		Pesavento et al. (2003)
Tunisian date stones	5.0 (293)	31.25	X		Bouhamed et al. (2012)
<i>Eucalyptus camaldulensis</i> <i>Dehnh</i>	5.0 (333)	53.98	X		Patnukao et al. (2008)
Biomass gasification	5.0 (298)	23.00		XX	Runtti et al. (2014)
Hazelnut husks	6.7 (291)	6.645		XX	Imamoglu and Tekir (2008)
<i>Ceiba pentandra</i> hulls	6.0 (303)	20.80	X		Madhava Rao et al. (2006)
Chestnut shell and	3.3 (298)	38.75			Özçimen and Ersoy-Meriçboyu (2009)
Grape seed	3.0 (298)	31.84	X		
Palm shell	3.0 (NR)	18.60		XX	Issabayeva et al. (2010)
	5.0 (NR)	30.80			
Hazelnut shell	5.0 (298)	199.4		XX	Milenković et al. (2009)
	5.0 (298)	239.4	X		
Rubber wood sawdust	5.7 (303)	5.72	X		Kalavathy et al. (2005)
Rice hulls	5.3 (293)	3.92		XX	Murat et al. (1999)

AC: activated carbon, SP: Phosphatic, SZ = Zinc Chloride.

copper (II) ions could easily be adsorbed by GVW-AC used in this work (see Fig. 3b). In addition, the results revealed that the prepared activated carbon could be considered as a promising material for the removal of copper (II) ions, even when compared with Filtrasorb 300-granular (Pesavento et al., 2003) reported in the literature (see Table 2) due to its high maximum adsorption (75.0 mg g<sup>-1</sup>). Although activated carbons derived from hazelnut shell (Demirbas et al., 2009; Milenković et al., 2009), Palm shell (Issabayeva et al., 2010) and Rice hulls (Murat et al., 1999) are economical like GVW-AC, the adsorption capacity of GVW-AC is higher than that of other activated carbons reported in the literature. The obtained results indicate that GVW-AC is a type of cost effective and promising adsorbent for the removal of copper (II) ions.

Despite the good potential demonstrated by activated carbon on adsorption of heavy metals, it is restricted for application on industrial scale due to its high regeneration cost and losses in the application processes. The accumulation of positively charged species on the surface of activated carbon lowers the adsorption capacity due to ionic repulsion. Therefore, regeneration and reuse studies of activated carbon for adsorption cycles can be another area of interest.

#### 4. Conclusions

The adsorption of copper (II) onto the GVW-AC is found to be dependent on the pH of the solution, contact time and adsorbent dosage. Adsorption process revealed that the initial uptake was rapid and equilibrium was achieved in about 90 min. The optimum parameters for this study were pH: 3.5, initial copper (II) ion concentration: 1.5 mg L<sup>-1</sup>, contact time: 90 min and adsorption dosage: 0.60 mg L<sup>-1</sup> with a maximum removal capacity of 75.0 mg g<sup>-1</sup>. Experimental results indicated that the pseudo second-order reaction kinetics provided the best description of the data. The isotherm study indicated that adsorption data correlated well with Langmuir isotherm model. Studies on the effects of other process parameters such as temperature, particle size and ionic strength can also be an interesting area of future study. This study demonstrated that the GVW-AC could be used as an effective adsorbent for the treatment of wastewater containing copper (II) ions.

#### Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. These authors, M.I. Sabela, K. Kunene, S. Kanchi, and K. Bisetty contributed equally to the experi-

mental design, preparation and discussion of the manuscript. The remaining authors N.M. Xhakaza, A. Bathinapatla, P. Mdluli, and D. Sharma contributed mainly to the experimental section.

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#### References

- Bouhamed, F., Elouear, Z., Bouzid, J., 2012. Adsorptive removal of copper (II) from aqueous solutions on activated carbon prepared from Tunisian date stones: equilibrium, kinetics and thermodynamics. *J. Taiwan Inst. Chem. E* 43, 741–749.
- Demirbas, E., Dizge, N., Sulak, M.T., Kobya, M., 2009. Adsorption kinetics and equilibrium of copper from aqueous solutions using hazelnut shell activated carbon. *Chem. Eng. J.* 148, 480–487.
- Dinçer, A.R., Güneş, Y., Karakaya, N., 2007. Coal-based bottom ash (CBBA) waste material as adsorbent for removal of textile dyestuffs from aqueous solution. *J. Hazard. Mater.* 141, 529–535.
- Feng, N., Guo, X., Liang, S., 2009. Adsorption study of copper (II) by chemically modified orange peel. *J. Hazard. Mater.* 164, 1286–1292.
- Flouty, R., Estephane, G., 2012. Bioaccumulation and biosorption of copper and lead by a unicellular algae *Chlamydomonas reinhardtii* in single and binary metal systems: a comparative study. *J. Environ. Manage.* 111, 106–114.
- Imamoglu, M., Tekir, O., 2008. Removal of copper (II) and lead (II) ions from aqueous solutions by adsorption on activated carbon from a new precursor hazelnut husks. *Desalination* 228, 108–113.
- Issabayeva, G., Aroua, M.K., Sulaiman, N.M., 2010. Study on palm shell activated carbon adsorption capacity to remove copper ions from aqueous solutions. *Desalination* 262, 94–98.
- Kalavathy, M.H., Karthikeyan, T., Rajgopal, S., Miranda, L.R., 2005. Kinetic and isotherm studies of Cu(II) adsorption onto H<sub>3</sub>PO<sub>4</sub>-activated rubber wood sawdust. *J. Colloid Interface Sci.* 292, 354–362.
- Kanchi, S., Bisetty, K., Gopalakrishnan, K., Lin, C.Y., Chin, T.S., 2014. Development of green energy waste activated carbon for removal of trivalent chromium: equilibrium and kinetic modeling. *Sep. Sci. Technol.* 49, 513–522.
- Kanchi, S., Bisetty, K., Gopalakrishnan, K., Sabela, M.I., 2017. Robust adsorption of Direct Navy Blue-106 from textile industrial effluents by bio-hydrogen fermented waste derived activated carbon: equilibrium and kinetic studies. *Arabian J. Chem.* 10 (S2), S3084–S3096.
- Kalyani, S., Srinivasa Rao, P., Krishnaiah, A., 2004. Removal of nickel (II) from aqueous solutions using marine macroalgae as the sorbing biomass. *Chemosphere* 57, 1225–1229.
- Kargi, F., Cikla, S., 2006. Biosorption of zinc(II) ions onto powdered waste sludge (PWS): Kinetics and isotherms. *Enzyme Microb. Technol.* 38, 705–710.
- Larous, S., Meniai, A.H., 2012. Removal of copper (II) from aqueous solution by agricultural by-products-sawdust. *Energy Proc.* 18, 915–923.
- Leone, N., Courbon, D., Ducimetiere, P., Zureik, M., 2006. Zinc, copper, and magnesium and risks for all-cause, cancer, and cardiovascular mortality. *Epidemiology* 17, 308–314.
- Madhava Rao, M., Ramesh, A., Purna Chandra Rao, G., Seshiah, K., 2006. Removal of copper and cadmium from the aqueous solutions by activated carbon derived from *Ceiba pentandra* hulls. *J. Hazard. Mater.* 129, 123–129.
- Milenković, D.D., Dašić, P.V., Veljković, V.B., 2009. Ultrasound-assisted adsorption of copper (II) ions on hazelnut shell activated carbon. *Ultrason. Sonochem.* 16, 557–563.
- Murat, T., Mustafa, I., Omer, S., 1999. Adsorption of copper and cadmium ions by activated carbon from Rice Hulls. *Turk. J. Chem.* 23, 185–192.
- Oliveira, D., 2013. Food waste costs SA R61.5-billion a year <<http://www.engineeringnews.co.za/print-version/food-waste-costs-sa-r615-billion-a-year-2013-08-23>> (accessed 27.05.16).
- Özçimen, D., Ersoy-Meriçboyu, A., 2009. Removal of copper from aqueous solutions by adsorption onto chestnut shell and grapeseed activated carbons. *J. Hazard. Mater.* 168, 1118–1125.
- Patnukao, P., Kongsuwan, A., Pavasant, P., 2008. Batch studies of adsorption of copper and lead on activated carbon from *Eucalyptus camaldulensis* Dehn. bark. *J. Environ. Sci.* 20, 1028–1034.
- Pesavento, M., Profumo, A., Alberti, G., Conti, F., 2003. Adsorption of lead(II) and copper (II) on activated carbon by complexation with surface functional groups. *Anal. Chim. Acta* 480, 171–180.
- Ricordel, S., Taha, S., Cisse, I., Dorange, G., 2001. Heavy metals removal by adsorption onto peanut husks carbon: characterization, kinetic study and modeling. *Sep. Purif. Technol.* 24, 389–401.
- Runtti, H., Tuomikoski, S., Kangas, T., Lassi, U., Kuokkanen, T., Rämö, J., 2014. Chemically activated carbon residue from biomass gasification as a sorbent for iron(II), copper (II) and nickel(II) ions. *J. Water Process Eng.* 4, 12–24.
- Schiever, S., Wong, M.H., 2000. Ionic strength effects in biosorption of metals by marine algae. *Chemosphere* 41, 271–282.
- Sha, L., Xueyi, G., Ningchuan, F., Qinghua, T., 2009. Adsorption of Cu<sup>2+</sup> and Cd<sup>2+</sup> from aqueous solution by mercapto-acetic acid modified orange peel. *Colloids Surf. B* 73, 10–14.
- Shen, L., Liu, Y., Paul, E., 2009. A simple geometric approach for simplification of Langmuir kinetics for adsorption. *Colloids Surf. A Physicochem. Eng. Asp.* 349, 78–82.
- Sheng, P.X., Ting, Y.P., Chen, J.P., Hong, L., 2004. Sorption of lead, copper, cadmium, zinc, and nickel by marine algal biomass: characterization of biosorptive capacity and investigation of mechanisms. *J. Colloid Interface Sci.* 275, 131–141.
- Tsai, W.T., Chang, C.Y., Lin, M.C., Chien, S.F., Sun, H.F., Hsieh, M. F., 2001. Adsorption of acid dye onto activated carbons prepared from agricultural waste bagasse by ZnCl<sub>2</sub> activation. *Chemosphere* 45, 51–58.
- Veit, M.T., Tavares, C.R.G., Gomes-da-Costa, S.M., Guedes, T.A., 2005. Adsorption isotherms of copper (II) for two species of dead fungi biomasses. *Process Biochem.* 40, 3303–3308.
- Wafwoyo, W., Seo, C.W., Marshall, W.E., 1999. Utilization of peanut shells as adsorbents for selected metals. *J. Chem. Technol. Biotechnol.* 74, 1117–1121.
- Wang, X., Liang, X., Wang, Y., Wang, X., Liu, M., Yin, D., Xia, S., Zhao, J., Zhang, Y., 2011. Adsorption of copper (II) onto activated carbons from sewage sludge by microwave-induced phosphoric acid and zinc chloride activation. *Desalination* 278, 231–237.