Studii şi Cercetări Ştiinţifice
Chimie şi Inginerie Chimică, Biotehnologii, Industrie Alimentară

2018, **19** (2), pp. 117 – 132

Scientific Study & Research
Chemistry & Chemical Engineering, Biotechnology, Food Industry

ISSN 1582-540X

ORIGINAL RESEARCH PAPER

REMOVAL OF METAL IONS FROM AQUEOUS SOLUTIONS USING ACTIVATED CARBON PREPARED FROM *ZEA MAYS* STEM

Mzukisi Matandabuzo, Peter A. Ajibade*

University of KwaZulu-Natal, School of Chemistry and Physics, Private Bag X01, Scottsville, Pietermaritzburg 3209, South Africa

*Corresponding author: ajibadep@ukzn.ac.za

Received: June, 03, 2017
Accepted: February, 28, 2018

Abstract: Activated carbon prepared from *Zea mays* stem using chemical activation was used as adsorbent for the removal of metal ions from aqueous solution. The results indicate that the adsorption of Pb(II), Cu(II) and Cr(III) ions is *p*H, contact time, and concentration dependent while the adsorption of Hg(II) is very different. The maximum removal percentages obtained at *p*H 5-6 were 97.44 % for Pb(II), 98.37 % for Cu(II), 89.37 % for Cr(III) and there was no adsorption for mercury ions. The metal ion removal trend follows the order Pb(II) > Cr(III) > Cu(II). The results show that Langmuir model fitted well in most cases with $R^2 > 0.99$. Consequently, the adsorption of Pb(II) and Cu(II) followed Langmuir isotherm model while that of Cr(III) best fitted on Freundlich isotherm model.

Keywords: *Activated carbon*, *adsorption*, *equilibrium isotherms*, *metal ions*

© 2018 ALMA MATER Publishing House, "VASILE ALECSANDRI" University of Bacău. All rights reserved.

INTRODUCTION

Activated carbon is a porous material with extremely large surface area and intrinsic adsorption to many chemicals [1, 2]. It is usually prepared from carbonaceous materials such as coal, agricultural wastes such as grape stalk [3], coffee husks [4], coconut shells [5], sugar beet pulp [6], rice straw [7], cotton stalks [8], soybean straw [9], tree fern [10], apple wastes [11], and *Moringa oleifera* [12]. Activated carbon have high surface area, sufficient pore size distribution, and variable surface chemistry that make them very useful in separation technology [13]. Activated carbons are useful in various applications such as water treatment, removal of harmful gases, solvent recovery, color removal, and as electrode materials in electrochemical processes [13 – 16]. Agricultural waste materials are useful as low-cost precursors for the preparation of activated carbons. Research have shown that many agricultural waste materials have been used to produce activated carbons with some promising results as environmental friendly material for metal ions remediation [3, 13]. Activated carbon can be prepared either by physical or chemical activation method [16]. The first step in the physical activation method involves the pyrolysis or carbonization of biomass material in an inert atmosphere at 500 - 700 °C and the second step involve the activation of the produced carbon at 800 - 1000 °C in the presence of CO_2. Chemical activation method is a single step process where carbonization and activation of the precursor material occurred simultaneously [13 – 15]. The precursor material impregnated with chemical dehydrating agent and heated in an inert atmosphere at 500 - 700 °C.

Common dehydrating reagents for chemical activation are H_3PO_4 [6], H_2SO_4 [3], Na_2CO_3 [5], $ZnCl_2$ [4], K_2CO_3 [8], KOH/NaOH [17], and citric acid [18]. The advantages of chemical activation technique over physical activation method includes lower temperatures for pyrolysis, one step process, high yield, and activated carbon with high surface area [19]. Awoyale *et al*. [19] in their study reported that activated carbon from bamboo and cocoa pod husk has comparable adsorption capacities. Gang and Wiexing [20] reported that activated carbon is only able to remove around 30 - 40 $mg \cdot g^{-1}$ of Cd, Zn, and Cr ions in water and is non-regenerable and this is quiet costly for application in wastewater treatment. Badmus *et al.* [21] reported the removal of lead ion from industrial wastewaters by activated carbon prepared from periwinkle shells (*Typano tonus fuscatus*). Singh *et al*. [22] studied the removal of Pb(II) from wastewater by activated carbon developed from tamarid wood activated with sulphuric acid. Recently, Zhou *et al*. reported the adsorption of divalent heavy metal ions from aqueous solution using pine sawdust modified by citric acid as adsorbent. They discovered the adsorption order of $Pb^{2+} > Cu^{2+} > Cd^{2+}$ in the competitive environment of metal ions [23].

In this work, Zea mays stem was used as precursor material for the chemical preparation of activated carbon using H_3PO_4, H_2SO_4, KOH and NaOH dehydrating reagents. A Zea mays is a large grain plant domesticated by indigenous peoples in Mesoamerica [24]. It is one of the most sensitive plant to drought, hence it is usually cultivated during summer and spring seasons in the temperate regions or zones. It consists of leafy stalk that produces ears containing grain. The maize plant is usually about 2.4 to 2.5 m long with the stem having the appearance of a bamboo cane. To the best of our knowledge, no work has been reported on the synthesis and characterization of activated carbon from *Zea mays* stem for the removal of metal ions. In this paper, we report the novelty

and innovative preparation of activated carbon from *Zea mays* stem and evaluation of its potential as adsorbent for the removal of Pb(II), Cu(II), Cr(III), and Hg(II) ions from aqueous solution.

MATERIALS AND METHODS

All chemicals and reagents were obtained from Sigma-Aldrich or Merck and used as received. *Zea mays* stem collected from the University of Fort Hare Research farm was washed thoroughly with distilled water to remove dirt and particulate materials attached to it. The biomass was then sun dried for about 20 days. It was then taken into the oven (Memmert oven Lasec SA) at 120 °C to dry. After being dried, it was chopped into smaller pieces suitable for grinding in YMSJ Super Fine Corn Grits Machine, Shandong Xingfeng Flour Machinery Co., LTD (2002) China, from animal traction centre to a powder-like form of about 0.85 - 0.1 mm internal diameter. The produced *Zea mays* stem material was stored in a desiccator for later use.

Preparation of activated carbons

Activated carbon was prepared from *Zea mays* stem using one-step chemical activation method as reported by Mohanty et al. [2]. Four different chemical activating reagents (H_3PO_4, H_2SO_4, KOH, and NaOH) were used in this study. In a typical experiment, about 10 g of dried-crushed raw Zea mays stem was impregnated with 100 mL of each of the four activating agents until an extensive swelling was observed. The mixture was then kept in an oven at 100 °C overnight. After that, it was removed from the oven and cool at room temperature. The mixture was then taken into electrical furnace for 1 hour 30 minutes at temperatures ranging from 400 - 600 °C. A deep black bubbles-like structure of activated carbon was produced and was allowed to cool. After cooling, it was cleaned with either hot distilled water to remove acid or HCl to neutral base from the activated carbon until the *p*H of the resulting solution was neutral, that is, *p*H = 7. The produced activated carbon was then dried further in an oven at 100 °C overnight.

Characterization of prepared activated carbon

The prepared activated carbon was characterized using Fourier transform infrared spectroscopy (Perkin Elmer, System 2000 FT-IR, USA), scanning electron microscopy/energy dispersive X-ray spectroscopy (Jeol, JSM-6390 LV SEM with Noran system Six software, USA). The infrared spectra were obtained from a Perkin Elmer Paragon 2000 FTIR spectrophotometer using the KBr disc method. Scanning electron microscope images were analyzed using Jeol JSM-6390 LV SEM, at different magnifications as shown on the SEM micrograph. Samples for SEM analysis were prepared by mounting the nanoparticles on a stub using carbon double-sided tape. The samples were coated with Au/Pd using the Eiko IB. 3 Ion coater for better imaging.

Iodine number

Iodine adsorption could be used to examine surface areas and pore size distribution of the four activated carbons prepared [25 – 30] as shown in equation 1.

$$Iodine\ number = \frac{V(Ti - Tf)Ci.Mi}{(Ti - g)} \quad (1)$$

where:
V = 25 mL (mL iodine solution)
Ti = 11.3 mL (mL Na2S2O3 solution used for titration of 10 mL iodine solution)
Tf = mL $Na_2S_2O_3$ solution used for titration of 10 mL filtrate solution
g = 0.1g (weight of the sample in grams)
Mi = 126.9044 $g \cdot mol^{-1}$ (molar weight of iodine)
Ci = 0.046 N (concentration of iodine)

Adsorption studies

Batch adsorption experiments were conducted using 20 mL of dilute solutions containing 200 ppm each of Pb(II), Cu(II), and Cr(III),) placed in 250 mL Erlenmeyer flask. The *p*H of each metal ion solution was adjusted using either 0.1N HCl or 0.1N NaOH solutions to the range of 2 - 7. The optimum *p*H was observed to be 5 - 6 and was used for all experiments. According to the results obtained from the preparation of activated carbons and their physicochemical and characterization techniques, activated carbon prepared with sulphuric acid was considered the better one out the three. 2 g of the adsorbent was added into 20 mL of each of the four flasks containing different metal ion solutions and were placed on the orbital shaker to be stirred for 2 hours at speed of 110 rpm. After a desired time, the activated carbon was removed using filter paper and molar concentrations for all metal ions were determined using atomic absorption spectroscopy. When studying the *p*H of the solution, initial concentration (200 ppm), contact time (2 hours), and shaking speed (110 rpm) were fixed. This procedure was applied to all experiments and depending on which of the fixed parameter(s) to be interchange.

RESULTS AND DISCUSSION

Characteristic properties of the activated carbon

Functional groups present in the prepared activated carbon, morphology and surface chemistry of the activated carbon, elements present on the surface of the carbon material (elemental analysis), crystallinity and amorphous structure of the material were all determined before and after adsorption. The carbon yield, adsorption capacity, moisture content and iodine number of the prepared carbon were determined before the adsorption.
The physico-chemical properties of the prepared activated carbon before adsorption shows that carbon yield percentage for H_3PO_4, NaOH, H_2SO_4, and KOH treated Zea mays stem was 76.52 %, 49.61 %, 33.75 %, and 13.16 %, respectively. The carbon yield percentage indicates the yield of the activated carbon relative to the amount of raw material used. Aygum *et al*. [31] reported carbon yields of 39.99 to 55.44 % for most activated carbon prepared from fruit stones and nutshells. They reported that phosphoric acid chemical activation method gave the highest carbon yield as compared to that of

sulphuric acid, sodium hydroxide, and potassium hydroxide. Yakout and El-Deen [25] reported activated carbon from olive stone-prepared using phosphoric acid with well-developed pore structure. The results obtained in this study indicates that activated carbon prepared from *Zea mays* stem using sulphuric acid as activating reagent has high adsorption capability, more effective, high surface area and pore volume than those produced using KOH, NaOH, and H_3PO_4 and can remediate a significant number of metal ions from wastewater. Adsorption percentage, that is, the amount of metal ions adsorbed per unit mass of activated carbon was determined and found to be 66.67 % for activated carbon obtained with H_2SO_4 from Zea may stem, 21.21 % for activated carbon prepared with KOH from Zea may stem, and 20 % for both NaOH and H_3PO_4 activated carbons, respectively. The adsorption capacity of the activated carbon was calculated using the adsorption percentage equation, as shown in eqn. (2):

$$\text{Adsorption} = \frac{W_a - W_b}{W_b} \cdot 100 \tag{2}$$

where: W_a and W_b are the weights of activated carbon after and before adsorption and ammonia solution was used as testing solution [26].

The iodine number determines the porosity of the activated carbon. The total surface area of the activated carbon prepared from *Zea mays* stem was determined by the iodine-adsorption number method. The iodine number for activated carbon prepared using sulphuric acid as activating agent is 348.7062 $mg \cdot g^{-1}$. This result indicates that activated carbon prepared with H_2SO_4 showed higher iodine removal. Higher surface area, micro and mesoporous structures have been reported with higher degrees of iodine adsorption as the indicators [24, 29 – 31]. Madu and Lajide [27] reported iodine number of 966 $mg \cdot g^{-1}$ for melon seed husk based activated carbon.

Metal ion adsorption

Effect of pH on metal ion adsorption

The results obtained from this study show that the *p*H of the aqueous solution does affect the adsorption of the metal ions. The effect of *p*H of the aqueous solution was studied from a range of *p*H 2 to 7 under fixed conditions at contact time of 120 minutes, 110 rpm shaking speed, initial concentration of 200 ppm, using 2 g of the adsorbent, and at room temperature. After careful study, the optimum *p*H 5 - 6 was chosen for all experiments and the results are presented in Figure 1. The maximum removal percentages that were obtained for all the metal ions at *p*H 5 - 6 are 97.44 % for Pb(II), 98.37 % for Cu(II), 89.37 % for Cr(III) and there was no adsorption for mercury ions. Pb(II) and Cr(III) also show a well-defined adsorption even at lower *p*H levels with 98.13 % and 69.92 %, respectively. The highest removal percentage of metal ions was obtained at higher *p*H, the adsorbent surface is usually deprotonated and negatively charged, which causes more attraction between the positively charged metal cations and negatively charged adsorbent. While at lower *p*H, the competition between H^+ and dissolved metal ions for ligands such as OH^-, CO_3^{2-}, SO_4^{2-}, Cl^-, S^{2-} and phosphates become more and more significant. Aggarwal *et al*. [32] reported a *p*H range of 6 - 7 for the adsorption of Cr(III), while Bernard *et al*. [33] reported that 100% adsorption of Pb(II) occur at *p*H of 2. As shown in Figure 1, the removal percentage of metal ions

increases as *p*H of the solution increases. It has been noted that the removal percentage of Cu(II) barely changes as *p*H increases from 2 to 5, but it drastically increases and reach 100 % when the *p*H is 6. This therefore indicate that Cu(II) can only be removed at high *p*H value when using activated carbon as adsorbent. Moreno-Pirajan and Giraldo [34] in their study reported that metal ion removal increases as *p*H value rises, reaching maximum around 5.0.

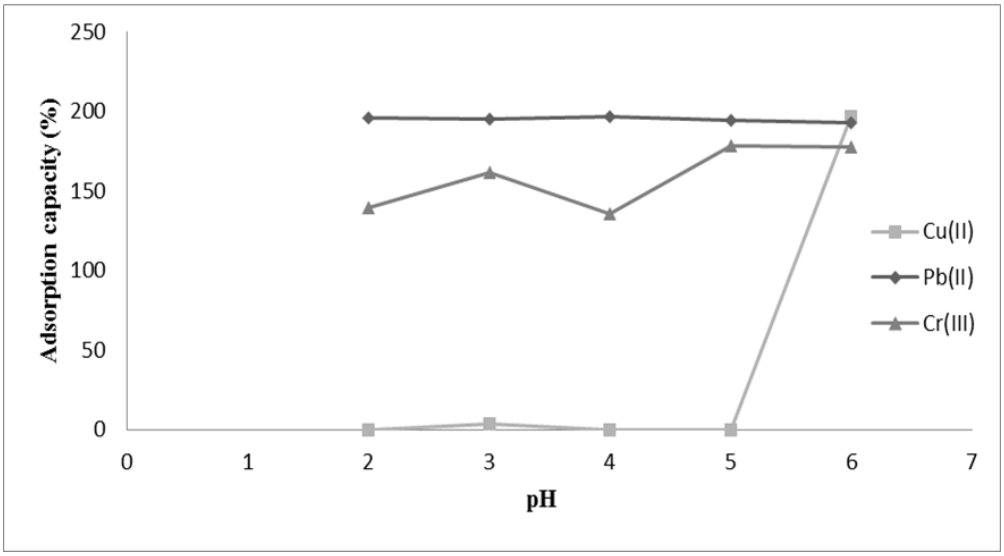

Figure 1. *Effect of pH on metal ion adsorption*

Effect of contact time on metal ion adsorption

The effect of contact on the removal of Pb(II), Cu(II), Cr(III) at fixed *p*H 5 - 6, and time intervals of 30 minutes is shown in Figure 2. The results indicate how long or fast it takes the adsorbent to adsorb metal ion or adsorbate to be diffused on the surface of the adsorbent. In this study, the adsorption immediately reach equilibrium at 30 minutes of adsorption for Pb(II) and Cr(III). From the results obtained, it is evident that the adsorption of metal ions increases as the contact time increases and it can be observed that the metal ion removal attained equilibrium at different times. The metal ions removal reached equilibrium at 30 min for Pb(II), 40 min for Cr(III), and 90 min for Cu(II), with Pb(II) attaining 97 %, Cr(III) 82 %, and Cu(II) 20 % removal. Bernard *et al*. [33] also reported 100 % removal of Pb(II) at 40 min using activated carbon produced from coconut shells.

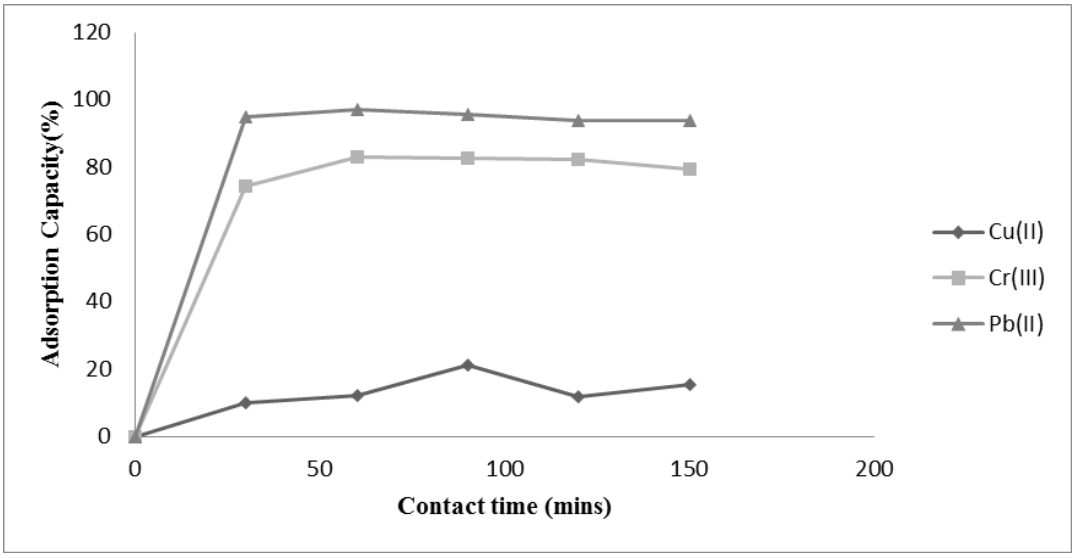

***Figure 2**. The effect of contact time on the removal efficiency*

Effect of initial concentration on metal ion removal

The effect of initial concentration was studied under specific conditions where *p*H was 5 - 6, maximum contact time was 2 hours, adsorbent dosage 2 g, shaking speed of 110 rpm (Figure 3).

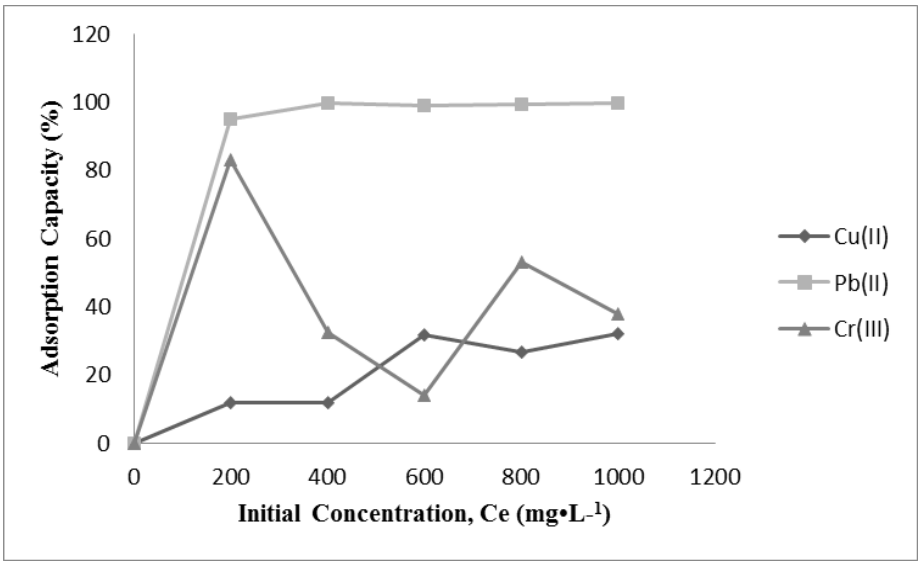

***Figure 3**. The effect of initial concentration on removal efficiency of the metal ions by the activated carbon*

The initial concentration for metal ion solutions was in range of 200 - 1000 ppm. It is evident that the adsorption of Pb(II) approached equilibrium even at lower concentrations of 200 ppm and it recorded 100 % removal for all concentrations. For Cr(III), 80 % removal was recorded at 200 ppm and then it declined at higher concentrations indicating that there is little or no further adsorption at higher metal ion concentrations (binding sites were already saturated). However, the increase in

adsorption capacity for Cr(III) at 800 ppm can be ascribed to the fact that the adsorbent was not uniform enough or being saturated at the same time by the metal ions and at higher concentrations, the adsorbent binding sites were overloaded. Maximum 30% removal for Cu(II) was recorded at 1000 ppm. This means that the removal of Cu(II) using this adsorbent can only be achieved at higher concentrations of 1000 ppm. Although previous studies conducted by Aggarwal *et al*. [32] and Bernard *et al*. [33] showed that removal of metal ions by activated carbon depends on concentration but we can conclude based on the results from this studies that dependency on concentration is relative to a particular metal ion.

Characterization after adsorption

FTIR analysis of Zea mays stem and activated carbon

The FTIR spectra of *Zea mays* stem-based activated carbon are shown in Figure 4. The cell wall of the plant is usually composed of complex structures consisting of hemicellulose, cellulose, and lignin with varying composition depending on the material resource and environment [12]. FTIR spectroscopy was used to determine the variation in the functional groups present before and after adsorption.

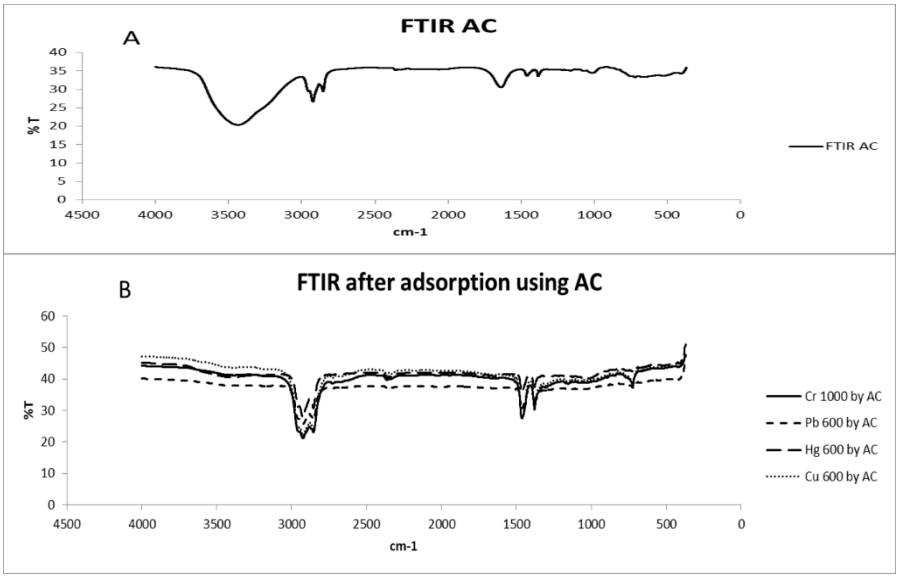

***Figure 4**. FTIR spectra for Zea mays stem- prepared activated carbon (A) and activated carbon after adsorption (B)*

A strong broad stretching vibration at 3467 cm^{-1} is observed for the prepared activated carbon, and this O-H stretching vibration can be assigned to hydroxyl functional groups O-H stretch for primary alcohol and phenols of the cellulosic activated carbon material [8]. C=C stretch related to aromatics at 1637 cm^{-1}, C-O-C stretching vibrations in ether, phenol and esters groups between 1041 – 1248 cm^{-1}. The less pronounced N-H stretch and reduction of O-H stretch can be credited to degradation or dehydration of cellulosic material by the use of activating reagents in the preparation of these activated carbons [30]. The absence of O-H stretch in Figure 4 (B) and pronouncement of vibration peaks at 3000 - 2800 cm^{-1} after adsorption of metal cations can be attributed to symmetric and

asymmetric C-H stretching vibration of aliphatic acids, new bond-formation between the metal cation and the adsorbent sites [36].

SEM surface morphologies of the prepared activated carbon

The SEM images for activated carbons prepared from *Zea mays* stem using sulphuric acid as chemical activating/dehydrating reagent are shown in Figure 5.

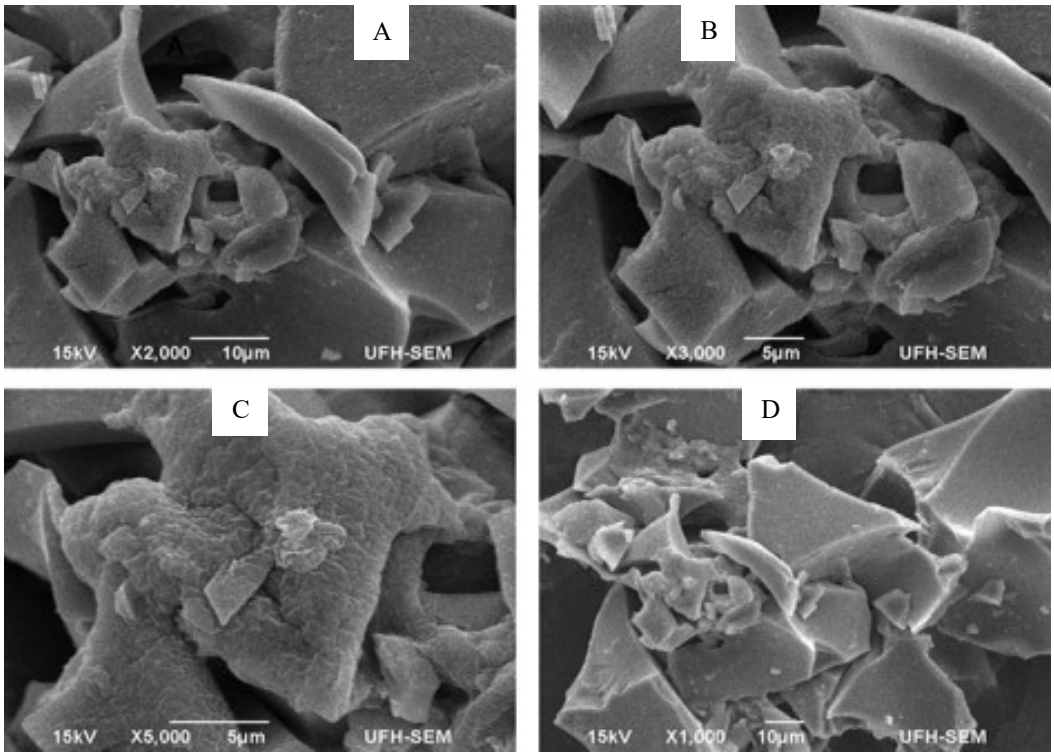

***Figure 5**. SEM images for the sulphuric acid prepared activated carbons with different magnifications, (A) 2000, B (3000), C (5000), and D (1000) scanning magnifications, respectively*

SEM images for activated carbon have some external surfaces with irregular cavities and pores. Cavities and cracks on the surface of the carbons resulted from the evaporation of the activating agent [36]. Some of these SEM images show some smooth morphology with very few cracks and voids external structures on the surface of the carbon. These cavities, cracks and voids are believed to be responsible for metal ion adsorption and diffusion [37, 38]. White irregular flakes or particles on the surface of the adsorbent can be observed and these irregular flaky attachments on the surface of the adsorbent signify the adsorbate being adsorbed by the adsorbent (Figure 6). Pores and voids that were seen before adsorption are now occupied with precipitates and complexes formed by metal ions with proton acceptors or binding site functional groups.

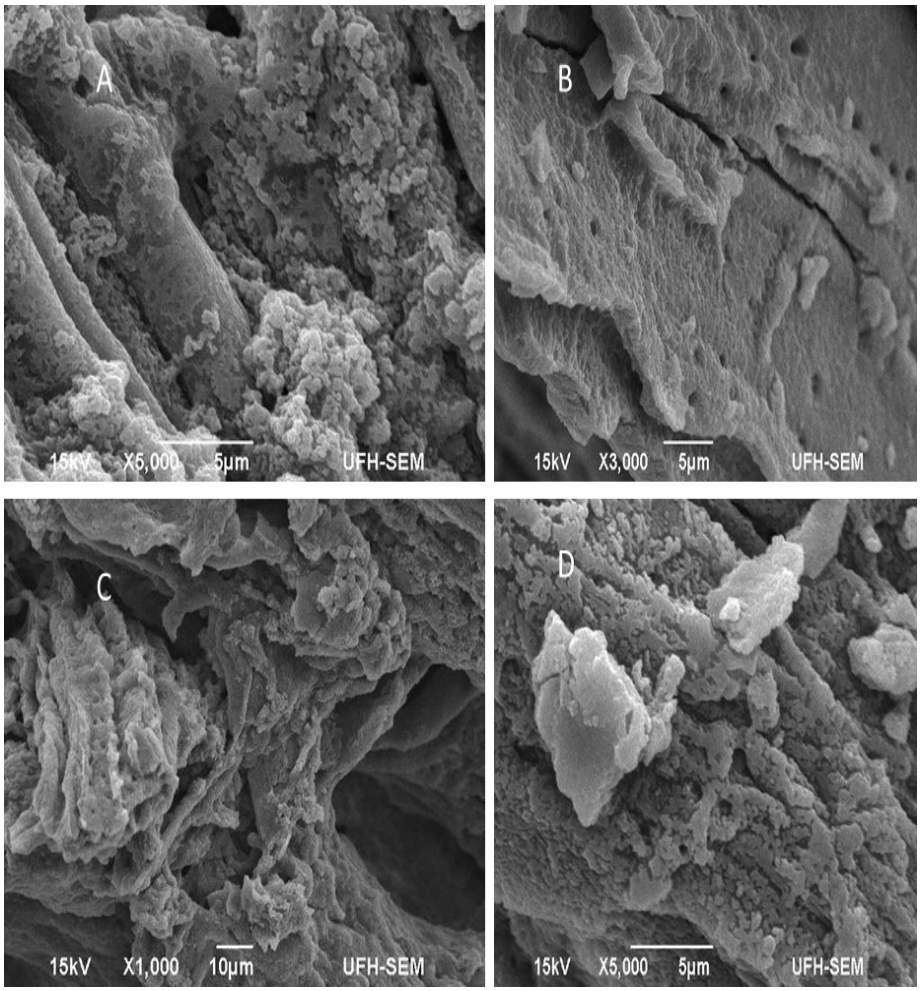

Figure 6. *SEM images for the sulphuric acid prepared activated carbons after metal ion adsorption: Pb^{2+} (A), Hg^{2+} (B), Cu^{2+} (C), and Cr^{3+} (D)*

Energy dispersive X-ray spectroscopy results for elemental determination and analysis for activated carbon

Energy dispersive X-ray spectroscopy (EDS) results were obtained in order to determine elemental composition of the activated carbon before and after adsorption, and confirm the presence of the metal ions in the adsorbent after adsorption. For example, some elements such as K, Na, Ca are believed to be the ones, which were responsible in exchanging sites with metal cations Pb(II), Cu(II), and Cr(III) respectively. Figure 7 shows EDS results obtained after adsorption of Pb(II), Cu(II), Cr(III), and Hg(II) using activated carbon as adsorbent. Elements C, O, S, and P detected in the EDS are believed to be part of hydroxyl, carbonyl and other proton acceptor group such as $–SO_3H$, which were also responsible for binding the positively charged metal cations during chemisorption [39, 40].

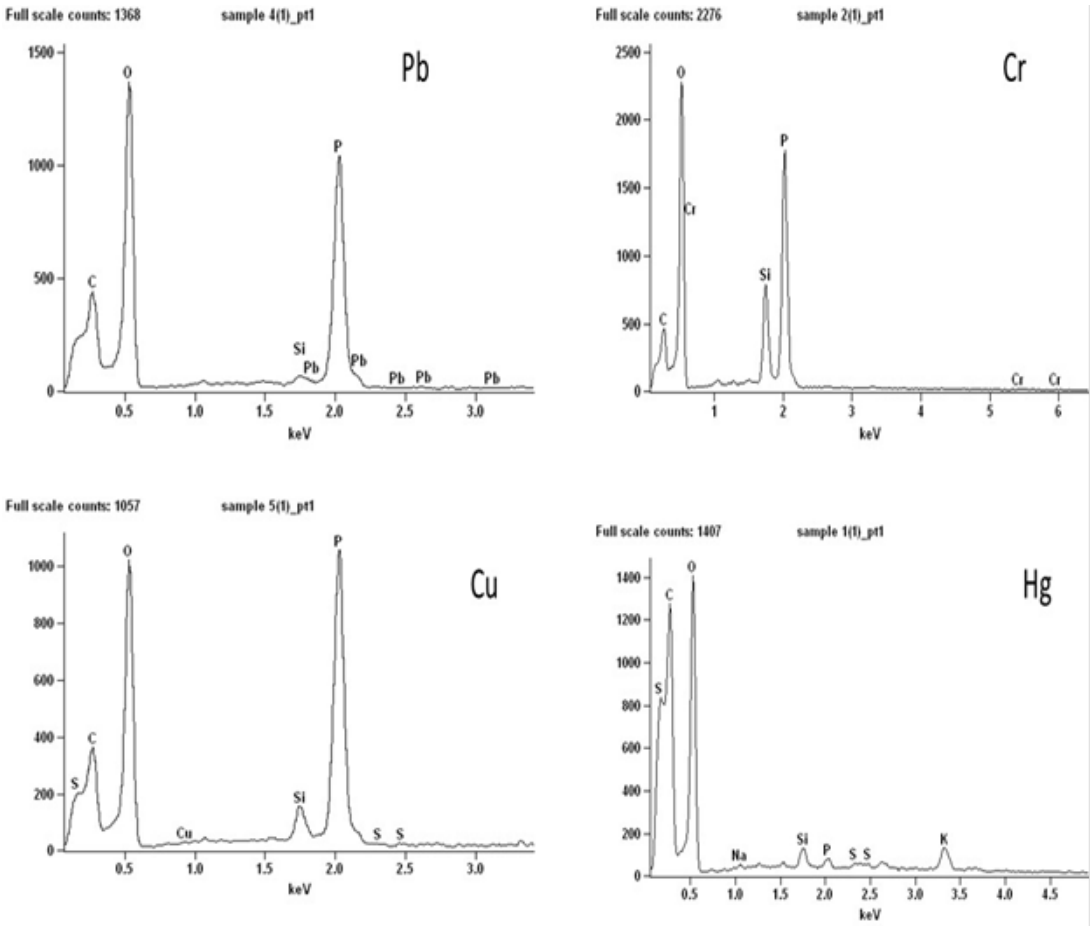

***Figure** 7. EDS results for adsorption of Pb(II), Cu(II), Cr(III), and Hg(II)*

Equilibrium isotherm model studies

Equilibrium isotherm models describe how adsorbate interacts with biosorbents and equilibrium is established between adsorbed metal ions on the biosorbent and the residual metal ions in the solution during the surface biosorption. The most common types of models describing this type of system are the Langmuir and Freundlich isotherms [41 – 44].

The Langmuir equation is represented as eqn. (3):

$$\frac{C_e}{q_e} = \frac{1}{q_{max} \cdot b} + \frac{C_e}{q_{max}} \tag{3}$$

Where q_{max} is monolayer capacity of the biosorbent ($mg \cdot g^{-1}$), q_e is the amount of metal ion in unit mass of adsorbent at equilibrium, C_e is the equilibrium concentration of the metal ions, and b is the biosorption constant ($L \cdot mg^{-1}$).

The Freundlich equation may be expressed as shown at eqn. (4):

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{4}$$

where: K_f and 1/n are the Freundlich isotherm constants related to biosorption capacity and intensity of biosorption, respectively.
Correlation co-efficient between 0 and 1 indicates favorable adsorption, whereas $R^2 = 1$ indicate linearity and RL > 1 which is for the dimensionless factor that describe the adsorption process whether is favorable or unfavorable [34]. Figure 8 shows the Langmuir models for Pb(II), Cu(II), and Cr(III) with $R^2 = 0.999$ for both Pb(II) and Cu(II) indicating favorable adsorption of these metal ions.

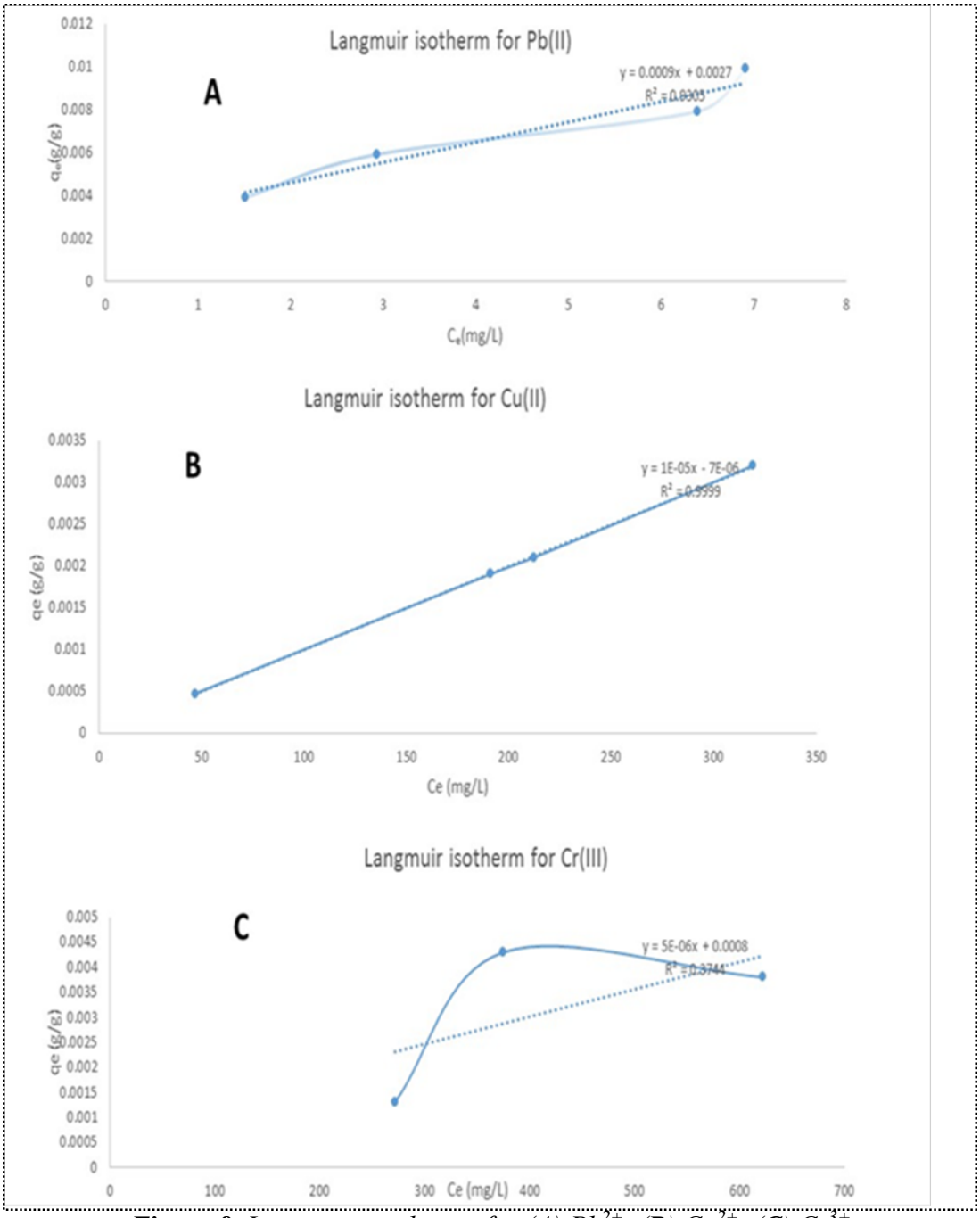

***Figure 8**. Langmuir isotherms for (**A**) Pb^{2+}, (**B**) Cu^{2+}, (**C**) Cr^{3+}*

Figure 9 shows the Freundlich models for the three metal ions and the $R^2 = 0.546$ for Cr(III) which indicates good adsorption. Moreno-Pirajan and Giraldo [34] also reported similar correlation co-efficient for Freundlich model of Cr(III) cations.

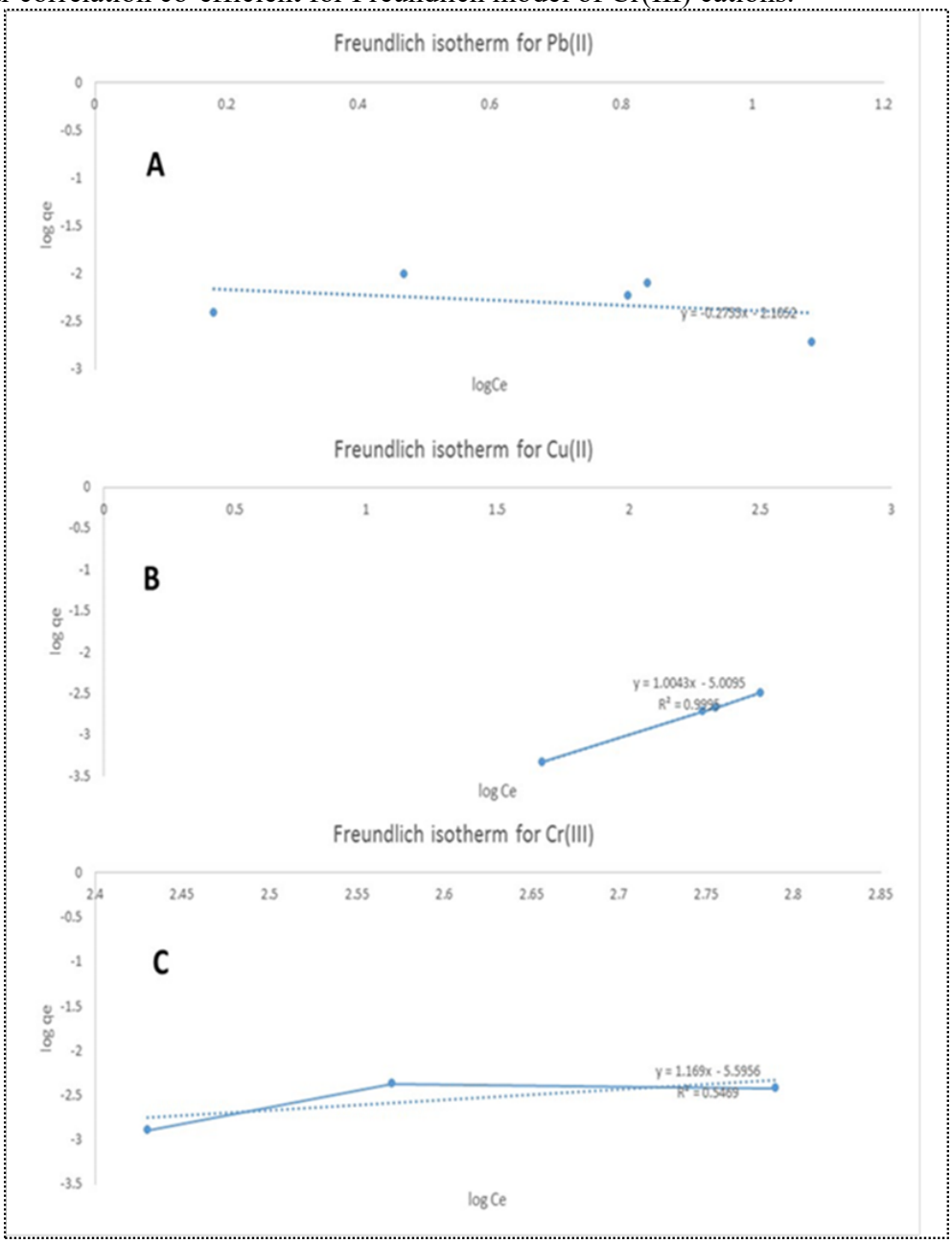

***Figure 9**. Freundlich isotherm for (**A**) Pb^{2+}, (**B**) Cu^{2+}, (**C**) Cr^{3+}*

Therefore, the Langmuir model fitted well in most of the cases with $R^2 > 0.99$. Consequently, the adsorption of Pb(II) and Cu(II) followed Langmuir isotherm model and that of Cr(III) best fitted on Freundlich isotherm model. This therefore suggests that the adsorption of these metal ions was more of monolayer process in most cases, though some were of multilayer due to variety in the surface chemistry of the adsorbent. Table 1 shows the summary of both Langmuir and Freundlich isotherm constants for adsorption of Pb(II), Cu(II), and Cr(III) by activated carbon used in this study.

The two mechanisms that are inferred based on the results from this study are the *metal ion-adsorbent complex model* due to the chemical interactions between the surface ligands mentioned above and metal cations dissolved. The second mechanism is the *metal ion – ion-exchange adsorbent complex model* that is due to the presence of ion-exchangeable elements (Ca, Mg, K, Na, C, and S) on the surface of some activated carbon.

Table 1. *Langmuir and Freundlich isotherm constants for adsorption Pb(II), Cu(II), and Cr(III) by activated carbon*

Adsorption of metal ions	**Langmuir isotherm constants**			**Freundlich isotherm constants**		
	q_{max}	**b**	R^2	**n**	K_f	R^2
Adsorption of Pb(II)	0.2	0.3	0.9305	0.23	4.7×10^{-5}	0.9059
Adsorption of Cu(II)	0.25	3.9×10^{-5}	0.9999	1.25	0.158	0.9995
Adsorption of Cr(III)	0.25	4.0×10^{-5}	0.3744	0.27	1.9×10^{-4}	0.5469

CONCLUSION

This work investigated the use of activated carbon produced from *Zea mays* stems using chemical activation method. Four different activated carbons were prepared from Zea mays stem using NaOH, H_3PO_4, H_2SO_4, and KOH. The results show that activated carbons are good adsorbent for the removal of Pb(II), Cu(II), and Cr(III) from aqueous solution but not good enough for the removal of Hg(II) and it was clear that the adsorption of Pb(II), Cu(II), and Cr(III) ions are *pH*, contact time, and concentration dependent. Compared with the untreated *Zea mays* powder, the activated carbons have high surface area and pore volumes with better adsorption capacity. The metal ions adsorption trend was Pb(II) > Cu(II) > Cr(III) and in terms of activated carbon adsorptive ability, activated carbon prepared using sulphuric acid and potassium hydroxide has proven to have high adsorption ability. The *p*H of the solutions still remains the most contributing factor on the adsorption of metal ions. It is believed that at low *p*H levels, the rivalry between hydrogen proton (H^+) in the solution and the dissolved metal ions for proton acceptor or ligands such as carbonyl, hydroxyl, aromatics, and carboxyl on the surface of the activated carbon turn out to be more significant such that it poses a negative impact on the removal of the metal ions. Electrostatic forces and Van der Waals forces are also believed to be the driving forces for the latter mechanisms as the ionic compound were intermingling with oppositely charged adsorbent surface though dipole interactions.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge ESKOM tertiary education support programme and Sasol South Africa. Mzukisi Matandabuzo acknowledges National Research Foundation (NRF)/ Sasol Inzalo Foundation for the award of postgraduate scholarship.

REFERENCES

1. Kannan, N., Devi, M.S.: Studies on removal of copper (II) and Lead (II) ions by adsorption on commercial activated carbon, *Indian Journal of Environmental Protection*, **2005**, **25**, 28-37;
2. Mohanty, K., Das, D., Biwas, M.N.: Adsorption of phenol from aqueous solutions using activated carbons prepared from Tectona grandis sawdust by zinc chloride activation, *Chemical Engineering Journal*, **2005**, **115** (1), 121-131;
3. Ozdemir, I., Sahin, M., Orhan, R., Erdem. M.: Preparation and characterization of activated carbon from grape stalk by zinc chloride activation, *Fuel Processing Technology*, **2014**, **125**, 200-206;
4. Oliveria, L.C., Pereira, E., Guimares, I.R., Vallone, A., Periera, M., Mesquita, J.P., Sapag. K.: Preparation of activated carbons from coffee husks utilizing $FeCl_3$ and $ZnCl_2$ as activating agents, *Journal of Hazardous Materials*, **2009**, **165** (1-3), 87-94;
5. Azevedo, D.C.S. Arujo, J.C.S., Neto, M.B., A.E.R. Torres, A.E.R., Jaguaribe, E.F., Cavalcante, C.L.: Microporous activated carbon prepared from coconut shells using chemical activation with zinc chloride, *Microporous & Mesoporous Materials*, **2007**, **100** (1), 361-364;
6. Aksu, Z., Isoglu, I.A.: Removal of Cu(II) ions from aqueous solutions by Biosorption onto agricultural waste sugar beet pulp, *Process Biochemistry*, **2005**, **40** (9), 3031-3044;
7. Gao, P., Liu, Z.H., Xue, G., Han, B., Zhou, M.H.: Preparation and characterization of activated carbon produced from rice straw by (NH4)2HPO4 activation, *Bioresource Technology*, **2010**, **102** (3), 3645-3648;
8. Deng, H., Yang, L., Tao, G., Dai, J.: Preparation and characterization of activated carbon from cotton stalk by microwave assisted chemical activation – application in methylene blue adsorption from aqueous solution, *Journal of Hazardous Materials*, **2009**, **166** (2-3), 1514-1521;
9. Tsai, W.T., Chang, C.Y., Lin, M.C., Chien, S.F., Sun, H.F., Hsieh, M.F.: Adsorption of acid dye onto activated carbons prepared from agricultural waste bagasse by zinc chloride activation, *Chemosphere*, **2001**, **45** (1), 51-58;
10. Ho, Y.S.: Removal of copper from aqueous solution by tree fern, *Water Research*, **2003**, **37** (10), 2323-2330;
11. Maranon, E.L., Sastre, H.: Heavy metal removal in packed beds using apple wastes, *Bioresource Technology*, **1991**, **38** (1), 39-43;
12. Cleids, S.T., Ara, U.J.O., Carvalho, D.C., Rezende, H.C., Ione, L.S., Coelho, L.M., Coelho, M.N.M., Marques, T.L., Aves, V.N.: Bioremediation of waters contaminated with heavy metals using *Moringa Oleifera* seeds as biosorbent, *Environmental Sciences: Bioremediation-Active and Passive Approaches*, **2013**, **953** (10), 227-255;
13. Kumar, A., Jena, H.M.: High Surface area microporous activated carbons prepapred from foxnut (Euryale Ferox) shell by zinc chloride activation, *Applied Surface Science*, **2015**, **356**, 753-761;
14. Arjmand, C., Kaghazchi, T., Latif, M.S., Soleimani, M.: chemical production of activated carbon from nutshells and data stones, *Chemical Engineering Technology*, **2006**, **29**(1), 986-991;
15. Yusufu, M.I., Ariahu, C., Igbadul, B.D.: Production and characterization of activated carbon from selected local raw materials, *African Journal* of *Pure Applied Chemistry*, **2012**, **6** (9), 123-131;
16. Amhadpour, A., Do, D.D.: The preparation of active carbons from coal by chemical and physical activation, *Carbon*, **1996**, **34**, 471-479;
17. Kin, J., Sohn, H.M., Kim, D.S., Kwon, Y.S.: Production of granular activated carbon from waste walnut shell and its adsorption characteristics for Cu(II) ion, *Journal* of *Hazardous Materials*, **2001**, **85** (3), 301-325;
18. Li, M., Wang, C., O'Connell, M.J., Chan, C.K.: Carbon nanosphere adsorbents for removal of arsenate and selenite from water, *Environmental Science nonamaterial*, **2015**, **2**, 245-250;
19. Awoyale, A.A., Eloka-Eboka, A.C., Odubiyi, O.A.: Production and experimental efficiency of activated carbon from local waste Bamboo for waste water treatment, *International Journal* of *Engineering* and *Applied Science*, **2013**, **3** (2), 8-17;
20. Gang, S., Weixing, S.: Sunflower stalk as adosrbents for the removal of metal ions from wastewater, *Industrial Engineering Chemistry Research*, **1998**, **37** (4), 1324-1328;
21. Badmus, M.A.O., Audu, T.O.K., Anyata, B.U.: Removal of Lead ion from industrial wastewaters by activated carbon prepared from Periwinkle shells (*Typanotonus Fuscatus*), *Turkish Journal Engineering Environmental Science*, **2007**, **31**, 251-263;

22. Singh, C.K., Sahu, J.N., Mahalik, K.K., Mohanty, C.R., Raj Mohan, B., Meikap, B.C.: Studies on the removal of Pb(II) from wastewater by activated carbon developed from Tamarind wood activated with sulphuric acid, *Journal* of *Hazardous Materials*, **2008**, **153** (1), 221-228;
23. Matandabuzo, M.; Remediation of metal ions in aqueous solution using activated carbon from *Zea* mays stem, *MSc Dissertation*, University of Fort Hare, Alice, South Africa, **2016**;
24. Igwe, J.C., Abia, A.A.: A bioseparation process for removing heavy metals from wastewater using biosorbents, *African Journal* of *Biotechnology*, **2006**, **5** (12), 1167-1179;
25. Yakout, S.M., Sharaf El-Deen, G.: Characteristics of activated carbon by phosphoric acid activation of olive stones, *Arabian Journal* of *Chemistry*, **2012**, **12**, 273;
26. Lamley, A., Wagenet, L., Kneen, B.: Activated carbon treatment of drinking water, Ithaca, NY: *Cornell Cooperative Extension*, *Fact Sheet* 3, **2011**;
27. Madu, P.C., Lajide, L.: Physicochemical characteristics of activated carbon derived from melon seed husk, *Journal* of *Chemical Pharmaceutical Research*, **2013**, **5**, 95-98;
28. Igwe, J.C., Abia, A.A.: Adsorption kinetics and intraparticulate diffusivities for bioremediation of Co(II), Fe(II) and Cu(II) ions from wastewater using modified and unmodified maize cob, *International Journal of Physical Science*, **2007**, **2** (5), 119-127;
29. Ioonnidou, O., Zabanitou, A.: A review on agricultural residues as precursors for activated carbon production, *Renewable* and *Sustainable Energy*, **2007**, **11**, 1966-2005;
30. Saeed, A., Akhter, M.W., Iqbal, M.: Removal and recovery of lead(II) from single and multimetal (Cd, Cu, Ni, Zn) solutions by crop milling waste (black gram husk), *Journal* of *Hazardous Materials*, **2005**, **117** (1), 65-73;
31. Aygam, A., Yenisoy, K.S., Duman, I.: Production of granular activated carbon from fruit stones and nutshells and evaluated of their physical, chemical, and adsorption properties, *Microporous Mesoporous Materials*, **2003**, **66** (2-3), 189-195;
32. Aggarwal, D., Goyal, M., Bansal, R.C.: Adsorption of chromium by activated carbon from aqueous solution, *Carbon*, **1999**, **37**, 1989-1997;
33. Bernard, E., Jimoh, A., Odigure, J.O.: Heavy metals removal from industrial wastewater by activated carbon prepared by Coconut shell, *Research Journal* of *Chemical Science,* **2013**, **3** (8), 3-9;
34. Moreno-Pirajan, J.C., Giraldo, L.: Heavy metal ions adsorption from wastewater using activated carbon from Orange peel, *E-Journal* of *Chemistry*, **2012**, **9** (2), 926-937;
35. Mittal, A., Kurup, L., Mittal, J.: Freundlich and Langmuir adsorption isotherms and kinetics for the removal of Tartrazine from aqueous solutions using Hen feathers, *Journal Hazardous Materials*, **2007**, **146**, 243-248;
36. Puzzy, A.M., Poddubnaya, O.I., Matines-Alonso,A., Suarez-Garcia, F., Tascon, J.M.D.: Characterization of synthetic carbon activated with phosphoric acid, *Applied Surface Science*, **2002**, **200**, 196-202;
37. Solum, M.S., Pugmire, R.J., Jagtogen, M., Derbyshire, F.: Evaluation of carbon structure in chemically activated wood carbon, *Carbon*, **1995**, **33**, 1247-1257;
38. Sugumaran, P., Susan, V.P., Ravichndran, P., Seshadri, S.: Production and characterization of activated carbon from Banana empty fruit bunch and *Delonix regia* fruit pod, *Journal Sustainable Energy* & *Environment*, **2012**, **3**, 125-132;
39. Kibami, D., Pongenr, C., Rao, K.S., Sinha, D.: Preparation and characterization of activated carbon from *Fagopyrum esculeuntum* Moench by nitric and phosphoric acids activation, *Pelagia Research Library*, **2014**, **5** (4), 46-55.
40. Won-Chun, O.H., Weon-Bae, B.: Physical properties of K-activated carbon and its removal efficiency for chemical factors, *Journal* of *Industrial* and *Engineering Chemistry*, **2006**, **12** (3), 373-379;
41. Langmuir, I.: The adsorption of gases on plane surfaces of glass, mica and platinum, *Journal* of *American Chemical Society*, **1918**, **40**, 361-1403;
42. Freundlich, H. Z.: Colloid and capillary chemistry, *Physical Chemistry*, **1907**, **57**, 388-470;
43. Mohanty, K., Jha, M., B.C. Meikap, B.C., Biswas, M.N.: Removal of chromium (VI) from dilute aqueous solutions by activated carbon developed from *Terminalla Arjuna* nuts activated with zinc chloride, *Chemical Engineering Science*, **2005**, **60**, 3049-3059;
44. Ketcha, J.M., Dina, D.J.D., Ngomo, H.M., Ndi, N.J.: Preparation & Characterization of activated carbons obtained from maize cobs by zinc chloride activation, *American Chemistry Science Journal*, **2012**, **2** (4), 136-160.