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Heavy Metals Removal from Industrial Wastewater by Activated Carbon Prepared from Coconut Shell

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Abstract

Activated carbon produced from coconut shell (ACS) was used as adsorbent to remove Cu^{2+}, Fe^{2+}, Zn^{2+} and Pb^{2+} ions from electroplating industrial wastewater. The activated carbon produced was chemically activated with zinc chloride. Batch adsorption experiment was conducted to examine the effects of adsorbent dosage, contact time, pH and stirring rate on adsorption of Cu^{2+}, Fe^{2+}, Zn^{2+} and Pb^{2+} from the wastewater. The obtained results showed that, the adsorption of the metal ions was adsorbent dosage, contact time, pH and stirring rate dependent. The optimum adsorbent dosage, stirring rate and pH, were found to be at 1 g, 350 rpm and pH 6 respectively. Kinetic studies showed that pseudo-second-order reaction model best described the adsorption process. The study also showed that activated carbon prepared from coconut shell can be efficiently used as low cost alternative for removal of metal ions.

Keywords: Activated carbon, heavy metals, adsorption, kinetic, wastewater.

Introduction

Wastewater from numerous industries such as paints and pigments, glass production, mining operations, metal plating, and battery manufacturing processes are known to contain contaminate such as heavy metal. Heavy metals such as Pb, Cd, Cr, Ni, Zn, Cu and Fe are present in industrial wastewater, these heavy metals in wastewater are not biodegradable and their existence in receiving lakes and streams causes bioaccumulation in living organisms, which leads to several health problems in animals, plants and human beings such as cancer, kidney failure, metabolic acidosis, oral ulcer, renal failure and damage in for stomach of the rodent[1]. As a result of the degree of the problems caused by heavy metals pollution, removal of heavy metals from wastewater is important[2]. Investigation into new and cheap methods of metal ions removal has been on the increase lately.

Recently efforts have been made to use cheap and available agricultural wastes such as coconut shell, orange peel, rice husk, peanut husk and sawdust as adsorbents[3-5] to remove heavy metals from wastewater[6].

For this research, activated carbon made from coconut shell was used as adsorbent to remove Cu, Fe, Zn and Pb present in electroplating wastewater. Parameters such as pH, stirring speed, adsorbent dosage and contact time, were investigated at 32°C. While the pseudo first-order and pseudo second-order models were used to analyze the kinetic data. The pore structure in activated carbon produced from coconut shell was investigated using Scanning Electron Microscope (SEM).

Material and Methods

Adsorbent Preparation: Coconut shell was obtained from fruits selling source, in Minna, Niger State. The coconut shell was cleaned using tap water to eradicate possible strange materials present in it (dirt and sands). Washed sample material was sun dried for 2-5 days and then crushed with a gun and crusher to reduce the size. 250g of the smaller pieces was carbonized at 400°C for 15mins and then subsequently activated using 1.0 M $ZnCl_2$ at 500°C for two to three hours. The sample was then brought out of the muffle furnace and cooled in a desiccators. It was then washed several times with distilled water until a pH range between 6 and 7 was obtained. The adsorbent was then dried in an oven at 105°C for a period of 24 h[7].

Metal Plating Wastewater: The wastewater sample used was collected from the effluent discharge point of electroplating section of the Scientific Equipment Development Institute (SEDI), Niger State. It was carefully bottled in a plastic container and was immediately taken to the laboratory for analysis.

Analysis: The heavy metals present in the wastewater sample, were analyzed using the atomic-absorption spectrophotometer[8]. It detected the concentrations of Cu^{2+}, Fe^{2+}, Zn^{2+} and Pb^{2+}. The initial concentrations of the metal ions present in the waste water are shown in table 1.

Table-1
Initial concentration of metal ions in wastewater

Heavy metals	Initial concentration (mg/L)
Cu^{2+}	43.500
Fe^{2+}	16.600
Zn^{2+}	17.400
Pb^{2+}	0.005

Characterization of Adsorbent: Scanning electron microscope (SEM) (JSM-5600model) machine was used to check the surface morphology of activated carbon produced from coconut shell.

Adsorption Study: Adsorption experiment was done by measuring 50 mL of the wastewater sample and poured into a 100 mL conical flask. 0.2 g of the previously prepared activated carbon was added to the wastewater. The conical flask containing the adsorbent and the wastewater was placed on a rotary shaker and shook at 150 rpm at a room temperature of (32°C) for a period of 120 min to ensure equilibrium. The suspension was filtered use Whatman filter paper. Atomic adsorption spectro-photometer was used to analyse the concentrations of the different metal ion present in the filtrate[9] (AAS). The amount of metal ions adsorbed by the adsorbent was evaluated using equation (1):

$$q_t = \frac{(C_o - C_t)\,V}{W} \tag{1}$$

The mass balance equation was used to determine the adsorption capacity (q_e) from equation[10] (2):

$$q_e = \frac{(C_o - C_e)\,V}{W} \tag{2}$$

Where, C_o and C_t are the initial and final concentrations of the heavy metals present in wastewater before and after adsorption, for a period of time t (mg/L) respectively: C_e represent the concentrations of heavy metals in wastewater (mg/L) when equilibrium was attained: the volume of wastewater used is represented by V(ml): while W represent the mass (g) of the adsorbent used. The percentage of metal ions removed was obtained from equation[11] (3):

$$R(\%) = \frac{(C_o - C_t) \times 100}{C_o} \tag{3}$$

Where (R %) is the ratio of difference in metal concentration before and after adsorption.

Effect of Contact Time: The effect of contact time on removal of metal ions was studied for a period of 120 min. 0.2 g of the adsorbents (activated carbon from coconut shell) was added to different conical flask containing 50 mL of wastewater, the flask was closed and placed in a rotary shaker, and agitated at 150 rotation per minute (rpm), for each of the different contact times chosen (20, 40, 60, 80,100 and120 minute). The content of each flask was filtered and analyzed after each agitation time[12].

Effect of Adsorbent Dosage: Different dosages of the adsorbents (0.2-1 g) were added in different conical flasks containing 50 mL of wastewater solution, corked and agitated in a shaker for 1 h at a speed of 150 rotations per minute (rpm) at a room temperature of 32°C. The content of each flask was then filtered and analyzed after the agitation time[13].

Effect of pH: Over a pH range of 2-6, the effect of pH on adsorption on metal ions was studied. For this particular study, 50 mL of wastewater was measured into different 250 mL conical flask and 1 g of the activated carbon being the optimum adsorbent from the previous experiment, was added and agitated at 150 rpm for one hour. The pH was adjusted from 2-6 using HCI. The Whatman filter paper was used to filter the mixture and the filtrate analyzed to determine the concentrations of metal ions.

Effect of Shaking Speed: Shaking speed was varied from 150 to 350 rpm, to study the effect of shaking speed on adsorption of metal ions. 1 g of the adsorbents was added to different conical flask containing 50 mL of wastewater sample, corked and agitated in a shaker for a period of 1hr at room temperature of 32°C. The content of each flask was then filtered and analyzed after the agitation time[14].

Kinetic Analysis: By analyzing the adsorptive uptake of heavy metals from wastewater at different time intervals, the kinetics of adsorption was studied. The pseudo-first-order and pseudo-second-order model equations are fitted to model the kinetics of heavy metals adsorption onto activated carbon[15]. The linearity of each model when plotted indicates whether the model suitably described the adsorption process or not. The general expression for pseudo-first-order equation model is shown in equation (3) and (4):

$$\frac{dq_t}{dt} = k(q_e - q_t) \tag{3}$$

The sorption capacities at equilibrium and at time t, are represented by q_e and q_t respectively (mgg^{-1}) and k_1 is the pseudo-first order sorption rate constant (Lmin^{-1}). Applying boundary conditions after integration, from $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the integrated form of equation becomes:

$$\log(q_e - q_t) = \log q_e - \frac{k}{2.303}t \tag{4}$$

The pseudo-second order chemisorption kinetic rate equation[16] is expressed as shown in equation (5):

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{5}$$

The sorption capacities at equilibrium and at time t, are represented by q_e and q_t (mgg^{-1}) respectively and k_2 is the rate constant of the pseudo-second order sorption (g.mg^{-1}.min^{-1}).

Results and Discussion

Effect of Contact Time on Adsorption of Heavy Metals: The relationship between contact time and the percentage removal of heavy metals from wastewater with activated carbon produced from coconut shell is shown in figure-1. The effect of contact time was studied at a room temperature of 32 °C, at intervals of 20 min. From the obtained result, it is evident that the removal of metal ions increased as contact time increases. Pb^{2+}, Fe^{2+}, $Cu^{2+}$and Zn^{2+} were removed using the produced adsorbent. The percentage metal ions removal approached equilibrium within 40 min for Pb (II), 80 min for both Fe (II) and Cu (II) and 60min for Zn(II);with Pb (II) recording 100% removal, Fe (II) 76.02% ,Cu(II) 71.26% and Zn(II) 26.15% removal. Having a trend of $Pb^{2+}>Fe^{2+}>Cu^{2+}>Zn^{2+}$, after which further increase in time did not bring about any further improvement for the metal ions, but resulted in desorption of some of the metal ions (zinc and copper) from the adsorbent surface. This experiment shows that the different metal ions attained equilibrium at different times.

Effect of Adsorbent Dosage: The availability and accessibility of adsorption site is controlled by adsorbent dosage[17]. Adsorbent dosage was varied from 0.2 g to 1 g, under the specific conditions (initial pH of 2, contact time of 80min, 150 rpm shaking speed and at room temperature of 32 ^oC). Figure-2, shows that increased adsorbent loading increased the metal ions percentage removal. The removal of Pb(II) attained maximum removal even at a lower adsorbent dosage of 0.2 g with 100% removal, increase in adsorbent dosage, also increased the percentage removal of Fe(II) until mass of the adsorbent reached 1 g, with 84.10% removal, while maximum removal of Cu(II) and Zn (II) was attained at 0.8 g with 78.16% and 34.77% removal of metal ions respectively, after which further increase in adsorbent dosage, brought no increase in adsorption, which was as a result of overlapping of adsorption sites due to overcrowding of adsorbent particles[18]. Hence 1 g was chosen as the optimum adsorbent dosage for removal of Cu (II), Fe (II) and Zn (II) metal ions and for further investigation of the work.

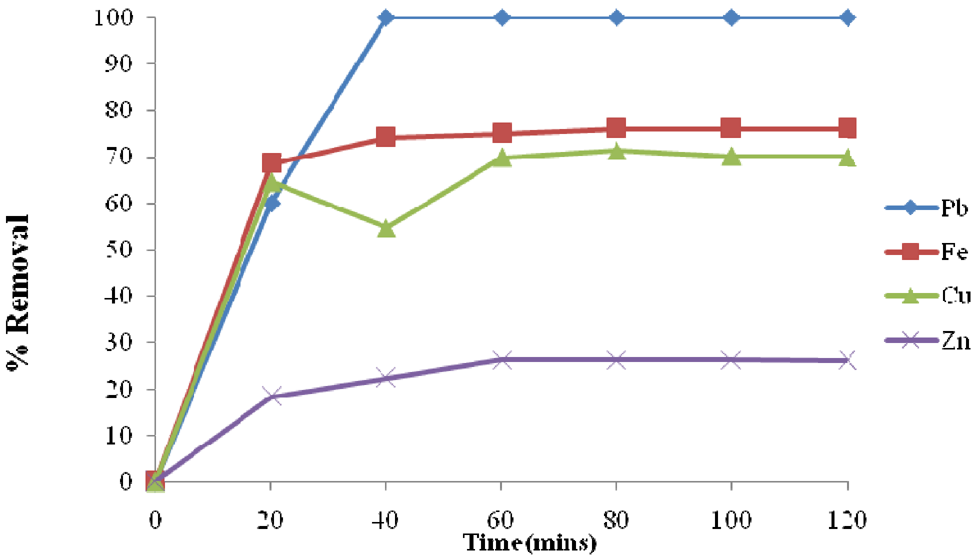

Figure-1
Effect of contact time on adsorption of heavy metals by activated carbon from coconut shell (pH =2, agitation speed =150 rpm, Mass =0.2 g and Temp = 32 ^oC)

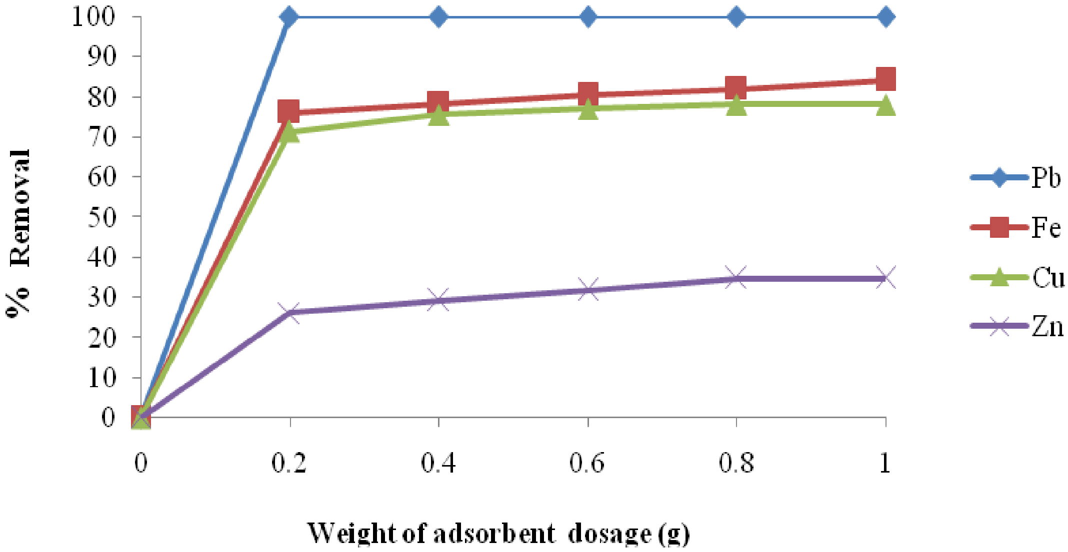

Figure-2
Effect of adsorbent dosage on the adsorption of heavy metals by activated carbon from coconut shell (Time =80 min, pH =2, agitation speed =150 rpm and Temp = 32^oC)

Effect of pH on Adsorption of Heavy Metals: The pH of the wastewater is one of the imperative factors governing the adsorption of the metal ions. The effect of pH was studied from a range of 2 to 6 under the precise conditions (at optimum contact time of 80 min, 150 rpm shaking speed, with 1 g of the adsorbents used, and at a room temperature of 32 ^oC). From Figure-3, with activated carbon from coconut shell used as adsorbent, it was observed that with increase in the pH (2-6) of the wastewater, the percentage removal of metal ions (iron, copper and zinc) all increased up to the pH 6 as shown above. At pH 6, maximum removal were obtained for all the three metal ions, with 88.07% removal of Fe (II), 84.29% of Cu(II) and 45.40% removal of Zn(II). While 100% removal of Pb (II) ion was achieved even at a low pH of 2 because of the low concentration of Pb (II) ion present in the wastewater. The increase in percentage removal of the metal ions may be explained by the fact that at higher pH the adsorbent surface is deprotonated and negatively charge; hence attraction between the positively metal cations occurred[19].

Effect of Shaking Speed on Adsorption of Heavy Metals: The effect of shaking speed was investigated under the specified conditions (at optimum contact time of 80 min, 150 rpm shaking speed, with 1 g of the adsorbents used, at pH 6 and at a room temperature of 32 ^oC) with activated carbon from coconut shell used as adsorbent; it was observed that increase in shaking speed from 150 to 350 rpm of the wastewater, the percentage removal of metal ions (iron, copper, and zinc) increased up to 350 rpm as shown in figure -4. Hence at a shaking speed of 350 rpm, maximum recoveries were obtained for all the three metal ions, with 93.37% removal of Fe (II), 92.22% of Cu (II) and 60.52 % removal of Zn (II). Also Pb (II) attained maximum removal of 100% at a lower shaking speed of 150 rpm. The increase in shaking speed resulting to increase in metal ions percentage removal, was due to the fact that, increase in stirring rate enhanced the metal ions diffusion to the surface of the adsorbent; and also caused reduction in the film boundary layer around the adsorbent.

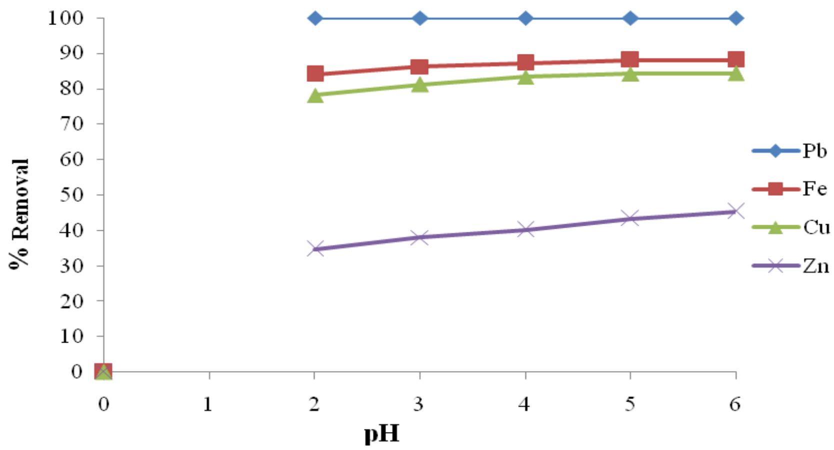

Figure-3
Effect of pH on the adsorption of heavy metals by activated carbon from coconut shell (Time = 80 min, agitation speed =150 rpm, Mass =1 g and Temp = 32 ^oC)

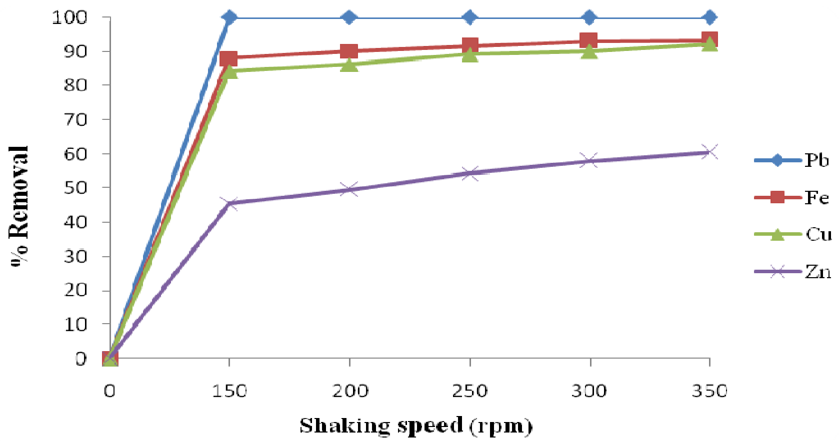

Figure-4
Effect of shaking speed on the adsorption of heavy metals by activated carbon from coconut shell (Time=80 min, pH=6, Mass =1 g and Temp = 32 ^oC)

Adsorption Kinetics: From the results of the fitted data, in figure-5 and figure-6, it is clear that pseudo-second-order reaction model (Ho model) yield very good straight line compared to the pseudo-first-order reaction model, which was significantly scattered (non linear). Also the theoretical (calculated) value of q_e of, pseudo-second-order reaction model, are closer to the experimental value of $q_{e,}$ for instance the calculated value of q_e of Fe(II) was 3.226 mgg^{-1}, which is in close agreement with the experimental value of 3.155 mgg^{-1}, compared to Fe(II) of pseudo-first-order reaction model, with calculated value of 47.619 mgg^{-1}, which differ greatly from the experimental value of 3.155 mgg^{-1}. These fact suggest that the adsorption of heavy metals by activated carbon from coconut shells follows the pseudo-second-order reaction model, which was as a result of chemisorptions. In chemisorption (chemical adsorption), the heavy metals stick to the adsorbent surface by forming a chemical (usually covalent) bond and tend to find sites that maximize their coordination number with the surface[20].

Surface Morphology: Scanning Electron Microscope (SEM) was used to observe the pore structure of the activated carbon. Pores present in activated carbon act as the active sites, where adsorption take place. The Scanning Electron Microscope images of activated carbon produced from coconut shell activated using zinc chloride ($ZnCl_2$) are shown in figure-1and figure-2 at 31 and 200 magnifications. SEM photograph showed that wide varieties of pores are present in the activated carbon which is more visible at 200 magnifications.

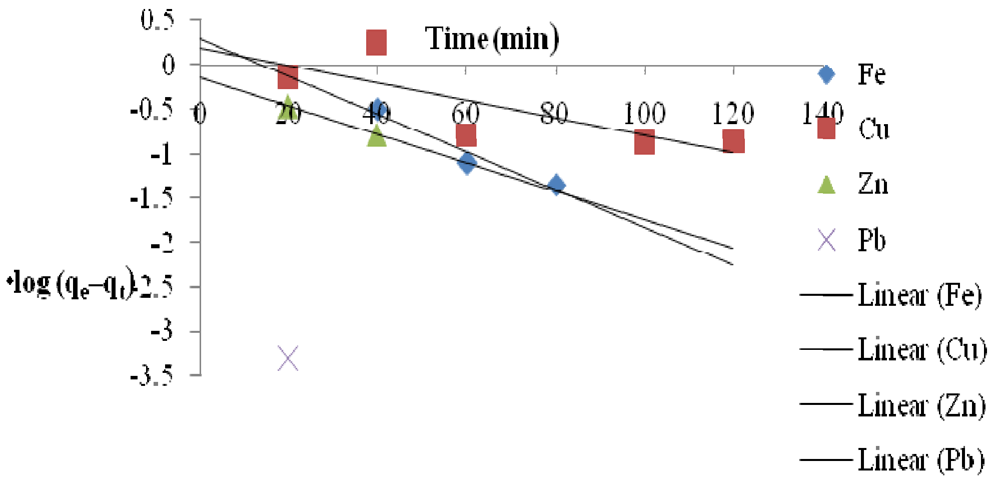

Figure-5
Pseudo-first-order reaction model for adsorption of heavy metals on activated carbon from coconut shell

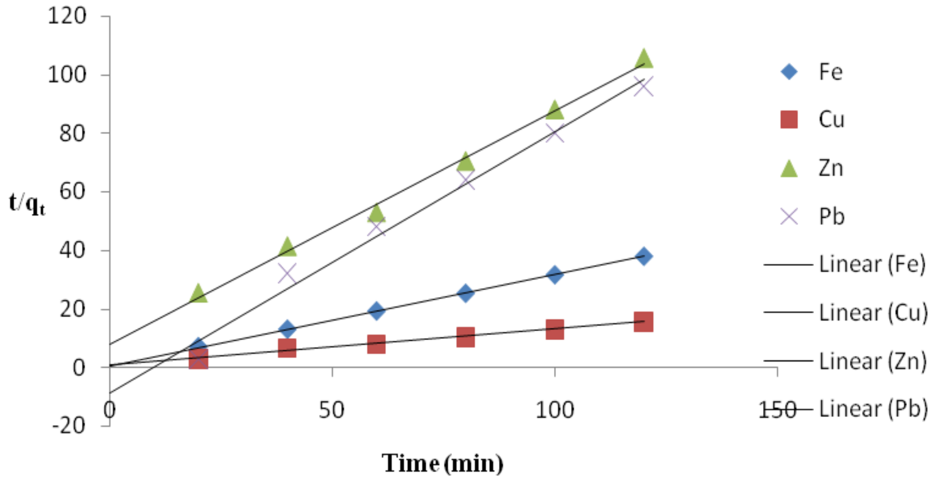

Figure-6
Pseudo-second-order reaction model for adsorption of heavy metals on activated carbon from coconut shell

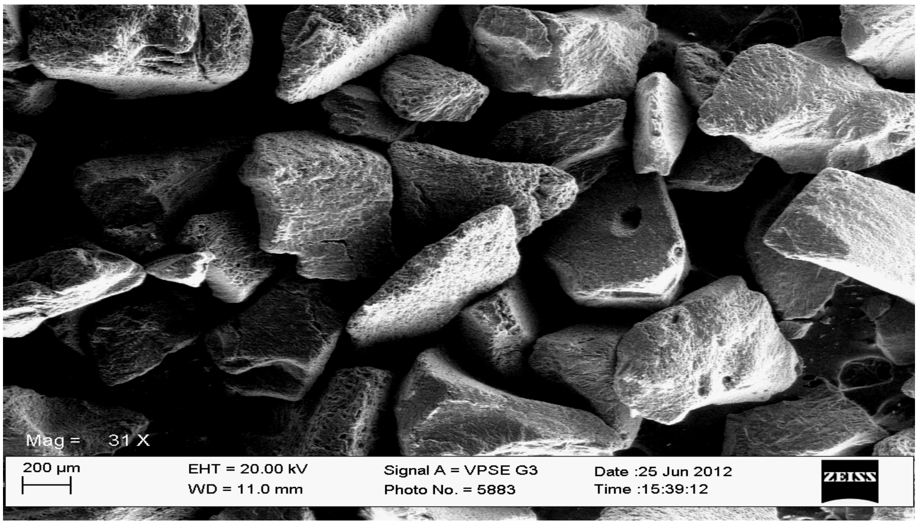

Figure-7
SEM image of activated carbon from coconut shell using zinc chloride ($ZnCl_2$), at 31 ×

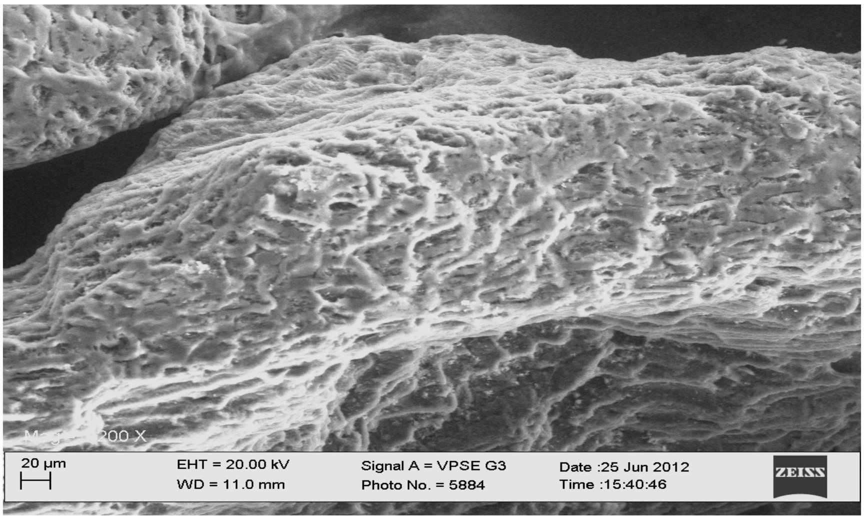

Figure-8
SEM image of activated carbon from coconut shell using zinc chloride ($ZnCl_2$), at 200 ×

Conclusion

From the obtained results, it is evident that activated carbon produced from coconut shell is a good adsorbent for removal of lead, iron, copper and zinc ions. Batch experiments were conducted and showed that the adsorption of lead, iron, copper and zinc ions are time dependent, adsorbent dosage dependent, pH dependent, and stirring speed dependent. Coconut shell (a waste) is inexpensive and readily available, thus this study provide a cost effective means for removing metal ions from contaminated water or effluents.

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