

## ADSORPTION OF Pb, Fe, Cu, and Zn FROM INDUSTRIAL ELECTROPLATING WASTEWATER BY ORANGE PEEL ACTIVATED CARBON

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### ABSTRACT

*The ability of activated carbon produced from orange peel (AOP) to adsorb Pb(II), Fe(II), Cu(II), and Zn(II) ions from electroplating industrial wastewater has been investigated through batch experiment. Batch adsorption studies was conducted to examine the effects of contact time, adsorbent dosage and pH on adsorption of Pb(II), Fe(II), Cu(II), and Zn(II) from the wastewater. The results obtained shows that, the adsorption of the metal ions is contact time, adsorbent dosage and pH dependent. The optimum contact time, adsorbent dosage and pH are found to be at 60min, 1 g and pH 6 respectively; for the activated carbon used (AOP). Kinetic studies show that pseudo-second-order reaction model best describes the adsorption process. The goal for this work is to develop inexpensive, highly available, effective adsorbents from orange peel as alternative to existing commercial adsorbents.*

**Keywords:** Adsorption, Activated carbon, Cu(II), Fe(II), Zn(II) and Pb(II), Kinetic, Wastewater

### 1.0 INTRODUCTION

Effluents from various processing industries such as electroplating industries is reported to contain high amounts of heavy metal ions, such as nickel, iron, lead, zinc, chromium, cadmium and copper (Konstantinos *et al.*, 2011). The presence of these heavy metals in industrial wastewaters is of serious concern because they are highly toxic, nonbiodegradable, carcinogen, and continuous deposition into receiving lakes, streams and other water sources within the vicinity causes bioaccumulation in the living organisms. These perhaps, could lead to several health problems like cancer, kidney failure, metabolic acidosis, oral ulcer, renal failure and many more (Booker., 2000). Effluent from electroplating industry is on serious concern because just about 30-40% of the metals used during plating processes are effectively utilized i.e. plated on the articles. The remaining percentage of the metals contaminates the rinsing waters used during electroplating process. The rinse waters used during electroplating process contains about 1000 mg/L toxic heavy metals,

which must be controlled to an acceptable level, in accordance to environmental regulations worldwide, before being discharged to the environment (Konstantinos *et al.*, 2011). Due to different degree of hazardous problems associated with heavy metals pollution, treatment of affected wastewater is very essential in order to allow human and industrial effluents to be disposed off without bringing about any of the mentioned associated dangers to human health, aquatics lives or causing avoidable damage to the natural environment (Li *et al.*, 2006).

Several treatment methods have been suggested, developed and used to remove heavy metals from wastewaters. These methods include chemical precipitation, ion exchange, cementation (Dean *et al.*, 1972), coagulation and flocculation (Amuda *et al.*, 2006) and membrane processes (Aydiner *et al.*, 2006). However, these techniques have been reported to be very expensive, making its adoption and application in a developing country like Nigeria very unrealistic. Ideally, heavy metals removal processes are expected to be simple, effective

and inexpensive. Investigation into new and cheap methods of metal ions removal from industrial wastewater is gaining continuous research attention, with adsorption process suggested has most economically viable method. Thus, this study intends to use adsorption process for heavy metals removal from industrial effluents because it has been reported to be inexpensive, widely applicable, efficient, and creates relatively little sludge (Kannan and Rengasamy, 2005).

Adsorption is one of the most useful methods to remove heavy metals from industrial effluents. This method explores the availability of different kinds of adsorbents associated with convenient procedures for obtaining high efficiency (Harland, 1994; Cooney, 1999). A large number of different adsorbent materials containing a variety of attached chemical functional groups have been reported for this purpose with activated carbon being the most popular material, however, its high cost restricts its large-scale use (Babel and Kurniawan, 2003; Bailey *et al.*, 1999).

Based on both environmental and the economical points of view, special attention has been focused on the use of natural adsorbents obtained from natural materials and waste agricultural products as an alternative to replace commercial activated carbon. The abundance and availability of agricultural by-products make them good sources of raw materials for natural sorbents.

In this paper, orange peel was treated with  $ZnCl_2$  solution to produce a carbonaceous adsorbent, which was subsequently used to treat effluent

obtained from electroplating industries. The capacity of the produced adsorbent to adsorb heavy metals like  $Pb(II)$ ,  $Fe(II)$ ,  $Cu(II)$ , and  $Zn(II)$  from the effluent with emphasis on the effects of contact time, adsorbent dosage, pH and stirring rate was carried out.

## 1.1 MATERIALS AND METHODS

### 1.1.1 Adsorbent preparation:

Agricultural waste used in this study is orange peel from orange fruit. The fruit was obtained from fruits selling source, in Minna, Niger State. The Orange was first peeled off to obtain the outer skin of the fruit and then removal of the inner fleshy layer after squeezing off the juice. The peel was washed with ordinary tap water to remove possible foreign materials present (dirt and sands). Washed sample material was sun dried for 2-5 days and then crushed with a mortar and pestle to reduce the size. 250g of the small pieces was carbonized at  $400^\circ C$  for 15mins and then subsequently activated using 1.0 M  $ZnCl_2$  at  $500^\circ C$  for two to three hours. The sample was then withdrawn from the furnace and cooled in a desiccator. After cooling, the sample was rinsed several times with distilled water until obtaining flushing water whose pH range between 6 and 7. The wet sample was dried at  $105^\circ C$  during 24 h (Gueu *et al.*, 2007).

### 1.1.2 Industrial effluent sample:

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 taken to the laboratory for analysis. The initial concentrations of the metal ions present in the waste water are shown in Table 1.

**Table1: Initial concentration of metal ions in waste water**

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

Pb<sup>2+</sup>

0.005

### 1.1.3 Adsorption experiment

Adsorption experiment was carried out in 100 mL conical flask containing 50 mL of wastewater. 0.2 g of the previously prepared activated carbon was added to the solution. The mixture was shaken on a rotary shaker at 150 rpm at room temperature (25 °C) for period of 120 min to ensure equilibrium. The suspensions were filtered and the concentrations of metal ions

$$q_t = \frac{V(C_o - C_t)}{M}$$

(1)

The adsorption capacity ( $q_e$ ) was determined using the mass balance equation (Horsfal 1 *et al.*, 2006; Zulkali *et al.* 2006).

$$q_e = \frac{V(C_o - C_e)}{M}$$

(2)

Where;  $C_o$  is the initial metal ions concentration,  $C_e$  is the concentration of metal ions in solution (mg/L) at equilibrium,  $C_t$  is the concentration of metal ions in solution (mg/L) at time,  $t$  in solution,  $V$  is volume of initial metal ions solution used (L) and  $M$  is mass of adsorbent used (g).

### 1.1.5 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 sample, corked and agitated in a shaker at 150 rpm, for different contact times (20, 40, 60, 80, 100 and 120 minute). After each agitated time, the content of each flask was then filtered and analyzed (Ekpet *et al.*, 2010).

### 1.1.6 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

in the filtrate were analyzed using the atomic adsorption spectro-photometer (AAS) (Chowdhury *et al.*, 2010)

### 1.1.4 Data analysis

The amount of metal ion ( $q_t$  at time  $t$ ) adsorbed per unit mass of the adsorbent was evaluated by using the following equation:

agitated in a shaker at 150 rpm for 1 h at room temperature. After the agitated time, the content of each flask was then filtered and analyzed (Onyeji and Aboje, 2011).

### 1.1.7 Effect of pH

The effect of pH on adsorption of metal ions was analyzed over the pH range from 2-6. In this study, 50 mL of wastewater solution 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 HCl. The solution was filtered using Whatman filter paper and the residual metal ions concentration analyzed (Onyeji and Aboje, 2011).

## 1.2 KINETIC ANALYSIS

The kinetics of adsorption was determined by analyzing adsorptive uptake of heavy metals from the waste water at different time intervals. The pseudo-first-order and pseudo-second-order model equations are fitted to model the kinetics of heavy metals adsorption onto activated carbon. The linearity of each model when plotted indicates whether the model suitably described the adsorption process or not. The pseudo-first-order equation is generally expressed as:

$$\log(q_e - q_t) = \log q_e - \frac{k}{2.303} t \quad (3)$$

Where  $q_e$  and  $q_t$  are the sorption capacities at equilibrium and at time  $t$ , respectively ( $\text{mgg}^{-1}$ ) and  $k_1$  is the rate constant of pseudo-first order sorption ( $\text{Lmin}^{-1}$ ).

The pseudo-second order chemisorption kinetic rate equation (Ho and Mckay, 1998a, b; Ho, 2004) is expressed as:

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

Where  $q_e$  and  $q_t$  are the sorption capacity at equilibrium and at time  $t$ , ( $\text{mgg}^{-1}$ ) respectively and  $k_2$  is the rate constant of the pseudo-second order sorption ( $\text{g.mg}^{-1}.\text{min}^{-1}$ ).

### 1.3 SURFACE MORPHOLOGY

The pore structure in activated carbon from orange peel was observed using Scanning Electron Microscope (SEM). Pores development in an activated carbon is important since pores act as active sites which played the main role in adsorption. Pores formed on surface of adsorbent are sites for metals to be adsorbed onto the adsorbent.

### 1.4 RESULTS AND DISCUSSION

#### Optimization of Adsorption Parameters:

Adsorption parameters such as contact time, adsorbent dosage and pH have immense effect on the heavy metal removal efficiency of an adsorbent. So these were optimized one by one keeping others constant.

#### Effect of contact time on adsorption of heavy metals:

From Figure1, with activated carbon produced from orange peel used as adsorbent. Pb (II), Cu(II) and Zn(II) all attained equilibrium within 60 min and 40 min for Fe(II). With Pb (II) recording 100 % removal, Cu(II) 51.47 %, Zn(II) 20.12 % and 56.63 % Fe(II) removal. After which further increase in time did not bring about any further improvement of the metal ions.

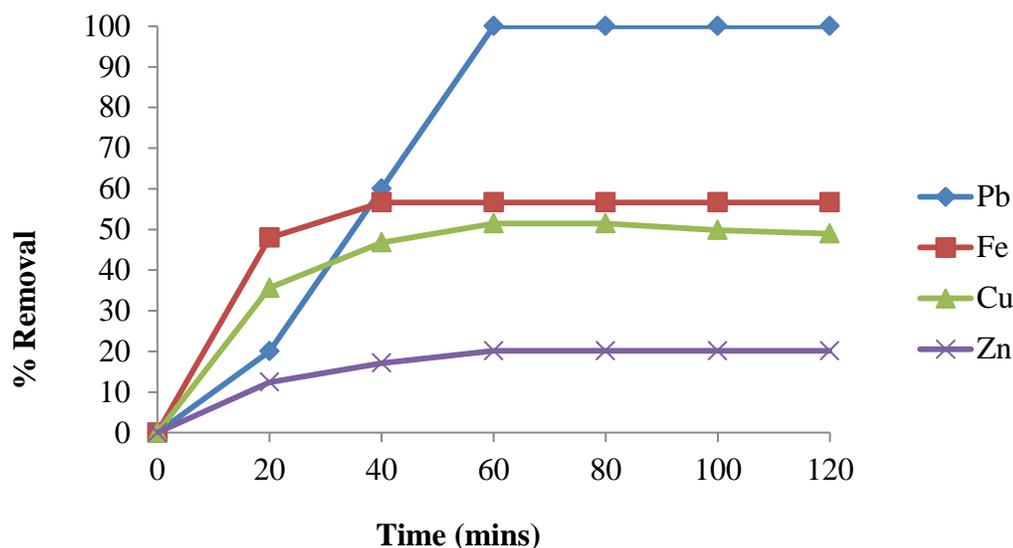


Figure 1: Effect of Contact Time on the Adsorption of Heavy Metals by Activated Carbon from Orange Peel (pH =2, Agitation Speed =150 rpm, Mass =0.2 g and Tem =32 °C)

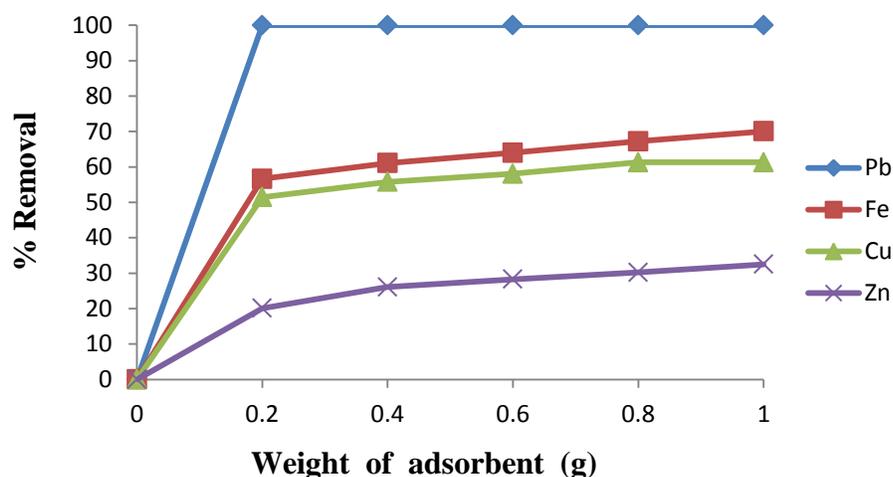


Figure 2: Effect of Dosage on the Adsorption of Heavy Metals by Activated Carbon from Orange Peel (Time = 60 min pH =2, Agitation Speed =150 rpm and Tem =32 °C).

The effect of adsorbent dosage with activated carbon produced from orange peel used as adsorbent for removal of heavy metals is shown in Figure 2, this shows that increased adsorbent loading increased the percentage removal of metal ions. The removal of Pb (II) attained maximum removal, even at a lower adsorbent dosage with 100 % removal, increase in adsorbent dosage also increased the percentage removal of both Fe (II) and Zn (II) until mass of the adsorbent reached 1 g with 70.06 % and

32.53 % respectively, while maximum removal of Cu (II) was attained at 0.8 g with 61.29 % removal, further increase in dosage did not bring about increase in adsorption. Hence 1 g was chosen as the optimum adsorbent dosage for removal of the Fe (II), Zn (II) and Cu (II) for further investigation of the work. Higher dosage of adsorbent increased the adsorption due to more surfaces and functional groups been available on the adsorbent (Esposito *et al.*, 2001).

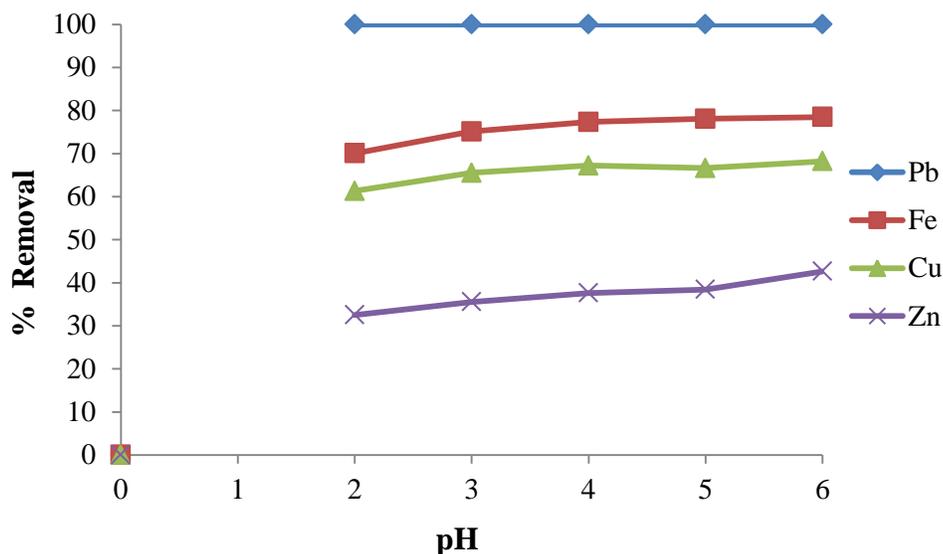


Figure 3: Effect of pH on the Adsorption of Heavy Metals by Activated Carbon from Orange Peel (Time = 60 min, Agitation Speed =150 rpm, Mass =1 g and Temp = 32 °C)

From Figure 3, with activated carbon from orange peel used as adsorbent, it was observed that with increase in the pH (2-6) of the waste water, the percentage removal of metal ions (iron, copper and zinc) all increased up to pH 6 as shown above. At pH 6, maximum recoveries

were obtained for all the three metal ions, with 78.49 % removal of Fe (II), 68.21 % of Cu (II) and 42.64 % removal of Zn (II), while 100 % removal of Pb(II) ion was obtained even at a low pH of 2.

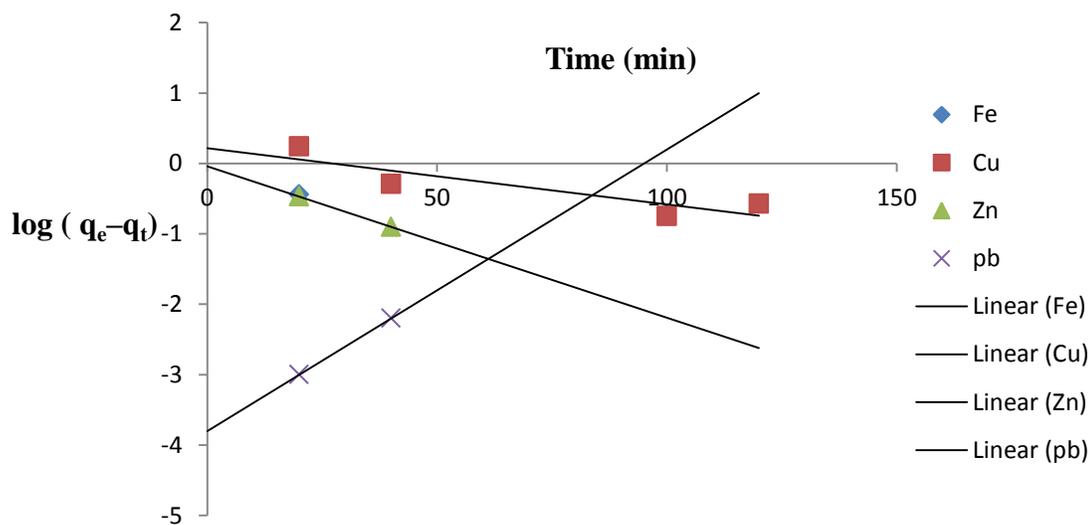


Figure 5: Pseudo-First Order Reaction Model for Adsorption of Heavy Metals on Activated Carbon from Orange Peel

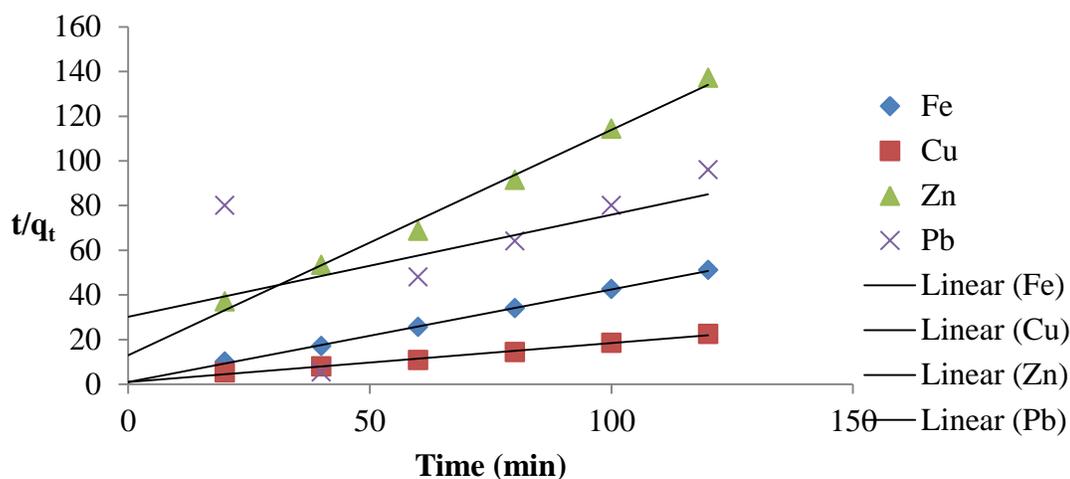


Figure 6: Pseudo-Second Order Reaction Model for Adsorption of Heavy Metals on Activated Carbon from Orange Peel

From the results of the fitted data, in Figure 5 and 6, show that pseudo-second-order reaction model (Ho model) yield very good straight line compared to the pseudo-first-order reaction model, which is 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  $q_e$  as shown in Table 2. For instance the calculated value of  $q_e$  of Cu(II) was  $5.74 \text{ mgg}^{-1}$ , which is in close agreement with the experimental value of  $5.598 \text{ mgg}^{-1}$ , compared to Cu(II) of pseudo-first-order reaction model, with calculated value  $125.000$

$\text{mgg}^{-1}$ , which differ greatly from the experimental value of  $5.598 \text{ mgg}^{-1}$ . These facts suggest that the adsorption of heavy metals by activated carbon from orange peels follows the pseudo-second-order reaction model, which relies on the assumption that chemisorption may be the rate-limiting step. In chemisorption, 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 (Atkins, 1995).

**Table 2: Coefficient of Empirical Kinetic Models for Activated Carbon from Orange Peel**

Pseudo-second-order reaction model				Pseudo-first-order reaction model	
Adsorbent	Metal ions	$q_{e,cal}$	$q_{e,exp}$	$q_{e,cal}$	$q_{e,exp}$
AOP	$\text{Fe}^{2+}$	2.416	2.350	-	2.350
AOP	$\text{Cu}^{2+}$	5.747	5.598	125.000	5.598
AOP	$\text{Zn}^{2+}$	0.992	0.875	47.619	0.875
AOP	$\text{Pb}^{2+}$	0.002	0.001	25	0.001

### Surface Morphology

The Scanning Electron Microscope images of activated carbon produced from orange peel

produced using zinc chloride ( $\text{ZnCl}_2$ ) is shown in figure 7 at 200 magnification. SEM photograph shows that wide varieties of pores are present in the activated carbon.

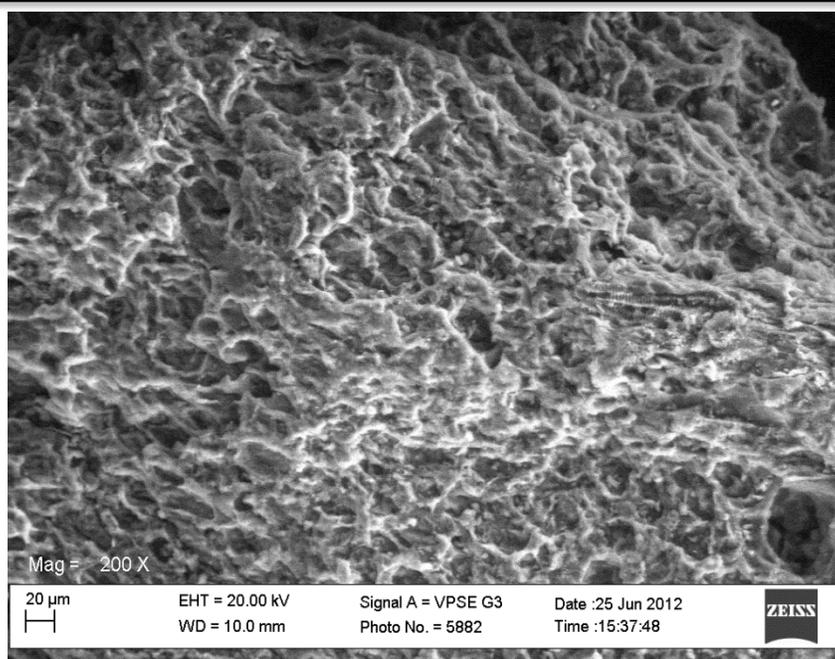


Figure 7: SEM Image of Activated Carbon from Orange Peel using Zinc Chloride ( $ZnCl_2$ ), at X 200

### 1.5 Conclusion

This study showed that a good adsorbent for the removal of Pb (II), Fe (II), Cu (II), and Zn (II) from wastewater of electroplating factory can be obtained from activated carbon prepared from orange peel. Batch experiments were conducted and showed that the adsorption of Pb (II), Fe (II), Cu (II), and Zn (II) are time dependent, pH dependent and adsorbent dosage dependent. Orange peel (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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