

# Cu<sup>2+</sup> removal from aqueous solution by *Platanus orientalis* leaf powders

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**Abstract**— An investigation steered to ascertain the adsorption potential of fallen *Platanus orientalis* leaf powder (FPOLP) as cost-effective adsorbent to remove Cu<sup>2+</sup> from an aqueous solution. The FPOLP was physically activated in two different forms (oxidation) and (N<sub>2</sub>) flow conditions. Batch operations for Cu<sup>2+</sup> adsorption were performed to ascertain adsorption characteristics of FPOLP and activated samples. The results indicated that the optimum activation temperature and time were 500 °C and 180 min, respectively, while the best Cu<sup>2+</sup> removal was achieved when the solution was controlled at pH 3 and the adsorbent dosage at 3 g/L. Additionally, an evaluation of the mechanism of adsorption fitted very well into pseudo-second-order. FTIR, scanning electron microscopy and BET measurements suggested that the new functional groups and the increased surface area related to the porous structure played a critical role in Cu<sup>2+</sup> removal by the activated leaf powder. FPOLP has a great potential to remove Cu<sup>2+</sup> in an aqueous solution.

**Keywords**— *Platanus orientalis* leaf; Cu<sup>2+</sup>; kinetics; isotherms; adsorption.

## I. INTRODUCTION

Industrialization certainly has come with many associated challenges and consequences, some of which include environmental pollution. Heavy metals pollution, as one of the contributory factors to the unending environmental contamination, has attracted global concerns in the past few decades (Özer et al. 2004). Among the wide range of pollution, wastewaters which contain heavy metals such as copper end up being discharge into the environment without appropriate and adequate treatments, resulting in severe environmental pollution (Argun et al. 2008). In addition, the pollution is coupled with increasing demand for freshwater, e.g. global water demand is estimated to increase by 55% as a result of industrialization and domestic use by 2050 (UN Water 2015). Copper, as a very valuable metal used in our daily lives such as pipes, valves and fittings (WHO 2010). However, the process of its

exploitation and refining result in the emission of sulfur dioxide gases (SO<sub>2</sub>) into the atmosphere. This phenomenon poses health hazards to humans like capillary damage, irritation, mucosal and hepatic (Yao et al. 2010, Solomon 2009, Zeitoun et al. 2014).

Based on World Health Organization's guidelines, when copper (Cu) concentration exceeds 1 mg L<sup>-1</sup> in drinking water, it becomes unsafe for humans (Gorchev and Ozolins 2011). In the manufacturing companies or industries, Cu effluents concentration above 3.0 mg L<sup>-1</sup> are not safe for discharge (Robert O. Pickard 2011), however not much has been achieved in terms of a viable and safe disposal method for Cu sludge. Therefore, it is very necessary to find effective remedies to curtail the risks associated with this problem. When Cu sludge is appropriately treated before discharge, it will prevent possible pollution of freshwater bodies or the environment. In the past few decades, several attempts aim at finding harmonious solution to the problems of wastewater purification have been made by a number of research works. The adopted approaches include but not limited to chemical precipitation ((USEPA 2013), reverse osmosis (Kurniawan et al. 2006), membrane filtration (Juang and Shiau 2000) and adsorption (Chen et al. 2010). Among the various methods listed, adsorption techniques appear to have comparative advantage over other techniques, these include high efficiency, environmentally friendly, simple operation, minimum complication (Sohn and Kim 2005). These merits make adsorption more suitable for wastewater treatment (Koumanova and Allen 2005, Erdem et al. 2004, Anagement 2014).

The use of waste materials (Wang and Guo 2011) and agricultural by-products (Venkata Ramana et al. 2012) for use as adsorbents to treat heavy metals is increasingly gaining attention, such as Neem leaves (Ibrahim and Sani 2015), (Nwabanne and Igbokwe 2012), bael leaves (Chakravarty et al. 2010), *Platanus orientalis* leaves (Abadian et al. 2015), teak leaves (Goswami et al. 2013) and *Elaeis guineensis* leaves (Soliman et al. 2016). Large quantities of waste (litter) from *Platanus orientalis*

are generated worldwide, most particularly in South-East Europe, Asia and Northern Iran, during winter season. This results in significant disposal challenges due to the sheer amount of waste generated from shed leaves.

The focus of this research is to use the un-activated (FPOLP) and activated (AC) leaf powder of *Platanus orientalis* to investigate the uptake of  $\text{Cu}^{2+}$  from the aqueous medium. The kinetics and mechanisms involved in the adsorption are subsequently discussed thoroughly.

## II. METHODS AND EXPERIMENTAL MATERIALS

### 2.1. Materials and chemicals

Samples of *Platanus orientalis* leaves (Fig. 1a) were obtained in December 2015, during pre-winter season from the West Mafangshang Campus of Wuhan University of Technology, Wuhan, Hubei Province, China. The dry leaves were

carefully cleaned using deionized water produced from Milli-Q Direct 16 distillation machine with Vent Filter MPK01, and oven-dried. An amount of 300 grams of these leaves were roughly crushed, washed using deionized water several times to purify the sample. Subsequently, the leaves were put in 101-1AB, manufactured by Tianjin Taisite Instrument Co. Ltd at 80 °C for 48 h to improve its brittleness. The dried samples were then crushed into fine powder smaller than 75  $\mu\text{m}$  using a mechanical grinder (RK/XPM – Ø 120 × 3, Wuhan Rock Comminution Instrument Co., Ltd). The leaf powder was repeatedly washed until its turbidity disappeared. After that, the mixture was decanted and filtered followed by another 24 h drying at 80 °C. The processed sample was kept in a moisture-free apparatus for use.

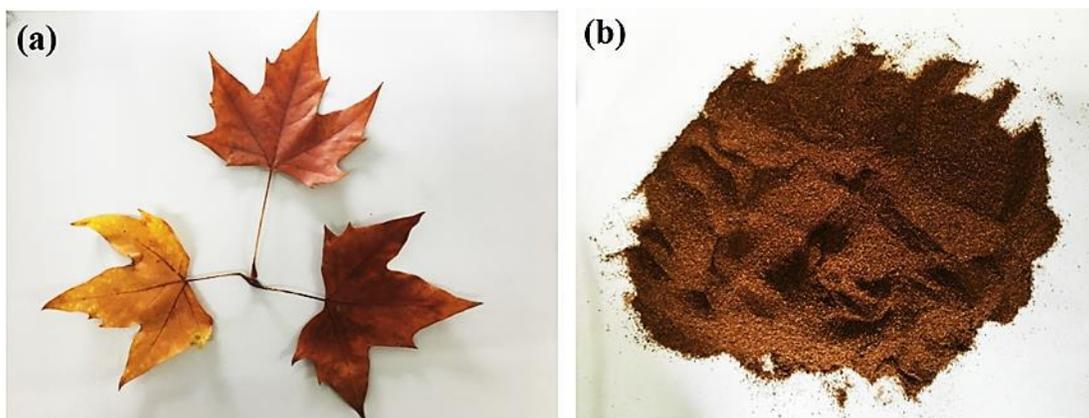


Fig. 1. (a) Leaves of fallen *Platanus orientalis* from West Mafangshang Campus, Wuhan University of Technology, Wuhan, Hubei province, China, and (b) ground FPOLP powder from (a).

A stock  $\text{Cu}^{2+}$  solution was prepared via  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , dilutions were made to meet the designed concentrations for the adsorption. Other chemicals used in the investigation were nitric acid ( $\text{HNO}_3$ ), hydrochloric acid ( $\text{HCl}$ ), potassium nitrate ( $\text{KNO}_3$ ), potassium bromide ( $\text{KBr}$ ), sodium hydroxide ( $\text{NaOH}$ ), ammonium citrate tribasic ( $\text{C}_6\text{H}_{17}\text{N}_3\text{O}_7$ ), ammonia solution ( $\text{NH}_3 \cdot \text{H}_2\text{O}$ ), ethanol absolute ( $\text{CH}_3\text{CH}_2\text{OH}$ ) and bis (cyclohexanone) oxalyldihydrazone (BCO) and neutral red. All the above chemicals and reagents listed were of standards, produced by China Sinopharm company,

### 2.2 Sample activation

Powdered FPOLP samples were physically activated at different temperatures of 300, 400, 500 and 600 °C for different time intervals at 60, 180 and 300 min, respectively, using both muffle furnace (SX2-5-12, Hubei Yingshan Jianli Electric Furnace Co., Ltd) and electric tube furnace (SK-

G06123K, Tianjian Zhonghuan Exp. Electric Furnace Co., Ltd). An amount of 40 g sample was activated (oxidation) and labeled as AC1 and another (under nitrogen) flow labeled as AC2, respectively. The samples were kept in crucibles and covered appropriately before carbonization to avoid direct contact of heat with samples.

### 2.3 Adsorption series

Different concentrations 25, 50, 75 and 100  $\text{mg L}^{-1}$  were examined with varied adsorbent load 1, 2, 3 and 4  $\text{g L}^{-1}$ . A fixed volume of 25 mL of various concentrations were put into 250 mL conical flask each to conduct the experiment. The preliminary pH of all solutions were accustomed in the range of 2 – 4 by adding either diluted  $\text{NaOH}$  or  $\text{HCl}$ . At each time, the explored mixtures were shaken in the thermostatic shaker bath (BS-S, Guohua Electrical Appliance Co., Ltd) at 150 rpm at designed temperatures for

120 min. After that, the suspensions were then filtered and both the adsorbate and residue used for subsequent analysis. The experimental kinetics regarding the amount of  $\text{Cu}^{2+}$  ions adsorbed  $q_s$  at a given period  $s$  ( $\text{mg g}^{-1}$ ) were evaluated by employing the following relationship:

$$q_s = V \frac{(C_0 - C_t)}{w_t} \quad (1)$$

where the parameters are initial concentration  $C_0$  and  $\text{Cu}^{2+}$  concentration  $C_t$  ( $\text{mg L}^{-1}$ ) at a given period  $s$  respectively, Volume of  $\text{Cu}^{2+}$  ( $\text{L}$ ) and  $w_t$  adsorbent mass ( $\text{g}$ ). The  $\text{Cu}^{2+}$  removal efficiency (RE) was examined via this relationship:

$$RE = \frac{(C_m - C_t)}{C_m} \times 100\% \quad (2)$$

where  $C_m$  represents initial  $\text{Cu}^{2+}$  concentration and ( $C_t$ )  $\text{Cu}^{2+}$  Conc. ( $\text{mg L}^{-1}$ ) at given period  $t$ .

### 2.5 Sample characterization

The interaction mechanisms between adsorbate and adsorbent are investigated through solid addition reported in (Wan Ngah and Hanafiah 2008). A 45 mL solution of 0.01 mol/L  $\text{KNO}_3$  prepared was pipetted six 250 mL flasks. To achieve the desired pH 0 – 12, diluted Sodium hydroxide and Hydrochloric acid were intermittently employed using pH meter (Cyberscan 2100, EUTECH INSTRUMENT). The controlled pHs were chronicled as  $\text{pH}_i$  (initial), 3 g  $\text{L}^{-1}$  mass is load in each  $\text{KNO}_3$  solution and tightly covered followed by mechanical agitation at a speed 150 rpm for 240 min at 25 °C. After the shaking completed, the resultant mixtures were re-examined and noted as  $\text{pH}_f$  (final). The differences in pH, thus  $\text{pH}_i$  and  $\text{pH}_f$  values were used to determine the change in pH ( $\Delta\text{pH} = \text{pH}_f - \text{pH}_i$ ). The  $\Delta\text{pH}$  values were plotted against the  $\text{pH}_i$ , and the  $\text{pH}_{\text{pzc}}$  was then determined. FTIR study was conducted using Thermo-scientific NICOLET (iS10) Spectrometer to analyze the surface functional groups, 0.01g dried sample from various adsorbents was ground into fine particles and mixed well with 0.05g potassium bromide (KBr) prior to being suppressed as pellets. The spectrum ranging from 500 to 4000  $\text{cm}^{-1}$ , it was allowed to standardize 32 times and the background set.

The SEM analysis was performed using analytical JSM-IT300 manufactured by JEOL Ltd. Japan. The BET was analyzed using ASAP 2020M indicating the specific surface area ( $\text{m}^2/\text{g}$ ) of FPOLP and AC1.

## III. RESULTS AND DISCUSSION

### 3.1 Activation temperature effect

An investigation into activation temperature was conducted from 300 to 600 °C using the muffle furnace for 180

min. After activation, 3 g  $\text{L}^{-1}$  sample was added into 25 mL solution of concentration 100  $\text{mg L}^{-1}$   $\text{Cu}^{2+}$  adjusted at pH 3 for the adsorption experiment. The results in Fig.2 showed that only approximately 23% of the  $\text{Cu}^{2+}$  was removed by using the unactivated powder sample (FPOLP). With the increment in activation temperature from 300 to 500 °C, the  $\text{Cu}^{2+}$  RE was increased apparently from around 26% to greater than 97%, however with a slightly decrease to around 95% being observed at 600 °C, indicating that 500 °C was the optimum temperature for activation.

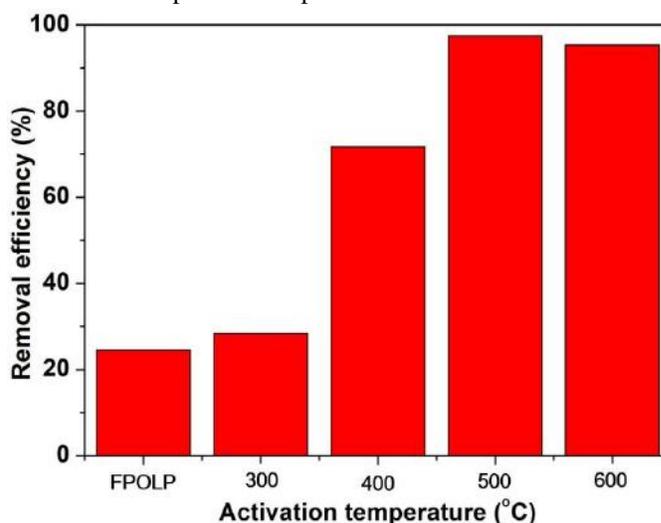


Fig.2:  $\text{Cu}^{2+}$  removal efficiency at pH 3 and different temperatures

### 3.2 Activation conditions and mass load

Investigation was conducted to understand the role of activation conditions for  $\text{Cu}^{2+}$  RE. The adsorption experiment was conducted by 100  $\text{mg L}^{-1}$  concentration of  $\text{Cu}^{2+}$  at pH 3, 25 °C and 150 rpm using FPOLP, AC1 and AC2 by way of adsorbents were conducted. The AC2 was also activated under 500 °C for 3 h but with nitrogen flow. FPOLP output (Fig. 3a) is in a way less efficient as compared to the AC1, but certainly more efficient than AC2. It is indicating that the use of electric furnace under (oxidation) condition was much more effective in producing activated samples for better  $\text{Cu}^{2+}$  adsorption, as compared to the tube resistance furnace which had nitrogen flow. The RE of  $\text{Cu}^{2+}$  increased very slowly when the amount of FPOLP load was varied beginning 1 up to 3 g  $\text{L}^{-1}$ , e.g.  $\text{Cu}^{2+}$  exhaustion increased to 33.38 % down from 21.98 %. Insignificant change was noted however when adsorbent mass was subsequently increased to 4 g  $\text{L}^{-1}$ . Similar  $\text{Cu}^{2+}$  removal behavior was observed for AC2, although with overall lower performance. The RE of  $\text{Cu}^{2+}$  using AC1 increased slightly to a maximum of 95.75% from 94.74%

with increasing adsorbent load from 1 up to 3 g L<sup>-1</sup> with no apparent increment in removing Cu<sup>2+</sup> when adsorbent mass

stood at 4 g L<sup>-1</sup>.

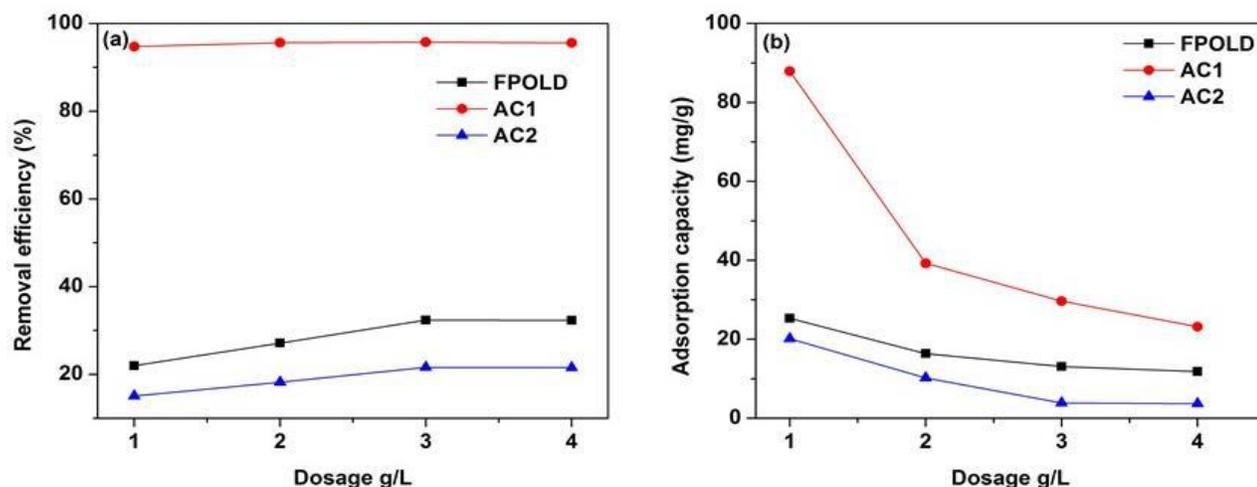


Fig.3: Activation conditions and mass load effect over Cu<sup>2+</sup> (a) removal efficiency and (b) adsorption capacity using 100 mg L<sup>-1</sup> Cu<sup>2+</sup> solution.

In contrast, Fig. 3b showed the effects of sample dosage on the adsorption capacity (q<sub>e</sub>). It is overall presented AC1 apparently greater compared to FPOLD, with AC2 having the lowest Cu<sup>2+</sup> up take capacity, e.g., adsorption capacity of AC2 decreased gradually from 20.18 to 3.70 mg g<sup>-1</sup> with varied adsorbent load of 1 to 4 g L<sup>-1</sup>. While FPOLD ability to adsorb Cu<sup>2+</sup> reduced from 25.33 to 11.85 mg g<sup>-1</sup>. Although showing the same declining trend for AC1, Cu<sup>2+</sup> adsorption capacity of AC1 reduced from 87.93 to 23.19 mg g<sup>-1</sup>. Therefore, activation under atmosphere conditions (oxidation) was used for subsequent investigations.

### 3.3 Activation time influence

Investigation carried out to determine Cu<sup>2+</sup> uptake efficiency using sample activated at 500 °C under atmosphere conditions (oxidation) for various times, e.g. 60, 180 and 300 min correspondingly. Noticeably, Cu<sup>2+</sup> RE gradually diminished when Cu<sup>2+</sup> concentration changed from 25 to 100 mg L<sup>-1</sup> for all three samples investigated, e.g. the removal percentage of Cu<sup>2+</sup> by the sample activated for 60 min decreased from around 70% to less than 60%. In addition, it is observed that Cu<sup>2+</sup> RE increased with increasing time for adsorption from 60 to 180 min. This was followed by a decrease when activation time was prolonged to 300 min, especially when Cu<sup>2+</sup> concentration was increased (e.g. 100 mg L<sup>-1</sup>) indicating a detrimental effect due to longer activation time. This informed the activation duration for subsequent sample preparations.

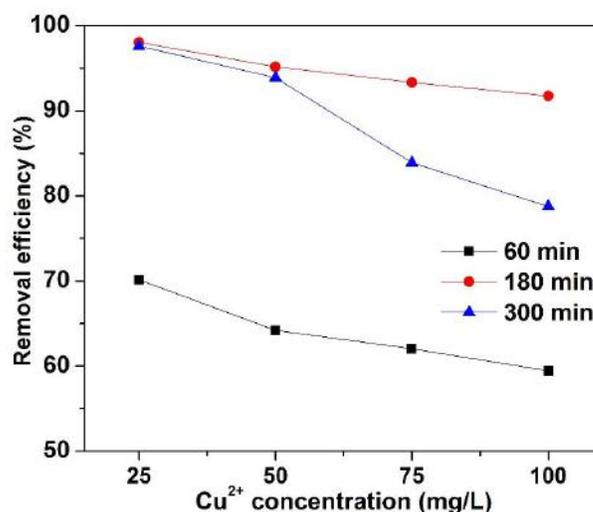


Fig.4: Influence of activation duration Cu<sup>2+</sup> removal efficiency via AC1 load

### 3.4 Influence of solution pH

Solution pH is a vital parameter that has appreciable influence on metal ions uptake (Reddy et al. 2012). An investigation into the effect of solution pH was conducted using 3 g L<sup>-1</sup> AC1 adsorbent (i.e. 75 mg AC1 sample was added into 25 mL solution) with Cu<sup>2+</sup> concentration 100 mg L<sup>-1</sup>. Fig. 5a shows a pH dependent adsorption since a change in pH from 2.0 up to 3.0 resulted in a significant improvement in Cu<sup>2+</sup> adsorption for all investigated adsorbent load but began to decline slightly with pH 4. It became evident therefore to use pH 3 as optimum since it yielded the highest removal efficiency of Cu<sup>2+</sup> investigated.

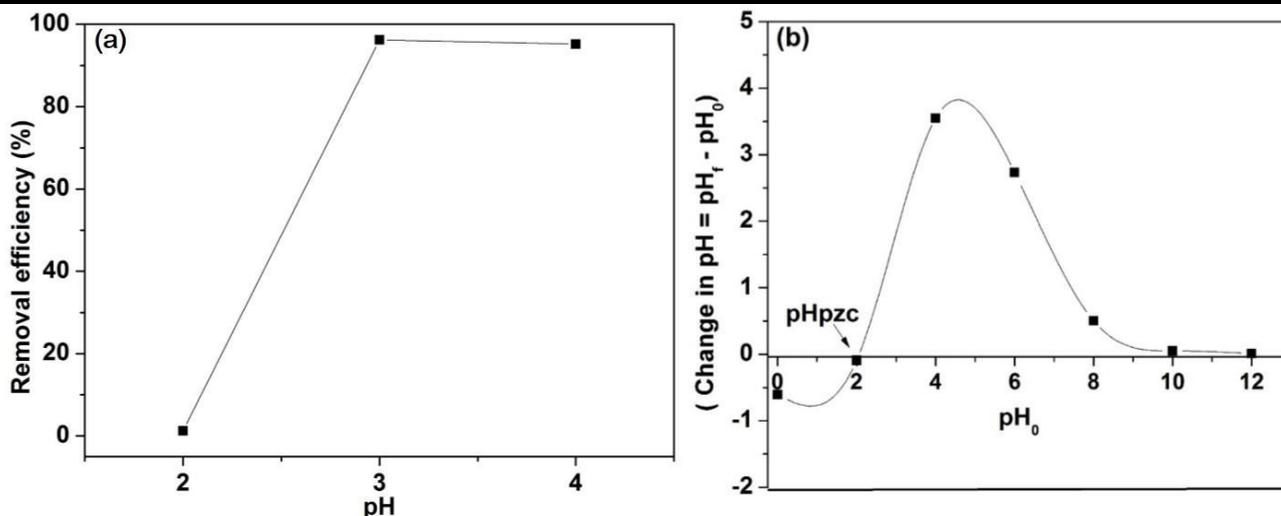


Fig.5: (a) pH effect on  $\text{Cu}^{2+}$  removal AC1 at 25 °C and 150 rpm; (b)  $\text{pH}_{\text{pzc}}$  of AC1.

Investigation based on pH at point zero charge ( $\text{pH}_{\text{pzc}}$ ) of the adsorbent was performed to ascertain the mechanisms of interaction in view of the interdependent roles  $\text{Cu}^{2+}$  and adsorbent both play (Pellera et al. 2012). Fig. 5b indicated that the  $\text{pH}_{\text{pzc}}$  of AC1 in this study was pH 2, indicating that at pH 2, the superficial charge of the loaded mass becomes nonaligned while the attraction force neutralized between the two interfaces. Once the solution pH is less than the  $\text{pH}_{\text{pzc}}$ , the charges on the adsorbent surface generally becomes positive. This will most likely result in a repulsive behavior when the various ions come into contact with each other. In the field of magnetism, like poles repels while unlike poles attract. The inverse leads to a negatively charged surface, thus, (Cardenas-Peña et al. 2012). In this case, cation attraction most likely would take place. In this investigation, the pH 3 at which maximum adsorption took place was greater than the  $\text{pH}_{\text{pzc}}$ , this could probably be responsible for the favourable adsorption due to electrostatic energy acting on both surfaces.

### 3.5 Role of contact time

As an important parameter, the role of contact time in this study was scrutinized as reported in Fig. 6. It was detected that, symmetry status was achieved beyond 40 minutes with a 96.6%. Moving forward,  $\text{Cu}^{2+}$  removal at the end of the 120 minutes cycle, with a given original concentration of 100 mg L<sup>-1</sup> at 25 degrees in AC1 3 g L<sup>-1</sup> evolved differently. This can be interpreted as two faces interaction e.g. the initial adsorption was risen from 75 to 92% in the early 20 minutes of the process (Fig. 6a), then, came much reduced rate of reaction until 40 minutes, consistent with other studies (Villaescusa et al. 2004). This is an indication of a high attraction force between the AC1 surface and the  $\text{Cu}^{2+}$  ions. Since all active sites were unoccupied initially with high solute concentration gradient (Abadian et al. 2015). The reduction in rapid uptake towards the final lap of the investigation may only point to a conclusion that, diminishing unoccupied adsorbent sites and the concentration gradient (Pathania et al. 2013). The adsorption capacity (Fig. 6b) followed a similar trend with that of the removal efficiency, showing an approximate 32 mg g<sup>-1</sup> being recorded at 120 min.

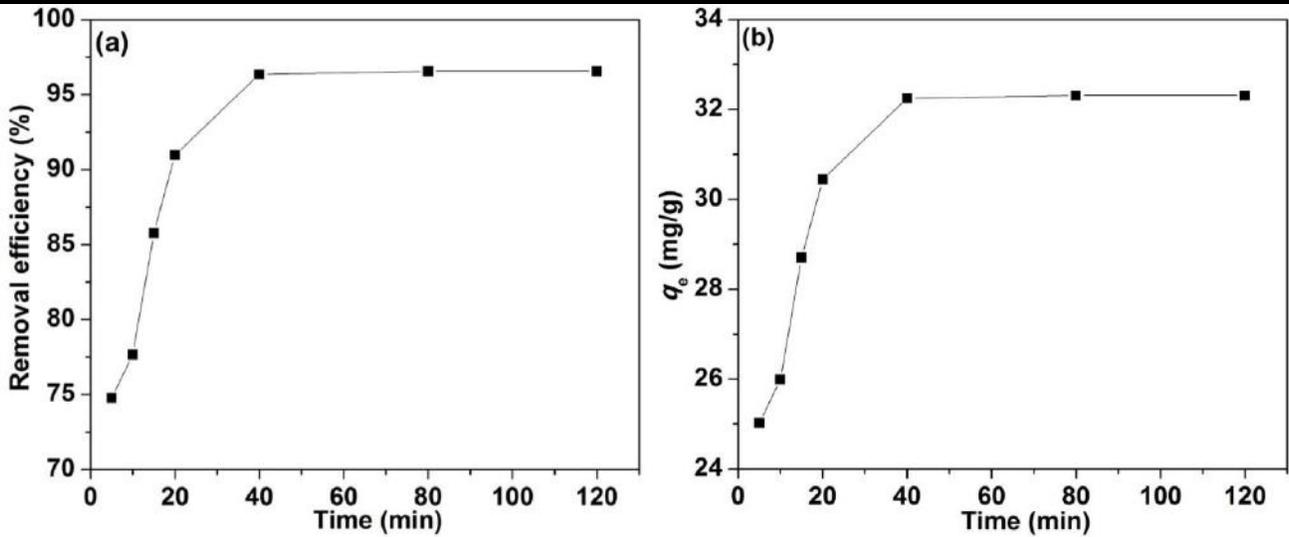


Fig. 6: Relationship of contact time with respect to  $\text{Cu}^{2+}$  concentration of  $100 \text{ mg L}^{-1}$  at  $25^\circ\text{C}$ ,  $150 \text{ rpm}$ , adsorbent concentration  $3 \text{ g L}^{-1}$  (a) removal efficiency and (b) adsorption capacity.

### 3.6 Kinetics phenomenon

There exists some relationship between adsorbent-adsorbate in the adsorption of  $\text{Cu}^{2+}$  on AC1 which can be expatiated using two different approaches. Firstly, Lagergren 1<sup>st</sup> order model relation is employed followed by 2<sup>nd</sup> order model formulation which represented by the parameters as follow:

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

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

where  $k_1$  and  $k_2$  are representing the Lagergren rate coefficients respectively,  $q_t$  and  $q_e$  ( $\text{mg g}^{-1}$ ) are quantities  $\text{Cu}^{2+}$  uptake at given time  $t$  and symmetry.

Adsorption kinetics were evaluated by using  $100 \text{ mg L}^{-1}$   $\text{Cu}^{2+}$  solution temperature at  $25^\circ\text{C}$  employing AC1 as made known in Fig. 7. Verification of Lagergren 1<sup>st</sup> order model revealed  $k_1$  ( $0.138 \text{ min}^{-1}$ ) in Fig. 7(a) and  $q_e$  ( $23 \text{ mg g}^{-1}$ ) as products of intercept and slope determined from the graph of  $\log(q_e - q_t)$  against time  $t$  ( $\text{min}^{-1}$ ) with  $r^2 = 0.96$ . The Lagergren 1<sup>st</sup> order model was not suitable for the first evaluation of  $\text{Cu}^{2+}$  adsorption onto AC1 as the calculated  $q_e$  ( $q_e, \text{cal}$ ) was significantly lower than the experimental  $q_e$  ( $Q_e, \text{exp}$ ) as indicated below, Table 1.

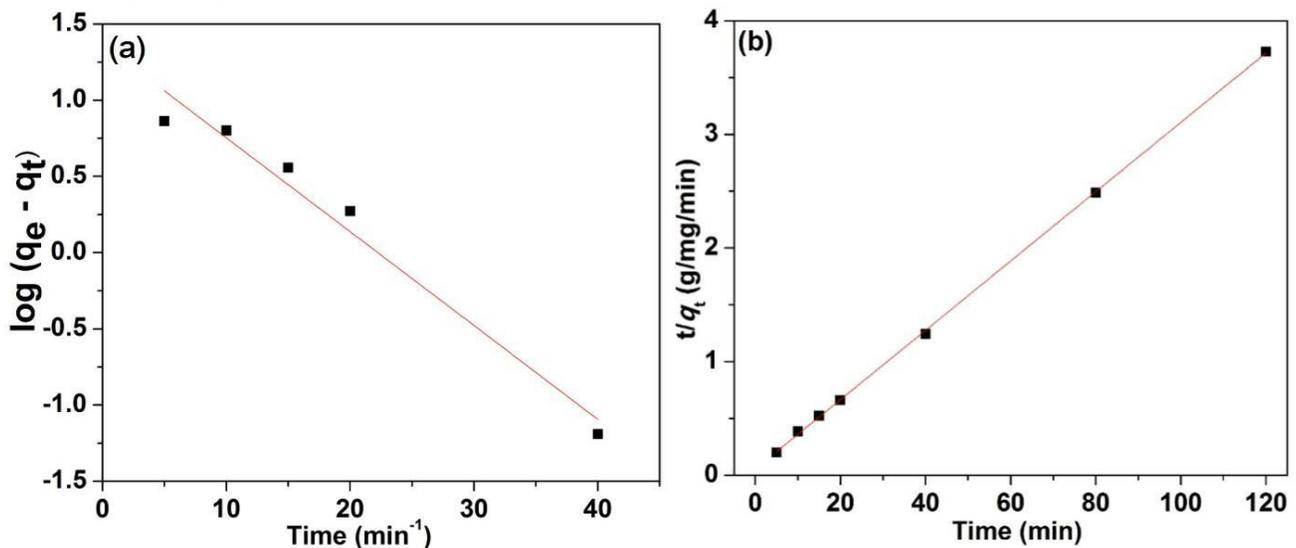


Fig.7: Kinetic model graphs on  $\text{Cu}^{2+}$  uptake adsorption by AC1: (a) Lagergren 1<sup>st</sup> order and (b) 2<sup>nd</sup> order model correspondingly.

The plotted yields, helped to determine the value for  $k_2$  which represented a demonstrating of pseudo 2<sup>nd</sup> order (Ho and McKay 1999) which stood at 0.0167 (g mg<sup>-1</sup> min) while  $q_e$  harmoniously stood at 32.78 (mg g<sup>-1</sup>). A plot of the coordinates  $t/q$  against  $t$  is presented in Fig.7b, with coefficient of  $R^2$  recorded 0.99. It has been reportedly severally through adsorption investigations that,  $k_2$  value usually is near or close to the experimental equilibrium while  $k_1$  in many scenarios are lower than

$k_2$ . Additionally, observation is that, the coefficient of correlation ( $r^2$ ) is mostly lower than 0.999. Adequate appreciation of kinetics of adsorption will greatly help to figure out appreciate strategy to employ in wastewater purification. As postulated already, in this investigation, the value for calculated  $q_e$  ( $Cq_e$ ) was in consonance with the experimental  $q_e$  ( $Exq_e$ ), this agrees with many survey findings (Simonin 2016).

Tab.1.: Kinetic models for Cu<sup>2+</sup> removal by AC1

Experiment	Pseudo-first-order			Pseudo-second-order		
	$k_1$ (min <sup>-1</sup> )	$Cq_e$ , (mg g <sup>-1</sup> )	$r^2$	$k_2$ (g mg <sup>-1</sup> min)	$q_e$ , cal (mg g <sup>-1</sup> )	$r^2$
Ex $q_e$ (mg g <sup>-1</sup> )						
32.17	0.138	23.00	0.96	0.0167	32.78	0.99

### 3.7 FT-IR spectral analysis

Fig. 8 shows the FT-Infrared bands consisting FPOLP, AC1 and AC1' (recovered residue). Recorded broad peaks between 3400 cm<sup>-1</sup> and 3550 cm<sup>-1</sup> on the adsorbents (Fig. 8a) may be assigned to high concentration of O-H functional group as a result of the vibration stretch effect, indicating availability of "free" hydroxyl elements within FPOLP surface as similarly (Li et al. 2007). Consequently, the peak magnitude reduced in AC1 sample after thermal treatment. The peaks at 2850 as well 2925 cm<sup>-1</sup> showed some attributes of aromatic compounds (Odewunmi et al. 2015) even though there was significantly reduction in the AC1 band (Fig. 8b) after thermal treatment at 500 °C under an oxidized medium for 180 min. As AC1 had better Cu<sup>2+</sup> adsorption capacity than FPOLP, the presumption is that these two peaks did not play roles in Cu<sup>2+</sup> adsorption. The peaks ranging from 1626 cm<sup>-1</sup> to 1629 cm<sup>-1</sup> may be attributed to the stretching modes of carbonyl groups in the forms of carboxylic acids (Jokar et al. 2016).

The peak at 1318 cm<sup>-1</sup> and 1400 cm<sup>-1</sup> were attributed different composition of aromatic nitriles (Li et al. 2012; Thusnavis K.P.V. K, and Sankara N. P. M. 2011), or the stretching effect of C-O and C-C stretch, respectively (Martin Chaplin 2013). After carbonization (Fig. 8b), band 1318 cm<sup>-1</sup> disappeared however, band 1048 cm<sup>-1</sup> may be credited to the stretching vibration effect of primary alcohol (Martin Chaplin 2013). It had undergone shifting to new band at 1100 cm<sup>-1</sup> (Fig. 8b) and further shifted to 1102 cm<sup>-1</sup> (Fig. 8c) probably due to C-O-C after thermal treatments and subsequent adsorption for AC1 and AC1'. The peaks at 874 cm<sup>-1</sup> could be ascribed to C-H bend as a feature of alkene compounds observed in Fig. 8a and Fig. 8b were

increased in Fig. 8c, indicating that this function group might contribute the combination with Cu<sup>2+</sup>.

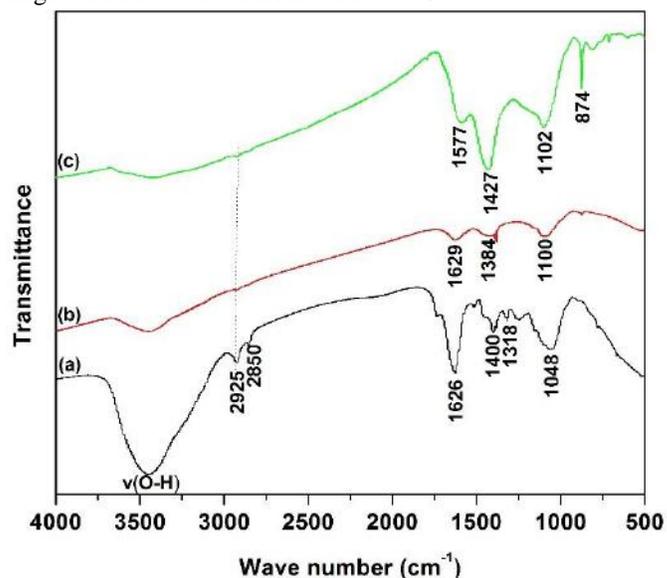


Fig. 8: FT-Infrared spectra (a) FPOLP, (b) AC1, (c) AC1'.

It should be noted that band shifts to lower wavelengths indicates weakening bonds, whereas shifts to higher wavelengths indicated increment in bond strength (Dwivedi et al. 2011). Band 1577 cm<sup>-1</sup> could be as a result of chemical interaction between Cu<sup>2+</sup> and the surfaces of the leaf powder. Other research has shown that, activation under oxygen condition has high yielding adsorptive capacity when it comes into contact with Cu<sup>2+</sup> (Klasson et al. 2009), this may partly account for the different adsorption potentials between FPOLP and AC1. Although the FT-Infrared examinations showed some differences in the samples before and after activation, the significant

variation in  $\text{Cu}^{2+}$  adsorption ability could possibly be due to activation influence under oxidized environment.

### 3.8 SEM analysis

Fig. 9 shows the SEM images of FPOLP and AC1 after examination. It is observed that the surface of the uncharacterized FPOLP looked 'blocked' (Fig. 9a).

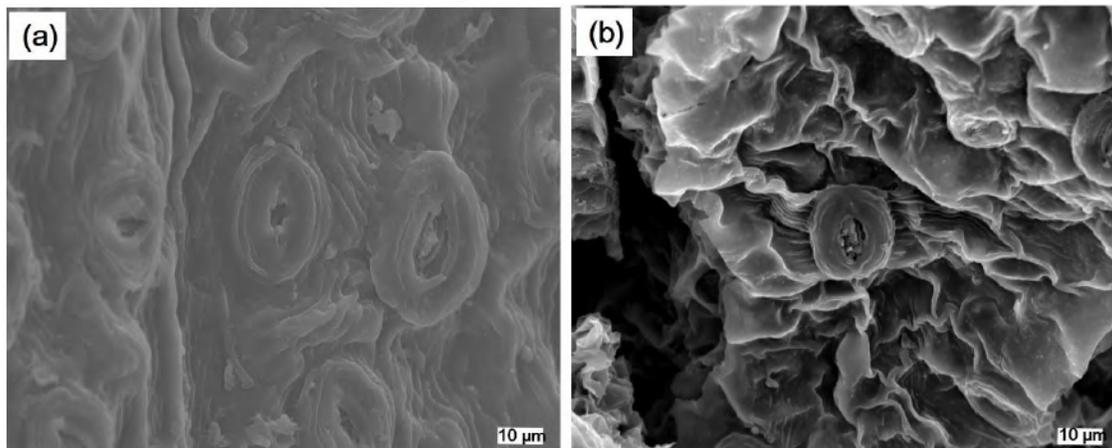


Fig.9: SEM images of (a) FPOLP and (b) AC1.

## IV. CONCLUSIONS

This study revealed that the *Platanus orientalis* litter (leaves) has good potential to be used as raw material for the production of AC for effective treatment of  $\text{Cu}^{2+}$  from aqueous solution. The outcome of this investigation partly fulfilled the objective of the study which among others was to exploit the benefits that could be driven from the large quantum of waste generated annually from this plant. The removal of  $\text{Cu}^{2+}$  was not independent of solution pH since maximum uptake had been achieved at pH 3.

As earlier stated, the evaluation of the mechanisms of interaction that occurred between the adsorbate and adsorbent, proved Lagergren 2<sup>nd</sup> order as the suitable model for this investigation.

Different adsorbent mass load 1, 2, 3 and 4  $\text{g L}^{-1}$  were investigated. Initial increment in adsorbent dosage to 3 from 1  $\text{g L}^{-1}$  led to a boost in  $\text{Cu}^{2+}$  removal from 94.74 to 95.75% when it was loaded with AC1, but beyond that, no significant changes were recorded. Similarly, when an increment in AC2 mass load to 3 from 1  $\text{g L}^{-1}$  resulted into an increase in  $\text{Cu}^{2+}$  removal efficiency from 15.08 to 21.61%. Therefore, activation of the leaves samples under an oxidized condition (pyrolysis) had proven to be much more effective compared to that under  $\text{N}_2$  condition. Additionally, SEM techniques were employed to examine the morphological attributes of the samples under investigation. The SEM images showed very good porosity

However, compared to AC1 which was carbonized in an oxidized condition, ended up having more pores on its surface (Fig. 9b). The BET measurements gave further insight into what could have possibly accounted for the adsorption differences even though under same controlled conditions, the specific surface dimensions were 2.1330 and 25.3165  $\text{m}^2 \text{g}^{-1}$  for FPOLP and AC1 correspondingly.

of the AC1 which had the best adsorption capacity of 87.93  $\text{mg g}^{-1}$ . Another aspect of this work considered was to evaluate the influence solution concentration would have in  $\text{Cu}^{2+}$  removal. The outcome of the investigation pointed to the fact that, when  $\text{Cu}^{2+}$  concentration was varied in the range of 25 and 100  $\text{mg L}^{-1}$ , using 3  $\text{g L}^{-1}$  mass of AC1, the depletion of  $\text{Cu}^{2+}$  reduced. It however brought about a rise in the adsorption capacity of all samples investigated. Results from pH<sub>pzc</sub> analysis recorded at pH 2 indicated a lower figure compared with the optimum adsorption at pH 3. It explained the mechanism of interaction that took place when the  $\text{Cu}^{2+}$  solution was loaded with the AC1 and FPOLD. In addition, the FTIR, BET and SEM results indicated that the greater surface area obtained after activation contributed greatly to the higher adsorption capacity.

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