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Tasnim Fahim CHYAD[1], Rasha AL-SAEDI[1*] and Zaman Ageel HAMMOOD[2]

COPPER(II) REMOVAL FROM WASTEWATER USING PINE CONE DERIVED ACTIVATED CARBON

Abstract: Inappropriate disposal of wastewater including heavy metals may lead to serious public health problems. Among conventional wastewater treatment methods, adsorption is the preferred treatment technique, due to its advantages such as cheapness, simplicity, and flexibility in design and operation. In recent years, there has been an urgent need toward the production of low-cost alternatives to the commercial activated carbon which has a greater adsorption capacity with high porous and large surface area. In this experiment, activated carbon that derived from pine cone (PCAC) has been investigated as a new adsorbent to remove copper(II) ion from wastewater. The adsorption process of copper(II) ion from aqueous solution was carried out in a batch mode to study the effects of adsorbent dose (0.5 g/50 mL - 2 g/50 mL), initial pH (2-8), and initial concentrations (5 mg/L - 20 mg/L). The results indicated that activated carbon obtained from pine cone was an efficient adsorbent for the copper removal from the aqueous solution. Removal of copper ion from aqueous solution was dependent on the adsorbent dosage, pH, and initial Cu concentration, achieving maximum adsorption efficiency (99 %) at 2 g/50 mL, 6, and 20 mg/L, respectively.

Keywords: Adsorption, activated carbon, pine cone, copper

Introduction

Heavy metals are hazardous pollutants, due to their non-biodegradable and bio-accumulation nature in the food chain. They are usually found in the wastewater streams of many industrial processes including: petroleum refining, mining, electroplating, paper, and rubber processing. Among others, copper is one of the most hazardous heavy metals, which commonly generates from chemical, electrical and mining industries. It can accumulate in the tissues of human body, creating adverse impacts in the eco-systems and organs of human body. Therefore, it is mandatory to remove copper from contaminated wastewater before discharge into water systems [1-4].

Different conventional techniques have been widely used for the removal of heavy metals from wastewater including: chemical precipitation, membrane filtration, coagulation-flocculation, and ion exchange. However, these techniques have their advantages and limitations in application [5]. Adsorption is a mass transfer process by which a solution of adsorbate (wastewater) adsorbs onto adsorbent surfaces (porous solid material). In last few decades, adsorption has outweighed other treatment techniques for the removal of metals from wastewater, owing to the following advantages: the non-sensitivity

[1] Department of Environmental Engineering, College of Engineering, Mustansiriyah University, Baghdad, Iraq, ORCID: TFC 0000-0002-0654-8355, RAS 0000-0002-5371-4715
[2] Department of Environmental Engineering, College of Engineering, University of Baghdad, Baghdad, Iraq, ORCID: ZAH 0000-0002-3094-8690,
[*] Corresponding author: rasha.az2013@gmail.com, rasha.azeez@uomustansiriyah.edu.iq

to contaminants and toxic compounds, high quality of effluent, and absence of hazardous byproducts, effective in removing heavy metals even at low concentrations [6].

Activated carbon (AC) is a widely used adsorbent for the removal and recovery of metal ions from aqueous solutions, due to its outstanding properties such as: high specific surface area and adsorption capacity [7-10]. Activated carbon is generated from commercial products such as, coal [11], peach pits [12], and wood [13]. However, the locally available and sustainable materials such as, coconut shell [14]; polyacrylonitrile fiber [15] that could serve as potential alternatives for commercial products [16]. Biosorption is a cost-effective option as the biosorbents are inexpensive and naturally available such as modified agricultural wastes (e.g. lignocellulosic materials like cellulose, hemicellulose and lignin), which have been frequently tested as alternatives of commercial adsorbents [17, 18]. Carboxylic, carbonylic, and aldehydic are specific organic groups situated at the sides of carbon layers which include the most powerful adsorption sites [16]. Lignin has some functions such as: strengthening the cell walls and protecting the microfibrils of cell wall from chemical, physical, and biological attacks. These characteristics of lignin may therefore clarify the low negative charges and the low carboxylic group contents produced from agricultural wastes with high lignin concentrations [19]. The selection of these wastes as adsorbents is based on the economic considerations, abundance of raw materials, and the positive footprints of adsorbent on the environment [20].

In this paper, activated carbon obtained from pine cones was studied to examine its capability as a cost-effective adsorbent to remove copper ions from wastewater. The effects of pH, initial concentration, and adsorbent dose on the removal efficiency of copper ions from aqueous solution were also assessed.

Materials and methods

Sieve analysis

Sieving analysis of PCAC was performed (on the basis of particle size) at Al-Esraa University/laboratory of soil, according to soil classification system/British standards (BS 5930: site Investigation), Figure 1 represents the distribution of PCAC grain size.

Preparation of pine cone derived activated carbon

The pine cones (PCs) were collected from the ground of plantation area in Ninavah, Iraq. 1 kg of PC was washed thoroughly using distilled water, and then dried under the sun for 48 h at a temperature of 30 °C. The dried PCs were crushed to powder using a blender. Sieving was performed for the resulted powder and particles below 300 μm were gathered and utilised for analysis. The PC activated carbon (bulk density = 0.18 g/cm^3) was then ready for use.

The measurement of bulk density was performed as follows: the powder was transferred to a 25 mL bottle, with a gentle tapping to make sure the settlement of the particles in the flask bottom with a complete saturation of air spaces. Then, the mass of density bottle filled with the powder was computed. The mass of the powder that occupied 25 mL was determined by taking off mass of the empty bottle from mass of the bottle and powder as shown in equation [21]:

$$\text{Bulk density} = M_d / V \quad (1)$$

where: M_d - mass of dry sample [g], V - total volume [mL].

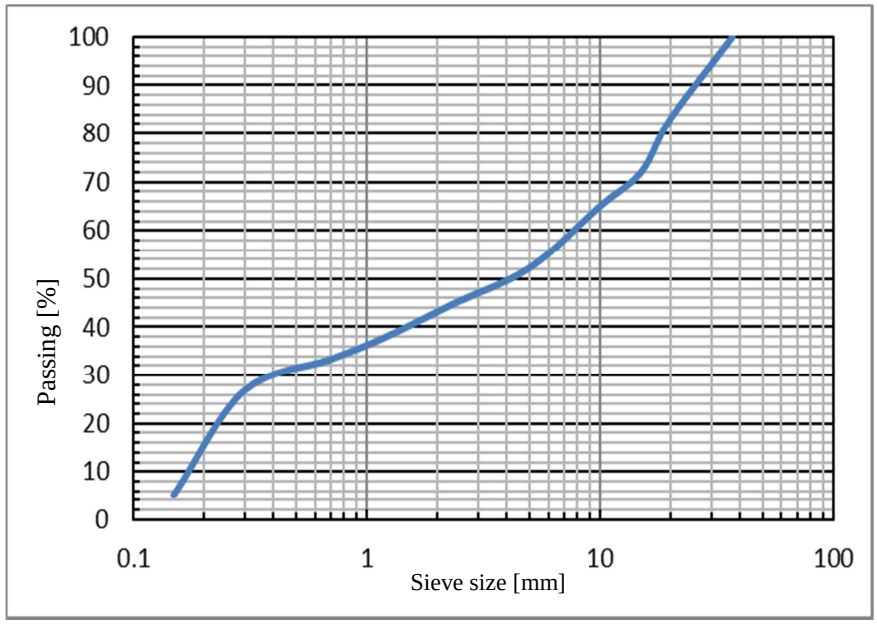

Fig. 1. Sieve analysis of PCAC

Table 1

Chemical composition of dried pine cone derived activated carbon porous media

Elemental analysis [wt.%] (on dry basis)			
Carbon [%]	**Hydrogen [%]**	**Nitrogen [%]**	**Sulphur [%]**
51	6.4	1.2	3.1
[wt.%] (as received)			
Moisture			6.7
Ash			8.2
Volatile			38
Main constituents [wt.%] (on dry basis)			
Lignin			26.4
Hemicellulose			25.1
Cellulose			45.3

Stock solution of Cu(II)

The aqueous solution of Cu(II) was prepared by dissolving 1 g (±0.001 g) $CuSO_4 \cdot 5H_2O$ (99 % purity) in 1000 mL distilled water. The sample of 5 mL was taken and analysed using atomic absorption spectrophotometer to determine the concentration of stock solution. The stock solution was diluted with distilled water into the predetermined concentrations of aqueous solution using general dilution formula.

Experiment of adsorption kinetics

To determine the equilibrium time of Cu(II) adsorption on PCAC, an experiment of Cu(II) adsorption onto PCAC was carried out in a batch mode. 50 mL of Cu(II) aqueous solutions, with different initial concentrations (5, 10, 15, 20) mg/L were transferred into

250 mL flasks, each concentration was mixed with different doses (0.5 to 3g PCAC), pH range (4 to 10) and stirred using a magnetic stirrer at 250 rpm, room temperature of 25 °C in order to determine the optimum conditions of the involved parameters. Based on the above experiment, the adsorption reached equilibrium at 180 min of contact time. Other conditions (initial concentration, adsorbent dose, and pH) were selected on the basis of the above experiment that demonstrated the equilibrium, which was established at 120 min contact time. After this period, the suspension was filtered using Whatman filter paper No. 1 in order to separate the sorbent from the aqueous solution. Thereafter, 10 mL of the filtered solution was obtained and analysed for Cu concentration, which was measured following the analytical procedure with (AA 7000 Shimadzu, Japan model) atomic absorption spectrophotometer at a wavelength of 325 nm [22].

The adsorption kinetics of Cu(II) on PCs activated carbon was investigated based on the optimal adsorption capacity of PCAC in terms of Cu(II) initial concentration. Data were presented in average values of the replicated results.

The weight of copper adsorbed by the adsorbent q_e [mg/kg] was computed using equation [23]:

$$q_e = (C_i - C_e / W) \cdot V \quad (2)$$

where: C_i and C_e - initial and final concentrations of wastewater [mg/L], W - weight of adsorbents [g].

Results and discussion

Effect of initial concentration

In adsorption, initial concentration is an important parameter for the removal of metal ions from wastewater. Figure 2 shows the effect of different initial Cu^{+2} concentrations (5, 10, 15, 20) mg/L on the removal efficiency under experimental conditions of: contact time = 180 min; dose of adsorbent = 2 g/50 mL; speed = 250 rpm; and pH = 6.

Concentration of 20 mg/L achieved rapid removal of Cu (60 %) at the first 20 min. of experiment. At 10 mg/L and 15 mg/L Cu initial concentration, the removal efficiencies were apparent (30 % and 40 % respectively), with the lowest removal (10 %) occurred at initial concentration of 10 mg/L. Afterward, the removal rates gradually promoted, having the maximum values at 160 min. of experimental time, reaching to an equilibrium state between 160 min. - 180 min.

Overall, the aqueous solution with initial Cu(II) concentration of 20 mg/L had the highest removal rate, indicating that the affinity of Cu(II) towards active sites of PCAC increases with increasing initial concentration [24].

Figure 3 shows an improvement in Cu(II) adsorption capacity over time, approaching maximum amounts of (90, 213, 350, 495) mg/kg at Cu(II) initial concentrations of (5, 10, 15, 20) mg/L respectively. This could be ascribed to sufficient access to the exchange sites and inadequacy in the resistance of internal diffusion [21]. After about 100 min, the adsorption intensity did not significantly vary, indicating no empty places for exchange.

The reason behind the increase in the adsorption amount is the production of driving forces (by initial concentration) to overcome the resistance to the mass transfer of metal between aqueous and solid phases. The increase also enhances the interaction between adsorbent and Cu [21].

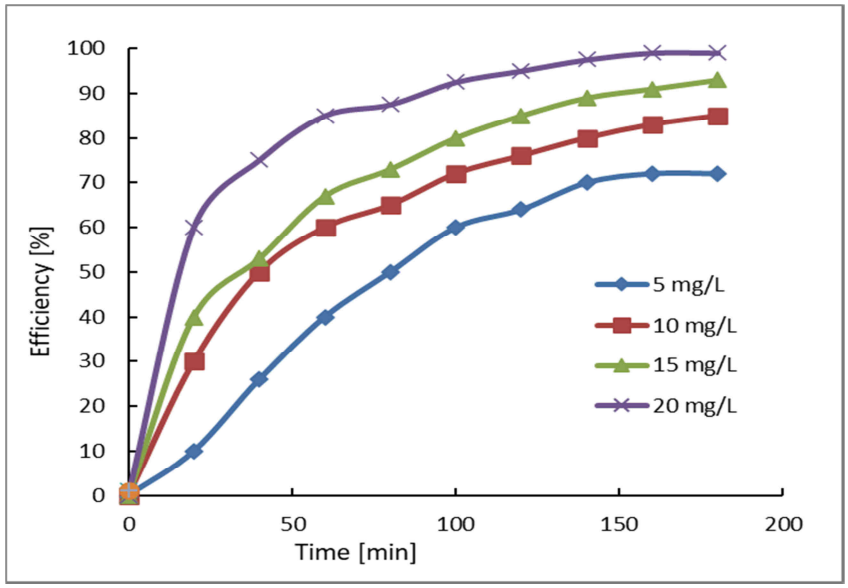

Fig. 2. Effect of Cu^{+2} concentration, C_i, on removal efficiency

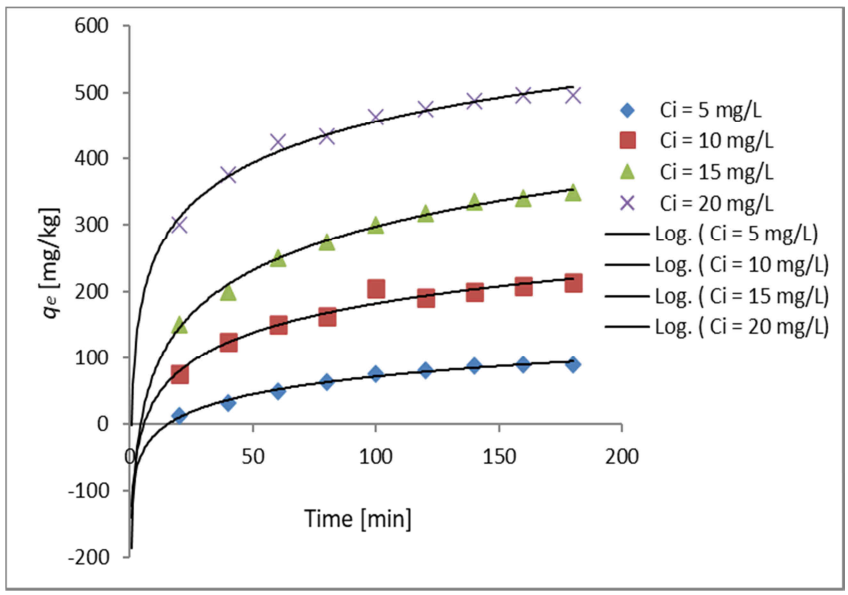

Fig. 3. Relation between adsorption capacity, q_e and time

Exchange of Cu was promoted with the increment in the initial concentration, resulting in excess molecules of Cu that are bounding the sorbent areas, finalising the mass transfer mechanism between adsorbent and solution. Furthermore, permeability and greater surface area might have enabled the remaining adsorption site to reach the saturation state, and

hence promoting the adsorption capacity from 90 mg/kg to 495 mg/kg with raising initial concentration from 5 mg/L to 20 mg/L. These results are in accordance with that previously published by Ofomaja et al. [25].

Enhanced adsorption capacity can be explained as follows: exchange of Cu cations takes place at higher energy sites but low Cu-cation/adsorption ratio. However, increasing the ratio saturated the higher energy sites, masking the effectiveness of cation exchange and hence lowered the adsorption process [19].

Effect of adsorbent dosage

This experiment was undertaken at a range of PCAC mass (from 0.5/50 mL to 3 g/50 mL) under initial concentration 20 mg/L, pH = 6, and agitation speed 250 rpm to investigate the effect of solid mass on the adsorption performance.

Adsorbent dosage is a critical factor in the sorption process, as it determines the capacity of adsorbent. The impact of adsorbent dose on the sorption efficiency of Cu (II) ions are demonstrated in Figure 4, which shows that the adsorption intensity enhanced (92 % to 99 %) with a more supplement of solid dose, due to increment in the specific surface area of adsorbent (active sites of exchange). By increasing the dose of PCAC, the number of sorption sites available for the interaction of sorbent-solute increased, thereby resulting in an increase in the percentage of copper(II) removal from solution. By increasing the adsorbent dosage, the active sites on the surface of PCAC would increase, which resulted in a further adsorption of metal ions on the adsorbent surfaces [25].

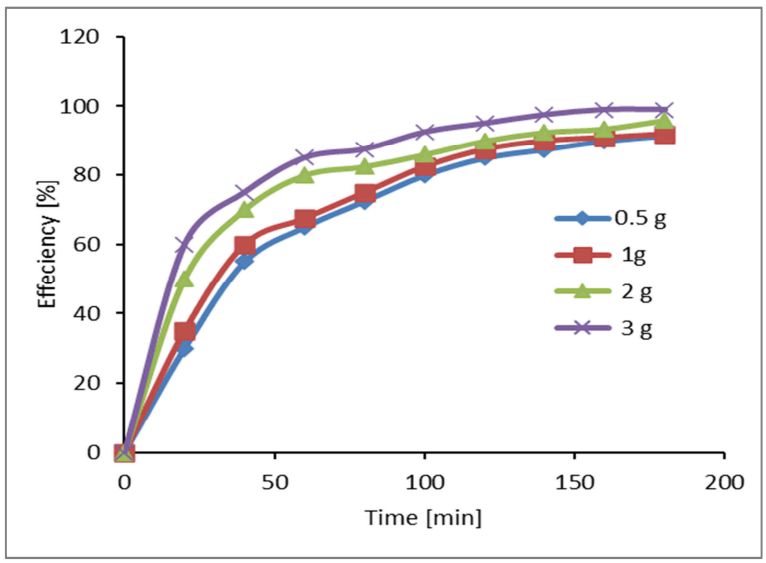

Fig. 4. Effect of ACPC dosage on removal efficiency of Cu^{+2}

As shown in Figure 4, the sorption efficiency clearly increased by increasing the dose from 1 g/50 mL to 2 g/50 mL. However, the dose between 0.5 g/50 mL - 1 g/50 mL showed no significant changes in the removal efficiency of Cu. For doses between 2 g/50 mL - 3 g/50 mL a slight change in the removal efficiency was noticed. Therefore, the

adsorbent dose of 2 g/50 mL was considered as the optimal value. In this adsorbent dose, the removal efficiency of Cu(II) was 96 % [9]. In addition, increasing the dose enhances the contact of surface area with the sorbate ions. For PCAC, when dose increased from 1 g/50 mL to 2 g/50 mL, the rate of copper(II) removal increased from 92 % to 96 %. The interpretation to this will be that the PCAC with 2 g/50 mL had a higher surface for contact with adsorbate ions than that dose with 1 g/50 mL. This result is in line with the results obtained from Ofomaja et al. [25]. A further increase in the adsorbent dose to 3 g/50 mL did not significantly change the adsorption efficiency. These presumptions are in accordance with the literature [16, 26].

Figure 5 shows that the amount of Cu adsorbed q_e [mg/kg] increased slightly with the addition of adsorbent mass, which is due to the split in the flux or the concentration gradient between solute concentration in the solution and the adsorbent surfaces [16].

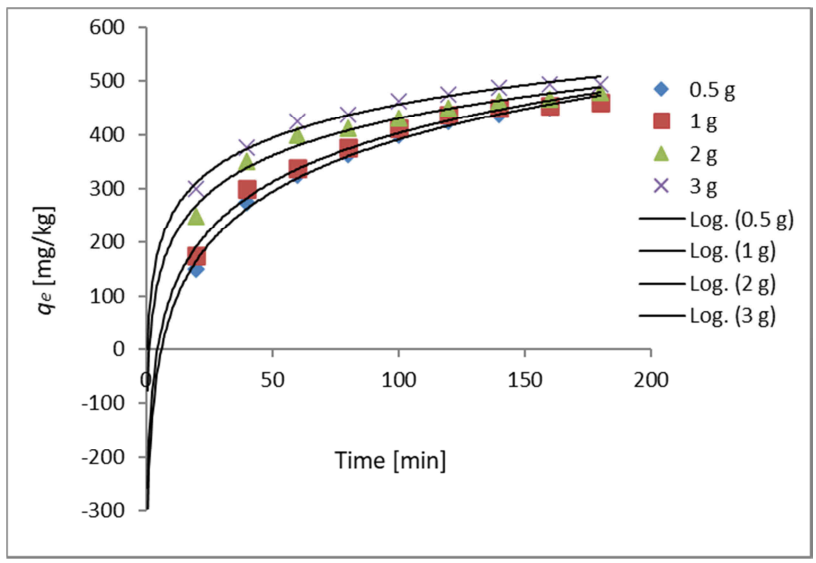

Fig. 5. Relation between adsorption capacity, q_e and time. Regression relations are: $y = 139.82 \ln(x) - 253.02$ (r^2 0.99) (dose 0.5 g), $y = 130.26 \ln(x) - 197.45$ (r^2 0.98) (dose 1 g), $y = 99.67 \ln(x) - 28.968$ (r^2 0.97) (dose 2 g), $y = 89.941 \ln(x) + 41.792$ (r^2 0.98) (dose 3 g)

Effect of pH

In this experiment, the effect of pH on Cu adsorption by PCAC was studied at a pH range of 4-10 (Fig. 6) at an initial Cu concentration 20 mg/L, contact time 180 min, and solid dose 2 g/50 mL. pH is a significant factor that manages the adsorption phenomenon, as it influenced the degree of ionisation and the surface charge of adsorbents. Generally, the shift in the pH level from 4 to 8 stimulated the adsorption efficiency of Cu(II) ions (Fig. 6). At high level pH, Cu ions usually precipitate through a combined micro precipitation-sorption. In this experiment at the highest applied pH value (10), adsorption capacity declined even less than the capacity at pH = 4. In general, a drop in the adsorption efficiency is noticed (99 % to 92 %), with the increase in solution pH from 6 to 10, which may be due to the inorganic micro-precipitation.

At pH 10, copper(II) removal efficiency was less than other tested pH values, which attributable to the competition between H^+ and ions of copper(II) for the biosorption sites. However, when solution pH increases from 4 to 6, the removal capacity of Cu increased. As solution pH rises to 8 and 10, the negative charges on the biosorbents surface increases with a decrease of H^+ ions in the solution, which takes part with copper(II) for the sorption sites [25].

Overall, the adsorption efficiency might be affected by a difference in the corresponding placement of C groups-surface charge and the balance of proton [16].

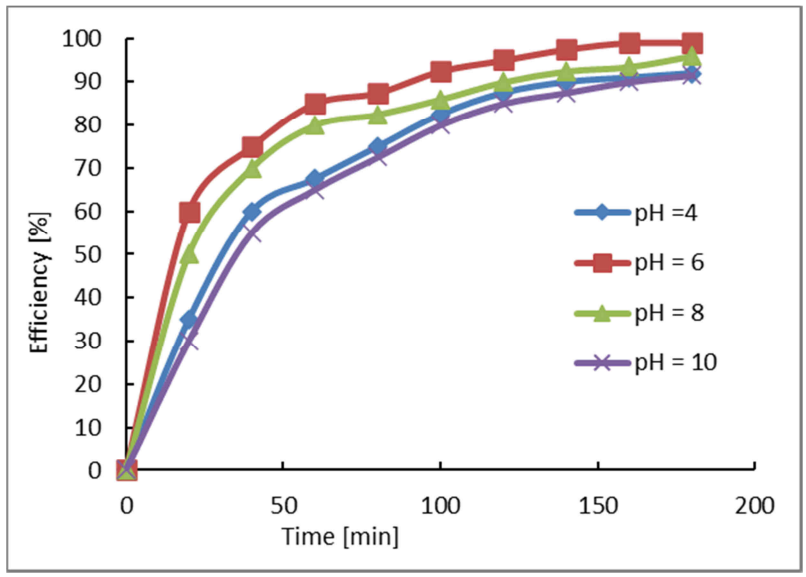

Fig. 6. Removal efficiency of Cu(II) with PCAC media at different pH levels

Figure 7 shows that the adsorption capacity of Cu generally improved as the pH level rose. However, the favoured adsorption was achieved at pH between 6 to 8. When pH upgraded from 4 to 6, the ion exchange enhanced from 460 mg/kg to 495 mg/kg at the end of the experiment. Typical adsorption occurred at pH of 6, which might be due to the electrostatic reaction between cationic copper and the charged medium. However, lower q_e magnitudes were apparent at low pH levels (4), due to the competitiveness between molecules of charged copper and H^+ for the unoccupied exchange areas. The results here is in alignment with that documented in the literature [26]. Nevertheless, the adsorption efficiency dropped from 495 mg/kg (at pH = 6) to 458 mg/kg at higher pH levels, reflecting that pH of 10 was not favoured for the optimum adsorption under these experimental conditions.

Surface charge is a limiting factor for the exchange process of the ionic and cationic copper molecules, which is primarily controlled by pH. As pH usually enhances the negative charge over the surfaces of PCAC, which could be advantageous in terms of adsorption capacity. In contrast, lowering the pH level promotes the positive charge over the surfaces of adsorbent and enhances the electrostatic attractiveness between cations and surfaces [19].

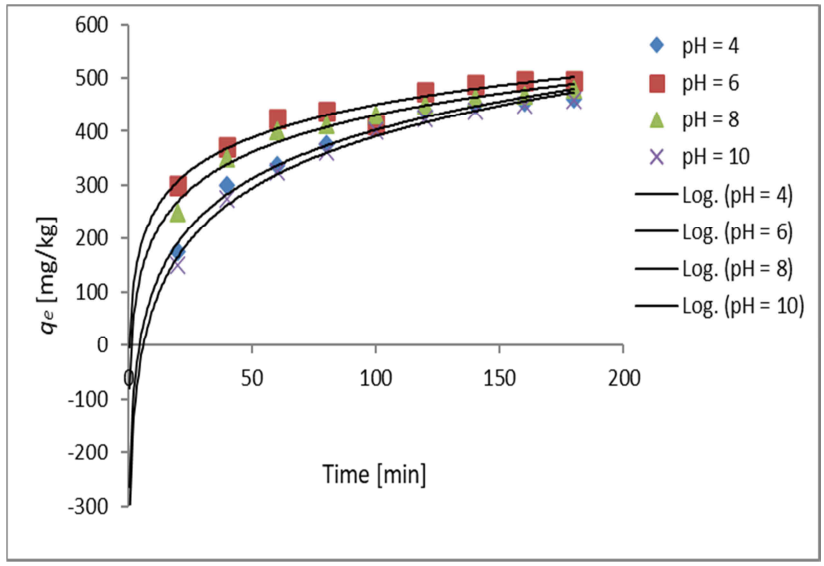

Fig. 7. Relation between adsorption capacity, q_e and time. Regression relations are: y = 130.26 ln(x) – 197.45 (r^2 0.98) (pH = 4), y = 88.563 ln(x) + 41.77 (r^2 0.94) (pH = 6), y = 99.67 ln(x) – 28.968 (r^2 0.97) (pH = 8), y = 139.82 ln(x) – 253.02 (r^2 0.99) (pH = 10)

Conclusion

Results showed that PCAC as a low-cost adsorbent can be efficiently used for the removal of Cu^{+2} under laboratory conditions of: contact time = 180 min., initial Cu concentration 20 mg/L, PCAC dosage 2 g/50 mL, and pH = 6. It was found that the percentage removal of Cu was dependent on: dose of adsorbent, pH, and initial concentration of adsorbate. The contact time of around 180 min was adequate for approaching an equilibrium state, which revealed a high affinity of pine cone derived activated carbon for Cu. The initial concentration had a significant effect on the amount of metal adsorbed q_e [mg/g] and percentage of Cu removal from aqueous solution. pH of the aqueous solution had a key role in the sorption process. A pH of 6 was favourable for the adsorption of Cu. The functional groups on the adsorbent sites and number of electrostatic charges on the metal ions are majorly manged by pH. Raising PCAC dosage stimulated the overall number of active sites causing an increase in the overall adsorption efficiency.

As the influence of solid dose (specifically between 0.5/50 mL - 1 g/50 mL and 2/50 mL - 3 g/50 mL) and pH (particularly between 6-8) did not significantly show a difference, a broad range of solid doses and pH thus requires further investigation.

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