

Synthesis of acid treated carbonized mandarin peel for purification of copper

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Abstract

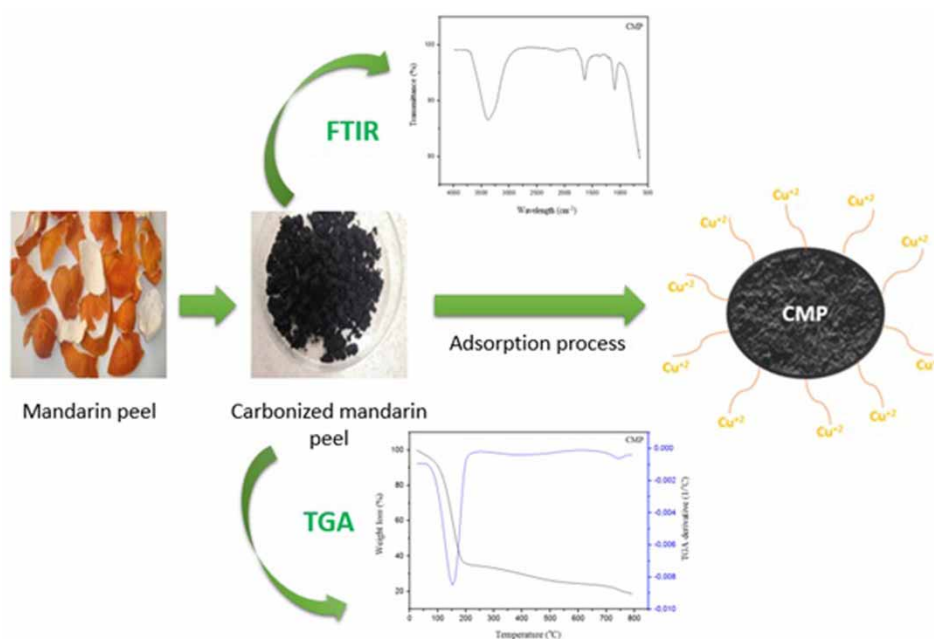
In this study; acid treated carbonized mandarin peel (CMP) adsorbent was prepared and the adsorption behaviour of the adsorbent for copper removal was investigated. In the adsorption studies the effects of initial metal concentration, solution pH, adsorbent dosage and contact time on the removal were investigated. As a result; the highest removal of 100% was achieved when the copper concentration in water was 5 mg/L and the adsorbent dosage was 3.75 g/L at a solution pH of 7. Isotherm studies were also done and the appropriate isotherm was obtained as the Freundlich isotherm. According to the kinetic studies, the copper adsorption onto CMP adsorbent was adopted to the pseudo-second-order adsorption kinetic. After HCl regeneration, the adsorbent maintained 94% of its activity.

Key words: copper removal, isotherm, kinetic, mandarin peel based activated carbon

Highlights

- An acid-treated carbonized mandarin peel (CMP) adsorbent was synthesized
- A complete copper removal was achieved
- The increasing adsorbent dosage increased the removal
- The CMP maintained 94% of its activity after HCl regeneration

Graphical Abstract



INTRODUCTION

Technological growth has led to a negative effect on the environment. Inorganic and organic pollutants cause environmental problems due to the industrial effluent of the mining, paint, leather and textile processes (Enniya *et al.* 2018). Industrial pollution can be categorized as soil, air, and water pollution. Especially, heavy metal contamination in water is crucial since they are non-biodegradable and affect the living organism. Various methods such as precipitation, coagulation and flocculation (Yi *et al.* 2017), reverse osmosis (Amuda & Amoo 2007), membrane filtration, ion exchange (Kurniawan *et al.* 2006), and adsorption (Thuan *et al.* 2017) can be used for heavy metal removal from wastewater. Adsorption is one of the effective, low-cost, modular processes for wastewater treatment. On the other hand, the performance of the method is limited by the performance of the adsorbent. Recently, studies on the development of reusable bio-based waste adsorbent have attracted attention. The carbon-based materials produced from the biological feedstock are defined as non-toxic and low-cost adsorbent sources (Hashemian *et al.* 2014). The efficiency of these materials can be improved by increasing their surface area, porous structure, and functional groups (Yahya *et al.* 2015; Thuan *et al.* 2017; Saidi *et al.* 2019). Many vegetable foods can be converted to effective adsorbents. In the literature, the peel of apple (Enniya *et al.* 2018), banana (Thuan *et al.* 2017), coconut (Gratuito *et al.* 2008), Litchi (Yi *et al.* 2017), orange (Hashemian *et al.* 2014), sugarcane bagasse (Foo *et al.* 2013), and mandarin (Koyuncu *et al.* 2018) is reported to be a good candidate for an effective carbon-based adsorbent.

According to the data of the United Nations Food and Agriculture Organization (FAO) 2013, 21 million tons of mandarin are produced in a year. Turkey is the biggest supplier of mandarins with a production capacity of 872 thousand tons. The amount of waste peel in the mandarin is approximately 8–14% by weight. Utilizing waste peels as valuable substances and reusing them as useful products positively affects the supplier economy. Valuable organic essences, oil species, and some other chemicals can be produced by the regeneration of these peels. These chemicals can be used in the cosmetic and pharmaceutical industries. However, after the removal of these important chemicals, mandarin peel residue still has a vast amount of biomass. The remaining biomass can be used as an effective adsorbent owing to the lignocellulosic and phenolic content (Mudyawabikwa *et al.* 2017; Koyuncu *et al.* 2018). In the literature, peels are converted to activated carbon by using a series of difficult, long and expensive processes. Thereby, the cost of the adsorbent increases depending on the process difficulty (Dod *et al.* 2012; Azharul-Islam *et al.* 2017; Shakoor & Nasar 2017). In this study, an alternative technique is proposed to produce a carbon-based adsorbent from the mandarin peel. In this study, the efficiency of the acid-treated carbonized mandarin peel (CMP) was tested to remove copper from a simulated copper-incorporated wastewater for the first time. The effects of initial copper concentration, solution pH, adsorbent dosage and contact time on copper removal were investigated.

EXPERIMENTAL

Materials

Copper sulfate pentahydrate was provided from Merck Chemicals, Turkey. Sulfuric acid (H₂SO₄) and sodium hydroxide (NaOH), which were used to convert the mandarin peels into functionalized carbon adsorbent, were provided from Merck Chemicals, Turkey.

Adsorbent preparation

The mandarin peel was washed with distilled water and dried in an oven (Santez SE-45F) at 100 °C for 24 hours. The functionalization was carried out in a hydrothermal reactor at 105 °C with 1 M of

H₂SO₄ solution for four hours. The acid treated carbonized mandarin peels (CMP) were dried in an oven at 70 °C for one day. Following the drying process, CMP was neutralized with 2 M NaOH solution. After the neutralization, CMP was dried in a vacuum oven at 70 °C for 2 hours.

Adsorbent characterization

In order to identify the active functional groups in CMP, Fourier-Transform Infrared (Perkin Elmer-Spectrum 100) spectra were studied between the wavelengths of 600–4,000 cm⁻¹. The thermal behavior and the degradation period of CMP were determined using Thermogravimetric Analysis (TGA-Mettler Toledo) in the temperature range of 25–800°C with a heating rate of 20°C/min.

Batch adsorption studies

In this study, the effects of heavy metal concentration, adsorbent dosage, pH, and the adsorption time on adsorption performances were investigated. Firstly, a stock solution of 1,000 mg/L Cu was prepared by diluting the copper sulphate pentahydrate. Then, varying concentrations of Cu (5, 15, 25 mg/L) were prepared from the stock solution. After determining the heavy metal concentration that gives the highest removal performance, the effect of the adsorbent dosage (0.625, 2.1875, 3.75 g/L) was investigated. The experiments were carried out in 100 mL Erlenmeyer with a total solution of 20 mL in a fixed mixer. Prior to performing the absorbance measurement, the solution was centrifuged and filtered. The absorbance of the purified solution was measured by means of a UV/visible spectrophotometer (Thermo Spectronic) with a wavelength of 790 nm. The metal removal (R) (%) and the adsorption capacity at the equilibrium state q_e (mg/g) were calculated using Equations (1) and (2), respectively.

$$R(\%) = \frac{(C_o - C_t)}{C_o} \times 100 \quad (1)$$

$$q_e = \frac{(C_o - C_e)}{W} \times V \quad (2)$$

where C_o, C_t, and C_e are the initial, at a given time t, and equilibrium heavy metal concentration (mg/L), V is the volume of the heavy metal solution (L), W is the weight of the adsorbent (g). The metal removal was calculated from the absorbance of the solution measured before and after the adsorption. The concentrations were calculated by means of Lambert Beer's law.

Isotherm investigations

Langmuir (Equation (3)) and Freundlich (Equation (4)) isotherms were adapted to the experimental results and the appropriate isotherm was determined by means of the following equations (Greenlee *et al.* 2009; Enniya *et al.* 2018):

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} \cdot K_L} + \frac{C_e}{q_{\max}} \quad (3)$$

where K_L is the Langmuir constant (mg/L), q_{max} is the maximum monolayer adsorption capacity of the adsorbent (mg/g).

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (4)$$

where K_F and n are the Freundlich constant. $1/n$ should be between '0' and '1'.

$$R_L = \frac{1}{1 + K_L C_0} \quad (5)$$

where R_L is the separation factor (Equation (5)). If the R_L value is between '0' and '1', then the adsorption isotherm is acceptable. If R_L is greater than 1, then the adsorption is define as unfavorable. If the R_L value equal to '0' or '1', then the adsorption is accepted as irreversible and linear, respectively (Ho & McKay 1998).

Kinetic studies

The amount of adsorbate which is adsorbed per unit mass of adsorbent q_t (mg/g) at a given time was calculated by using Equation (6). The adsorption kinetics of copper ions on the mandarin peel was investigated by accepting the kinetics as pseudo-first-order (Equation (7)), pseudo-second-order (Equation (8)).

$$q_t = \frac{C_0 - C_t}{W} \times V \quad (6)$$

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad (7)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} \times t \quad (8)$$

where q_t is the amount of adsorbate that is adsorbed per unit mass of adsorbent (mg/g), t is time (minute), K_1 and K_2 are pseudo-first order, pseudo-second order kinetic model rate constants (Ponnusami *et al.* 2009).

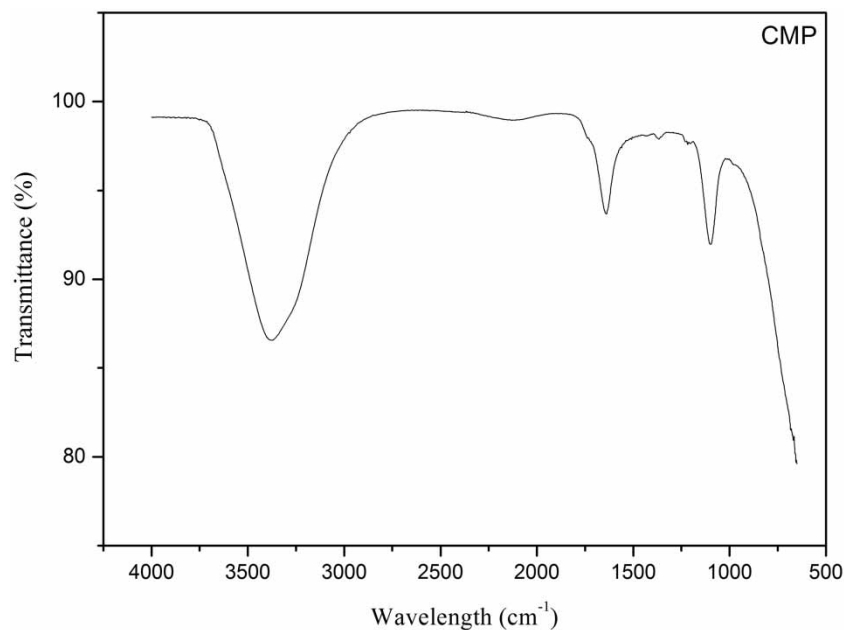


Figure 1 | FTIR spectra of adsorbent.

RESULT AND DISCUSSION

Characterization of the adsorbent

Figure 1 shows the FTIR spectra of CMP adsorbent. The peak at $3,360\text{ cm}^{-1}$ is assigned to the presence of -OH groups. The alkene stretching vibration of C = C is observed at $1,642\text{ cm}^{-1}$. The peaks at $1,229\text{ cm}^{-1}$ and $1,218\text{ cm}^{-1}$ should be assigned to the C-O stretching of ether and ester groups, respectively. The peak at $1,100\text{ cm}^{-1}$ is corresponding to the C-H stretching vibration (Rout *et al.* 2015; Zhang *et al.* 2014; Rattanapan *et al.* 2017).

The thermal stability of the CMP was determined by means of the TGA test. Figure 2 shows the weight loss of CMP depending on the temperature. It is clear from the figure that the degradation of CMP occurs in three steps. The degradation before the temperature of $100\text{--}105\text{ }^{\circ}\text{C}$ is corresponding to the moisture inside the adsorbent. The first decomposition temperature from $100\text{ }^{\circ}\text{C}$ to $200\text{ }^{\circ}\text{C}$ is due to the volatile organic compounds in CMP. The second decomposition temperature from $200\text{ }^{\circ}\text{C}$ to $450\text{ }^{\circ}\text{C}$ is corresponding to the decomposition of the cellulose and hemicellulose in the adsorbent. The last degradation temperature from $450\text{ }^{\circ}\text{C}$ to $700\text{ }^{\circ}\text{C}$ should be attributed to the degradation of lignin (Gaur *et al.* 2018; Sabela *et al.* 2019). After $700\text{ }^{\circ}\text{C}$, there is no significant weight loss.

Contact time is one of the effective parameters of the low-cost adsorption process. It directly affects the adsorption performance. For a high-performance and cost-effective process, it is desired to complete the adsorption process in a short adsorption time. Figure 3 shows the effect of contact time on copper removal; when the metal concentration was 5 mg/L , the adsorbent concentration was 3.75 g/L and the solution pH value was 7.

The copper removal was 87.51% in the first 90 minutes and then reached 100% of removal within 150 minutes. As shown in the figure, the removal of heavy metal ions showed a significant increase up to 90 minutes. After 90 minutes, the adsorption layer became saturated. The driving force between the adsorbent and metal ions maximized the mass transfer (Souza *et al.* 2018). The optimum contact time was determined as 150 minutes by providing a dynamic balance.

Heavy metal concentration is an important parameter for mass transfer during the adsorption process. (King *et al.* 2006; Mobasherpour *et al.* 2014). The appropriate metal concentration leads to an increase in the adsorption efficiency by increasing the interaction between the adsorbent surface and metal (Semerciöz *et al.* 2017). In this study, the effect of initial metal concentration on the

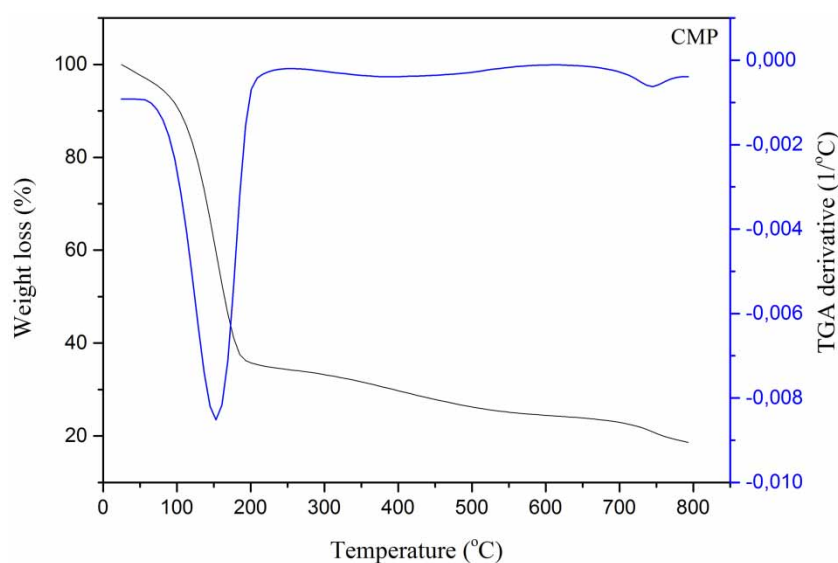


Figure 2 | TGA curve of adsorbent.

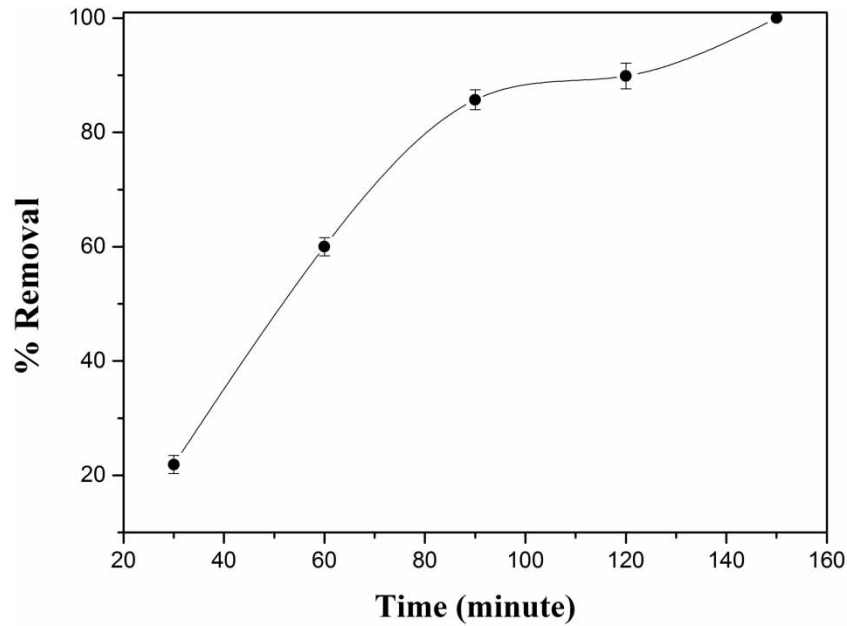


Figure 3 | Effect of contact time (5 mg/L Cu, 3.75 g/L adsorbent, pH: 7).

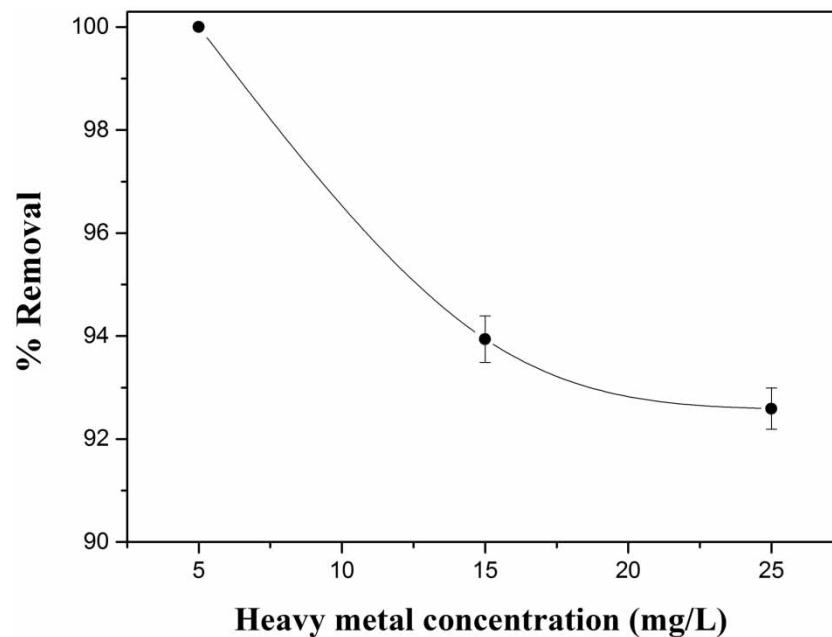


Figure 4 | Effect of metal concentration (3.75 g/L adsorbent, pH: 7, 150 min).

removal of copper from a copper-water solution was evaluated. Experiments were conducted with a constant adsorbent concentration of 3.75 g/L when the solution pH was 7 and the contact time was 150 minutes. The initial metal concentrations were changed from 5 mg/L to 15 mg/L and 25 mg/L. The effect of metal concentration on removal is illustrated in [Figure 4](#).

[Figure 4](#) shows that 100% of copper removal was achieved at low metal concentrations (5 mg/L). As the metal concentration was increased from 5 mg/L to 25 mg/L, the removal gradually decreased from 100% to 92.59%. The decrement should be attributed to the saturation of the active sites of the adsorbent with the metal ([Moghadam et al. 2013](#); [Semerjian 2018](#)). Therefore, increasing metal concentration in the solution caused a decrease in the removal.

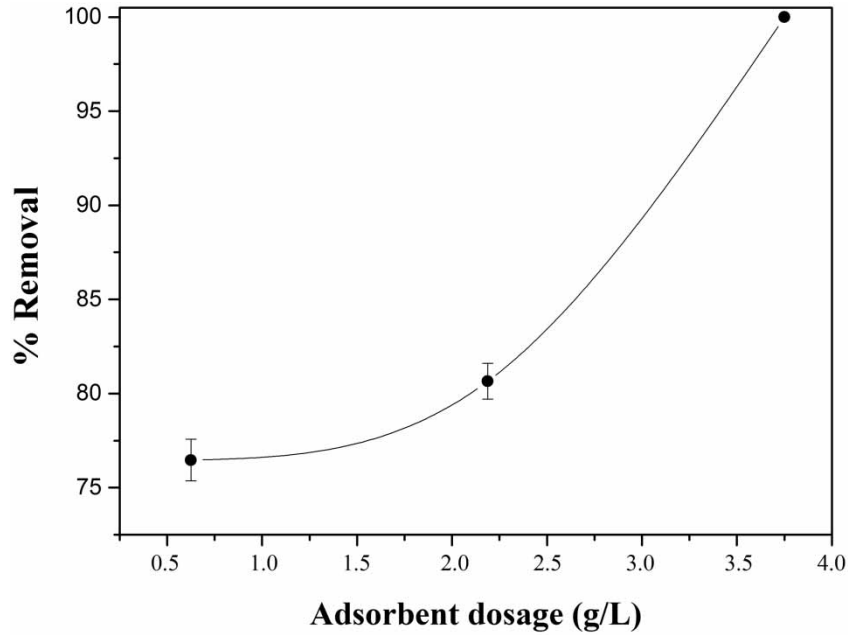


Figure 5 | Effect of adsorbent dosage (5 mg/L Cu, pH: 7, 150 min).

The adsorbent dosage or adsorbent concentration is another important parameter for the performance of the adsorption process. An increase in the adsorbent dosage directly affects the total cost of the adsorption process and recycling. Figure 5 displays the effect of adsorbent concentration on the copper removal process when the metal concentration was 5 mg/L, the solution pH value was 7 and the contact time was 150 minutes.

The removal enhanced from 76.47% to 100% when the adsorbent dosage increased from 0.625 g/L to 3.75 g/L. The concentration of the adsorbent determines the number of binding sites for adsorption. As the amount of the adsorbent increases in the adsorption media, the total surface area and the empty adsorption sites increase (Tadepalli *et al.* 2016). Therefore, adsorption performance increases as it was also obtained in the present study.

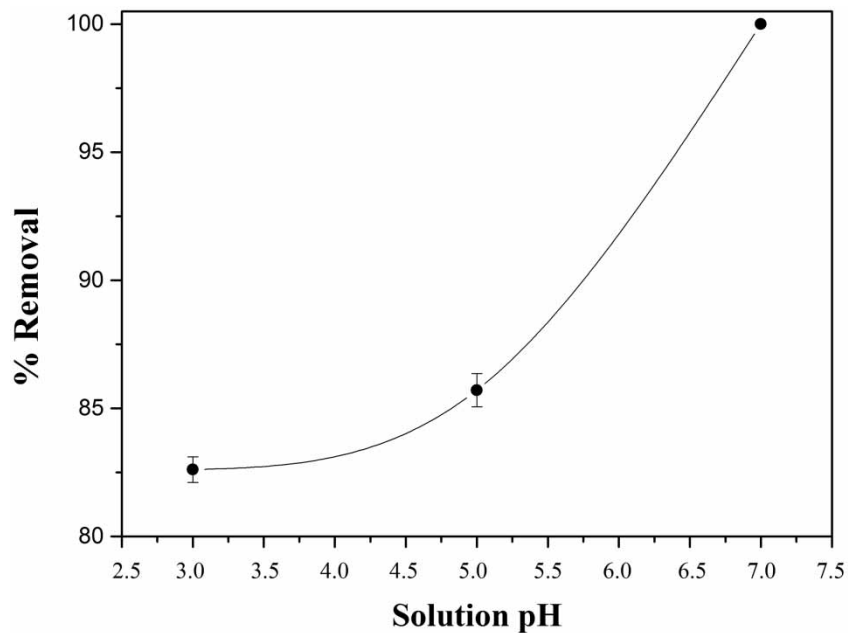


Figure 6 | Effect of the solution pH (5 mg/L Cu, 3.75 g/L adsorbent, 150 min).

The surface charge of the adsorbent affects the ion concentration and the degree of ionization of functional groups (carboxyl, hydroxyl, amino) in the adsorbent (Othman *et al.* 2012). The active surface sites of the adsorbent also change with the pH of the media. Since the adsorption performance is directly related to the active sites on the adsorbent, the varying pH also affects the adsorption performance (Ali *et al.* 2016). The effect of solution pH (pH:3, pH:5, pH:7) on the removal of Cu was investigated when the metal concentration was 5 mg/L, the adsorbent dosage was 3.75 g/L and the contact time was 150 minutes. The removal results are illustrated in Figure 6. As shown in the figure, 82.61% of copper removal was obtained when the pH of the solution was 3. At the same conditions (adsorbent dosage, copper concentration and contact time), 100% of removal was achieved when the pH was 7. In a strongly acidic environment, the adsorbent surface is positively charged while in a basic environment the adsorbent is charged negatively. This difference affects the adsorbent surface chemistry and leads to a significant change in the adsorption efficiency. As the pH decreases, the concentration of H_3O^+ ions increases and the adsorption of copper ions decreases. Similar results have also been obtained and reported by Ali *et al.* (2016).

Adsorption isotherm studies

The adsorption isotherm shows the distribution of adsorbate molecules between liquid and solid phases while the adsorption process is in an equilibrium state. The different isotherm models and isotherm data can be used to determine a suitable model for design purposes (Ali *et al.* 2016). Adsorption isotherms are used to optimize how the adsorbent interacts with the adsorbate. It gives information about the adsorption mechanism and surface properties of adsorbents. In the present studies, Langmuir (Figure 7(a)) and Freundlich (Figure 7(b)) isotherms were studied by using the removal data obtained from the different metal concentrations (5, 15 and 25 mg/L), a constant adsorbent dosage of 3.75 g/L, a constant adsorption time of 150 minutes, and a constant solution pH of 7. The isotherm data are shown in Table 1. According to the R^2 values, the most suitable isotherm was determined as the Freundlich isotherm. Therefore, it can be evaluated that the adsorption processes through the CMP occurred on heterogenous surfaces.

Adsorption kinetics

Kinetic models help to estimate the rate constants of adsorption and to explain the mechanism of the adsorption. In the present study, kinetic studies were performed using the metal concentration of 5 mg/L. In this concentration, the highest copper removal was achieved and with the highest

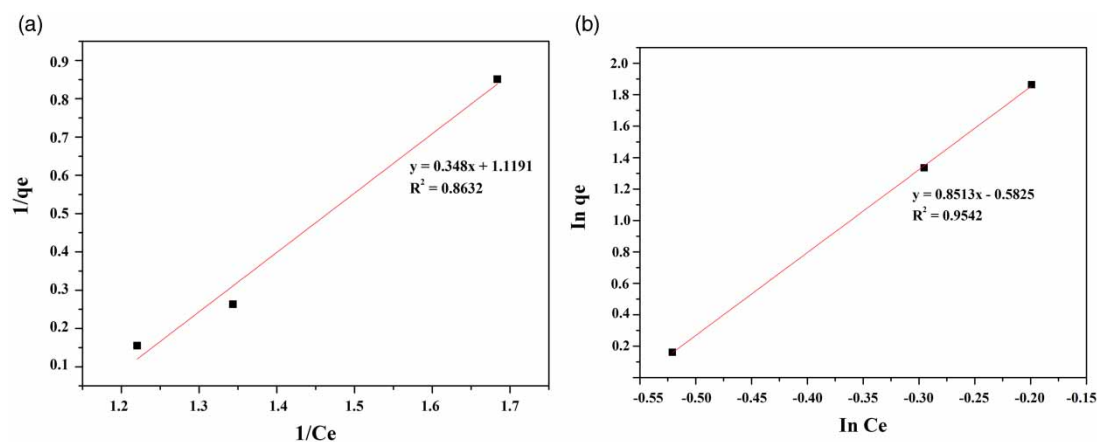


Figure 7 | Langmuir isotherm (a) and Freundlich isotherm (b).

Table 1 | Langmuir and Freundlich isotherm data

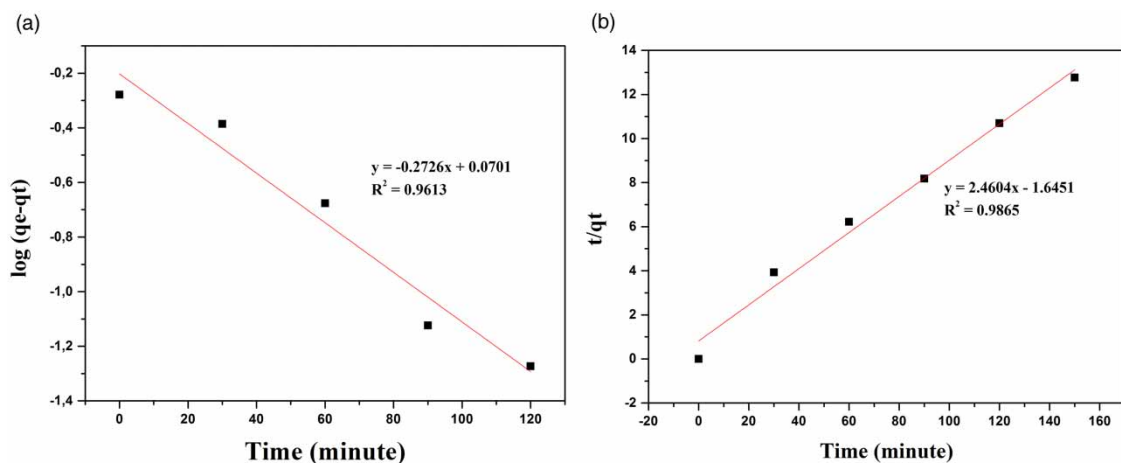
Heavy metal		Cu
Langmuir	q_m	0.8936
	K_L	3.2158
	R^2	0.8632
Freundlich	$1/n$	0.8513
	K_F	0.5585
	R^2	0.9542

adsorption rate. In order to estimate the adsorption mechanism, pseudo-first-order and pseudo-second-order models were applied. The kinetic model parameters are shown in Table 2 (C_0 : 5 mg/L, adsorption dose: 3.75 g/L, pH: 7).

For determining the appropriate kinetic model, both the experimental and calculated q_e values accompanied with the R^2 value should be taken into account. Figure 8 shows the kinetic plots. According to the results obtained in this study, the pseudo-second order kinetic was suitable. The kinetic model was acceptable since the q_e value that was calculated from the figure and obtained from the experiment were close to each other. The pseudo-second order kinetic model confirmed that the adsorption rate was independent from the adsorbate concentration and was dependent on the adsorption capacity (Lim *et al.* 2017).

Table 2 | Kinetic parameters for the adsorption of copper onto CMP

Heavy metal		Cu
Pseudo 1st order	K_1 (min^{-1})	0,6278
	$q_{e,\text{exp}}$ (mg/g)	1,17496
	$q_{e,\text{cal}}$ (mg/g)	1,1751
	R^2	0,9613
Pseudo 2nd order	K_2 (g/mg min)	3,6804
	$q_{e,\text{exp}}$ (mg/g)	1,17496
	$q_{e,\text{cal}}$ (mg/g)	0,4064
	R^2	0,9865

**Figure 8** | Pseudo 1st order kinetic model (a); pseudo 2nd order kinetic model (b).

Adsorption stability and comparison of results with literature

In this study, the removal of copper metal from wastewater by using acid-treated carbonized mandarin peels was investigated. The highest copper removal of 100% was achieved when the copper concentration was 5 mg/L, the adsorbent dosage was 3.75 g/L, and the solution pH was 7. After the adsorption test, the adsorbent was treated with 1 M HCl for four hours, dried and used for the same condition (5 mg/L Cu, 3.75 g/L adsorbent dosage, 7 solution pH). As a result, 94% of removal was achieved with regenerated adsorbent. Table 3 gives the adsorbents and experimental parameters used in copper removal. In the literature, there are no reported studies on heavy metal removal using the acid-treated mandarin peel. Therefore, the adsorbent results obtained from different fruit peels are included in the table.

Table 3 | Studies removal of copper metal by using agricultural wastes

Adsorbent	Initial metal concentration (mg/L)	pH	Time (min)	Removal (%)	Reference
Peanut husk	10	7	180	60	Salam <i>et al.</i> (2011)
Henna leaves	10	7	90	91	Shanthi & Selvarajan (2013)
Origanum	10	7	16 h	93	Al-Senani & Al-Fawzan (2018)
Cotton plant	25	6	90	81	Kamble <i>et al.</i> (2018)
Mandarin peel	10	7	150	100	This study

CONCLUSION

In the present study, a new acid-treated and factionalized carbonized adsorbent was synthesized from the mandarin peels and used for the adsorption of simulated copper solution. As a result, it was obtained that the CMP was very effective to remove copper from simulated metal-containing water solution. The highest removal of 100% was obtained when the copper concentration was 5 mg/L, the adsorbent dosage was 3.75 g/L, and the solution pH was 7. After HCl regeneration, the adsorbent maintained 94% of its activity. The Freundlich isotherm was more appropriate to explain the removal of copper from the solution. The kinetic of the heavy metal adsorption onto CMP was obtained as pseudo-second-order. As a result, it can be evaluated that the adsorbent synthesized from the waste mandarin peels is an effective candidate to be used as a low-cost adsorbent.

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