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Effect of pH on Adsorption of Cu^{2+} by Using Composite of Polyvinyl Alcohol (PVA)/Kaolin

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Abstract. The existence of copper ions in the aquatic environment at a high level can cause negative repercussions for living organisms due to the toxic effect of bioaccumulation in the food chain. Hence, a profound effort is imperative to remove them from water effectively. Among feasible alternatives, a composite film made of PVA and kaolin is reviewed for copper removal via an adsorption mechanism. In this paper, the removal of copper ions from aqueous solution using PVA/Kaolin composite film has been studied with initial copper ions concentration within the range of 50 and 100 ppm and pH of the aqueous solution being controlled at 4, 7, and 9. The loading of 3 wt% kaolin in PVA shows the best adsorption performance in removing 99.14% of 50 ppm copper with an equilibrium adsorption capacity of 5.379 mg g^{-1} at pH 7. The composite can maintain the adsorption performance for the removal of 100 ppm copper solution at 96.26%.

Keywords: Composite, Copper, Heavy metal, Kaolin, Polyvinyl alcohol

INTRODUCTION

Heavy metal contamination in the water body has been an arising global environmental issue with a consequential threat to the ecosystem and public health. The origin of contamination can be traced from industrial sectors, agricultural applications, domestic effluents, and natural activities (Rasheed et al. 2019). Industrial sectors such as mining, semiconductor manufacturing, and metal plating contribute severely to the heavy metal pollution, which the characteristics are non-biodegradable, toxic, and persistent (Azimi et al. 2017; Burakov et al. 2018). Heavy metals can accumulate in living tissues, causing multiple diseases even at a low level of exposure. The degree of toxicity from the heavy metals is significantly high since their accumulation in living organisms is followed by bio-amplification in the food chain (Rasheed et al., 2019). Copper is one of the trace elements necessary for humans, plants, and animals at low concentrations. Copper, as a component of metalloenzymes, donate or accept electron in the human body, and it has a significant part in producing hemoglobin, collagen, and

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melanin for human health (Osredkar, 2011). However, a high concentration of copper is normally found in wastewater due to its great value and application in industrial sectors. The primary industrial sources which contribute heavily to the contamination of copper in wastewater are metal finishing, electroplating, and mining activities (Renu et al. 2016). Copper ions need to be removed before discharging them to the environment in pursuance of preventing negative repercussions. In fact, World Health Organization deduced that the content of copper ions in drinking water must be lower than 2 mg/L (Team, 2017).

Several methods have been used to treat heavy metal ions from industrial or domestic wastewater, such as ion exchange, membrane separation, absorption, coagulation / flocculation, photocatalytic degradation, and biological treatment (Ngulube et al. 2017; Van Aken 2008; Zhu et al. 2017). Among those technologies, adsorption is one of the most widely used for industrial applications due to its effectiveness, selectivity, and cost-efficiency. To date, activated carbon, natural or modified biochar, and clay minerals are the main kind of adsorbents used as adsorbents for industrial applications. Compared to other commercial adsorbents such as activated carbon, clay mineral is considered superior due to their low cost, wide availability, and excellent adsorption performance (Han et al. 2019).

Kaolin, one kind of clay mineral, is a structured hydrated aluminum silicate having units of one layer of silica tetrahedrons and one layer of alumina octahedrons with the finest particle size (Tan et al. 2020; Uddin 2017). Kaolin is a natural mineral, hydrated aluminosilicate, and broadly consumed in various industries such as cosmetic, pharmaceutical, and agriculture sectors. Kaolin has a small particle size and complex structure of porous, allowing strong physical and chemical interactions with dissolved species (Uddin 2017). Chemical modification by acid and base compounds also has been introduced to alter the structure, surface functional groups, and surface area of kaolin (Boukhemkhem & Rida, 2017). Acid treatment has been known as a method to disaggregates the kaolin particles, eliminate impurities of minerals and cause dissolution of the external layers (Behnamfard et al. 2019; Niu et al. 2021).

Meanwhile, alkali treatment facilitates the increasing of active centers of kaolin when treated with sodium hydroxide (Boukhemkhem & Rida, 2017). In the past few years, the usage of kaolin as an adsorbent has escalated rapidly due to its great adsorption capacity and ion-exchange capability for organic and inorganic molecules. The utilization of kaolin to adsorb heavy metals have been used in the case of copper, iron, lead, chromium, and cadmium in the form of pure kaolin, modified kaolin, and composite fibers (Al-Makhadmeh & Batiha 2016; Bahah et al. 2020; Belachew & Hinsene 2019; Huang et al. 2016; Roque-Ruiz et al. 2016). Hence, kaolin can serve as an alternative to the low-cost adsorbent. However, as an adsorbent, kaolin is generally used in powder form, which limits its application due to the limited reusability and recyclability, and may cause secondary pollution. One way to solve this problem is by making a polymer composite film that will provide high surface area to volume with flexibility (Simón-Herrero et al. 2018).

PVA is a synthetic hydrophilic polymer with wide application in the wastewater treatment industry due to its great properties such as high hydrophilicity, non-toxic, bio-compatible, biodegradable, and possess good mechanical properties (Ben Halima 2016). PVA has been utilized for heavy metal removal since it consists of unpaired electrons, while the heavy metals contain valence shells (Al-Hwaiti et al. 2019). Thus, according to the 18-electron rule, PVA unpaired electrons will bond with the valence shells of heavy metal ions, which ease the removal of heavy metal ions from water (Al-Hwaiti et al. 2019). In addition, PVA is a semi-crystalline polymer having hydroxyl groups that easily create hydrogen bonds with other molecules (Abu-Saied et al. 2017). Thus, the combination of kaolin and PVA is not only expected to improve the adsorption of copper than solely use of material. In addition, the use of this PVA-Kaolin composite can eliminate the separation step of the used adsorbent from water. Hence the reusability and recyclability can be improved. Therefore, in this study, the compatibility of kaolin and PVA as a composite film is being addressed in the direction of assessing their potential for the removal of copper from an aqueous solution.

In the interest of measuring the removal efficiency using the composite film, variant samples are being prepared with different concentrations of copper at 50 and 100 ppm. In addition, the pH of copper solutions is being controlled from acidic to basic for the evaluation of the effect of solutions' pH on copper removal.

METHODOLOGY

Materials

PVA (99+% hydrolyzed) and sodium hydroxide (NaOH) were purchased from Sigma-Aldrich (USA), kaolin (Kaolin (M) Sdn. Bhd., Malaysia), hydrochloric acid (HCl) 37% was purchased from Fischer Scientific (UK), sodium chloride (NaCl) was purchased from Merck (Germany), copper (II) sulfate was purchased from Bendosen. All chemicals were used without further purification. De-ionized (DI) water (18.2 MΩ) from PureLab Flex was utilized for the whole experiment.

Pretreatment of Kaolin

Kaolin was pretreated using an acid-alkali solution based on the previous method with some modifications (Boukhemkhem & Rida, 2017). Around 10 g of kaolin was dried in the oven for 1h at a temperature of 100 °C, followed by acid treatment using 50 ml of 2.5 M HCl solution at a temperature of 80 °C for 7 h. Then, the acid-treated kaolin was cooled and rinsed with distilled water using vacuum filtration three times. Subsequently, the rinsed sample was placed in an oven at 110 °C for 3 h to obtain dry solid kaolin. Later, an alkali treatment was conducted on the dried sample with 50 ml of 0.5 M NaOH solution, following the exact procedures used in acid treatment.

Synthesis of composite PVA/Kaolin

PVA solution was prepared by dissolving 1.25 g of PVA powder into 25 ml of DI water on the heating plate at 100^0C with constant stirring overnight. Then, 3, 5, 7, and 10 wt% of pretreated kaolin were added to the PVA solution, and samples were then labeled as PVA/Kao3, PVA/Kao5, PVA/Kao7, and PVA/Kao10, respectively. Each mixture of kaolin and PVA was stirred until a uniform suspension was observed. The mixture samples were then cast on the flat petri dish and left at constant room temperature to dry for 2 days. Finally, the resultant composites were peeled off from the petri dish and kept in the desiccator for upcoming testing.

Characterization of kaolin and composite

The crystallinity of kaolin was analyzed using X-ray Diffraction (XRD) (Bruker D8), X'Pert3 Powder, and Empyrean PANalytical with Cu Kα diffraction angle (2θ) from 10 to 80° with a step size of 2°/step and exposure time of 1s/step. The morphology of kaolin was done using Field Emission Scanning Electron Microscopy (FESEM) analysis (Zeiss Supra55). The surface area of kaolin was investigated by using N_2 sorption isotherm analysis (Micromeritics ASAP 2020). Around 1 g of the composite was cut with the dimension of 4 cm x 2.5 cm and characterized by using the Fourier Transform Infrared (FTIR) analysis (Perkin Elmer Spectrum One Spectrophotometer, USA). The spectra were recorded using a wavenumber range of 4000 – 500 cm^{-1} with 8 scans and a resolution of 4 cm^{-1}. Zeta Potential analysis was conducted to determine the Point Zero Charge (PZC) for each composite (Malvern, Zetasizer Nano ZSP, UK). Firstly, the composite films were cut and weighed at 0.125 g using the weighing balance. Then, the pH of the solution was adjusted to 2, 4, 6, 8, and 10 by adding 0.1 M of HCl or NaOH. The composite films were then submerged in 10 ml of 1 M NaCl solution in the capped vials. The set of solutions was left for 24 h before the final pH was recorded. The PZC value was determined as the point on the graph, at the position where the initial pH vs. final pH curve intersected the y = x line. Contact angle measurement was carried out to evaluate the hydrophilicity property of composite films using a Goniometer at the temperature of 25 °C (Rame Hart, 260, USA). The settings for this characterization testing, including the selection of water as the droplet liquid, air as the external phase, and the composite films, were introduced as the solid phase.

Removal of copper ions

The concentration of the copper solution was prepared at 50 and 100 ppm by dissolving the respective weight of copper (II) sulfate powder in the determined volume of DI water. Next, 0.5 g of the composite film was submerged into 50 ml of copper solutions for 30 min, 1 h, 2 h, and 4 h. Eventually, a vis spectrophotometer (Hach DR3900, USA) was used to determine the concentration of copper ions that remained in the aqueous solution (Yotova et al. 2019). Then, the removal test continued by varying the pH of copper solutions at 4, 7, and 9 through the addition of 0.1 M HCl or NaOH. Similarly, after 30 min, 1 h, 2 h, and 4 h of submerging the composite, the spectrophotometer measured the remaining concentration of the copper solution. Finally, the removal efficiency of copper was calculated using the following equation:

Removal efficiency (%) = $\frac{Co-Ce}{Co}\ x\ 100\%$

Where Co represents the initial concentration of copper solution (mg/L) and Ce is the concentration of copper solution at equilibrium (mg/L). The experiment was performed at room temperature of around 23 – 26 °C.

RESULTS AND DISCUSSION

Characteristic of pretreated Kaolin

The XRD pattern of pretreated kaolin is shown in Fig. 1a with diffraction peaks of kaolinite are shown at 2θ of 19.85°, 26.7°, 31.7°, 34.4°, 39.4°, and 45.7° which are matched with the JCPDS database file (PDF 01-089-6217). The XRD analysis is consistent with previous studies on kaolin (Caponi et al., 2017; Dewi et al. 2018). According to the N_2 adsorption-desorption isotherms curve in Fig. 1b, the surface area of kaolin is found to be around 21.49 m^2/g. Whereas, from the hysteresis loop, this kaolin has the characteristic of mesoporous material. The surface area of Kaolin prepared from our method is higher compared to those prepared by sol-gel, which is around 18.16 m^2/g (Dissanayake et al. 2021). The pretreatment of kaolin was carried out using acid and alkali solution with the aim of dissolving the impurities, disturbing the kaolin structure, and improving the surface area, which is eventually expected to enhance the adsorption of heavy metals (Cheng et al. 2021; Niu et al. 2021). FESEM image shows that kaolin has a layered structure of flake-like sheets stacked closely together (Fig. 2a). The release of H^+ ions from the edge of the flake-like structure could promote the adsorption of heavy metals (Gu et al. 2019). A smaller structure of fragmented flakes also appears which can be due to the pretreatment condition using acid-alkali solution (Cheng et al. 2021). The casted composite film of PVA/Kaolin is shown in Fig. 2(b), with few agglomerations of kaolin that can be observed on the surface of the composite.

Characteristics of PVA/Kaolin

The FTIR spectra of the composite show the peaks related to functional groups belonging to kaolin (Fig. 3). The bands at 1001 and 1123 cm^{-1} represent Si-O stretching, and the vibration of Si-O-Si groups originated from kaolin (Cheng et al. 2021; Mustapha et al. 2019). The band at 912 cm^{-1} is attributed to the stretching of Al-OH groups (Cheng et al. 2021; Mustapha et al. 2019). The band at 798 cm^{-1} is assigned to the Si-O stretching vibrations of kaolin (Cheng et al. 2021). The presence of kaolin also contributed to the peak detection at the band of 743 cm^{-1} due to the Si-O-Al bond coming from the tetrahedral and octahedral layers (Boukhemkhem & Rida, 2017). Finally, the band region at 689 cm^{-1} is attributed to the bending and symmetric deformation vibrations of Si-O-Si groups of kaolin (Cheng et al. 2021).

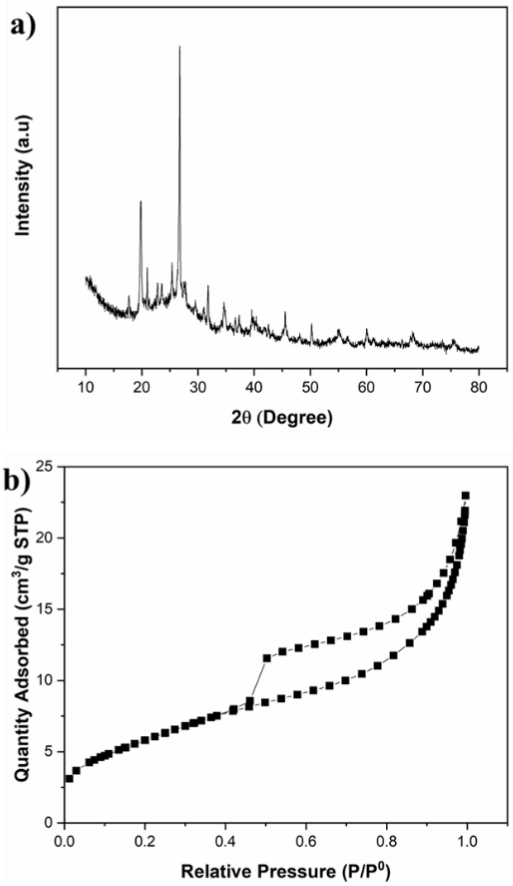

Fig. 1: a) XRD pattern and b) N_2 adsorption-desorption isotherms of Kaolin.

The wavenumbers at 3615 and 3696 cm^{-1} represent the hydroxyl group sitting at the clay platelets' edges. The hydroxyl group interaction happens at the surface of the octahedral layers, with the oxygen atoms of the adjacent tetrahedral layers and the internal hydroxyl groups (Boukhemkhem & Rida, 2017). The incorporation of PVA decreased the band intensity, as seen in Fig. 3, with a small peak appearing at around 1442 cm^{-1}, representing bending vibrations of C-H (Hendrawan et al. 2019).

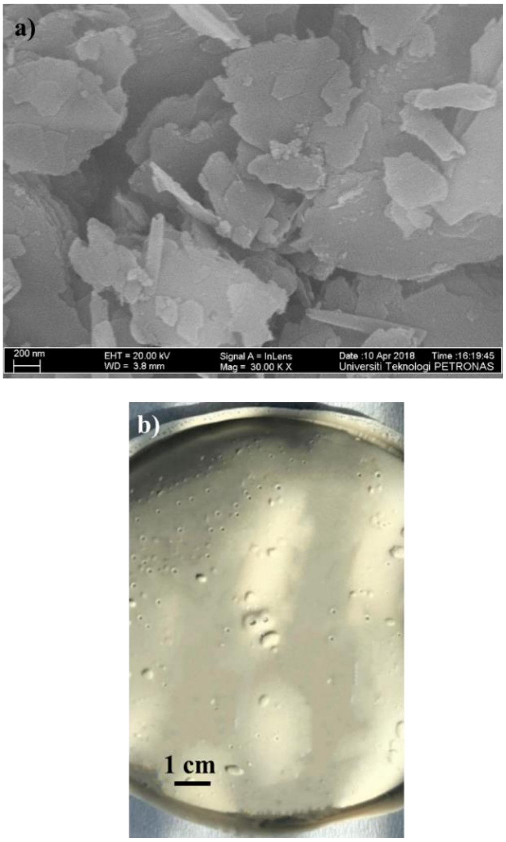

Fig. 2: a) FESEM image of Kaolin, and b) Image of PVA/Kao film.

Fig. 4 shows contact angle values for PVA/Kao3, PVA/Kao5, PVA/Kao7, and PVA/Kao10 at around 39.7°, 41.49°, 48.32°, and 56.78°, respectively, which indicate that all synthesized composites have a hydrophilic surface. A previous study on the composite of polypropylene and kaolin shows the contact angle of film at around 39.9° (Yusoff et al., 2010). A slight increase in contact angle with the increasing percentage of kaolin can be caused by the aggregation of particles and increasing loading (Hu et al. 2020). The contact angle of kaolin was reported at around 45° to 60° (Liu et al., 2015; Mgbemena & Mgbemena, 2013). The hydrophilicity of composite helps the interaction of the material with polar solvents such as water, which is beneficial for the application of composite for adsorption in aquatic environment.

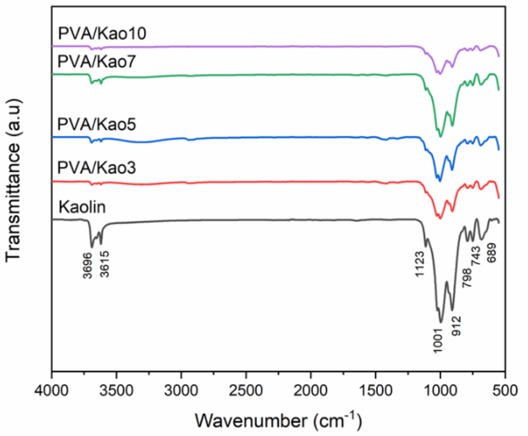

Fig. 3: FTIR spectra of Kaolin and PVA/Kaolin samples.

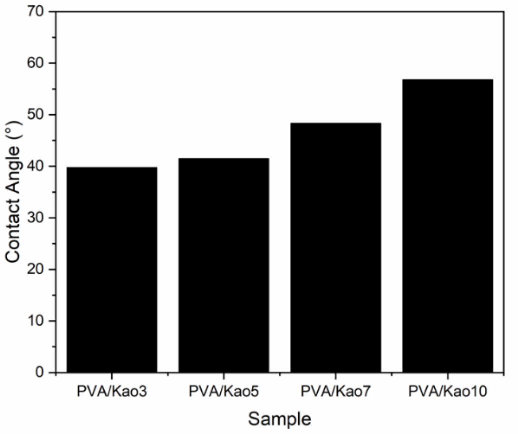

Fig. 4: Contact angle of PVA/Kaolin samples.

Adsorption performance of PVA/Kaolin

The adsorption behavior of PVA/Kaolin composite is observed through PZC analysis, in which PZC values for PVA/Kao3, PVA/Kao5, PVA/Kao7, PVA/Kao10 are measured at pH 6.3, 6.6, 7.8, and 7.9, respectively (Fig. 5). The PZC value signifies that the net surface charge of the composite is zero. Below the PZC, the composite will be positively charged, while above the PZC, the composite will be negatively charged (Aragaw & Angerasa 2020). Hence, we can see this effect on the adsorption of copper, where the adsorption at pH 7 is higher than at pH 4 (Figs. 6(a) and 6(b)).

Previous studies in using tamazert kaolin for the removal of methylene dye show a similar range of PZC from pH 6 to 7.4. Hence alkaline environment provides higher adsorption performance from a negatively charged surface (Boukhemkhem & Rida, 2017). In removing heavy metals, acid-activated kaolin has shown significant improvement in the adsorption of Cu(II) and Ni(II) at pH higher than PZC of 5.3 (Chai et al., 2020). In this study, pH 7 shows the most conducive environment for the adsorption of copper. pH is an important factor affecting the adsorption performance of kaolin, due to the protonation effect, which affects the availability of active sites (Abbar et al., 2017).

At a pH value lower than PZC, the surface of kaolin is protonated, and there is competition between Cu^{2+} and H^+. When the pH is higher than PZC, the sorption sites become available because they turn more negatively charged, which increases the electrostatic force and attraction (Abbar et al. 2017; Chai et al. 2020).

However, the increase of pH to 9 in this study shows a slight decrease in adsorption performance (Fig. 6(c)). This can be due to the precipitation of copper that can happen at pH higher than 7 in the form of hydroxide (Abbar et al. 2017; Chai et al. 2020). The highest adsorption of Cu^{2+} can be achieved by using PVA/Kao3 at around 99.14%. However, the adsorption performance of other composites only slightly decreased, which can still be maintained at above 80%. The increasing kaolin loading in PVA might increase the agglomeration of particles inside the polymer matrix, hence decreasing the availability of sorption sites (Manyangadze et al. 2020).

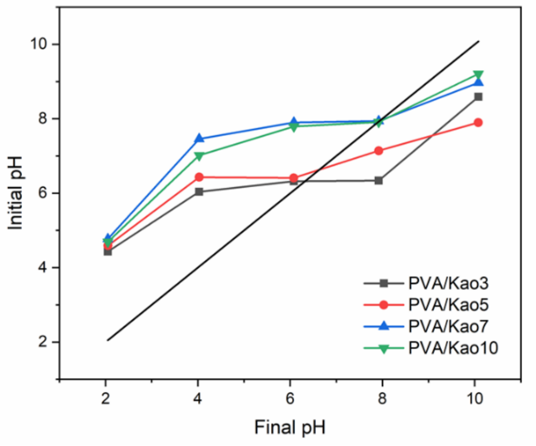

Fig. 5: Point of zero charge of PVA/Kaolin samples.

The adsorption ability of PVA/Kao3 was then tested by using a higher Cu^{2+} concentration at 100 ppm by performing the experiment at pH 7 to avoid the precipitation of metal at higher pH (Figure 7). The adsorption of 100 ppm copper solution still can be maintained above 90%, at around 96.26%, which shows a satisfying performance of composite for removal of copper in an aquatic environment at high concentration.

Kinetic of adsorption

The adsorption of copper fits the pseudo-second-order kinetic (Figure 8) following Eq. (1) (Tan et al. 2020):

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \qquad (1)$$

Table 1. Parameter of pseudo order kinetic model for copper removal.

Sample	Parameter (pH 4)		Parameter (pH 7)		Parameter (pH 9)	
PVA/Kao3	q_e (calc., $mg.g^{-1}$)	5.35	q_e (calc., $mg.g^{-1}$)	5.379	q_e (calc., $mg.g^{-1}$)	4.975
	q_e (exp., $mg.g^{-1}$)	4.818	q_e (exp., $mg.g^{-1}$)	4.957	q_e (exp., $mg.g^{-1}$)	4.409
	k ($g.mg^{-1}.min^{-1}$)	0.0086	k ($g.mg^{-1}.min^{-1}$)	0.0105	k ($g.mg^{-1}.min^{-1}$)	0.0089
	h (kq_e^2, $mg.g^{-1}.min^{-1}$)	0.247	h (kq_e^2, $mg.g^{-1}.min^{-1}$)	0.304	h (kq_e^2, $mg.g^{-1}.min^{-1}$)	0.22
	R^2	0.981	R^2	0.993	R^2	0.966
PVA/Kao5	q_e (calc., $mg.g^{-1}$)	5.373	q_e (calc., $mg.g^{-1}$)	5.42	q_e (calc., $mg.g^{-1}$)	4.693
	q_e (exp., $mg.g^{-1}$)	4.749	q_e (exp., $mg.g^{-1}$)	4.945	q_e (exp., $mg.g^{-1}$)	4.288
	k ($g.mg^{-1}.min^{-1}$)	0.0074	k ($g.mg^{-1}.min^{-1}$)	0.0098	k ($g.mg^{-1}.min^{-1}$)	0.0135
	h (kq_e^2, $mg.g^{-1}.min^{-1}$)	0.213	h (kq_e^2, $mg.g^{-1}.min^{-1}$)	0.287	h (kq_e^2, $mg.g^{-1}.min^{-1}$)	0.297
	R^2	0.971	R^2	0.989	R^2	0.981
PVA/Kao7	q_e (calc., $mg.g^{-1}$)	4.933	q_e (calc., $mg.g^{-1}$)	5.429	q_e (calc., $mg.g^{-1}$)	4.782
	q_e (exp., $mg.g^{-1}$)	4.31	q_e (exp., $mg.g^{-1}$)	4.918	q_e (exp., $mg.g^{-1}$)	4.333
	k ($g.mg^{-1}.min^{-1}$)	0.0076	k ($g.mg^{-1}.min^{-1}$)	0.0086	k ($g.mg^{-1}.min^{-1}$)	0.0116
	h (kq_e^2, $mg.g^{-1}.min^{-1}$)	0.185	h (kq_e^2, $mg.g^{-1}.min^{-1}$)	0.254	h (kq_e^2, $mg.g^{-1}.min^{-1}$)	0.266
	R^2	0.952	R^2	0.987	R^2	0.978
PVA/Kao10	q_e (calc., $mg.g^{-1}$)	5.084	q_e (calc., $mg.g^{-1}$)	5.26	q_e (calc., $mg.g^{-1}$)	4.697
	q_e (exp., $mg.g^{-1}$)	4.572	q_e (exp., $mg.g^{-1}$)	4.837	q_e (exp., $mg.g^{-1}$)	4.348
	k ($g.mg^{-1}.min^{-1}$)	0.0091	k ($g.mg^{-1}.min^{-1}$)	0.011	k ($g.mg^{-1}.min^{-1}$)	0.015
	h (kq_e^2, $mg.g^{-1}.min^{-1}$)	0.235	h (kq_e^2, $mg.g^{-1}.min^{-1}$)	0.305	h (kq_e^2, $mg.g^{-1}.min^{-1}$)	0.328
	R^2	0.976	R^2	0.99	R^2	0.985

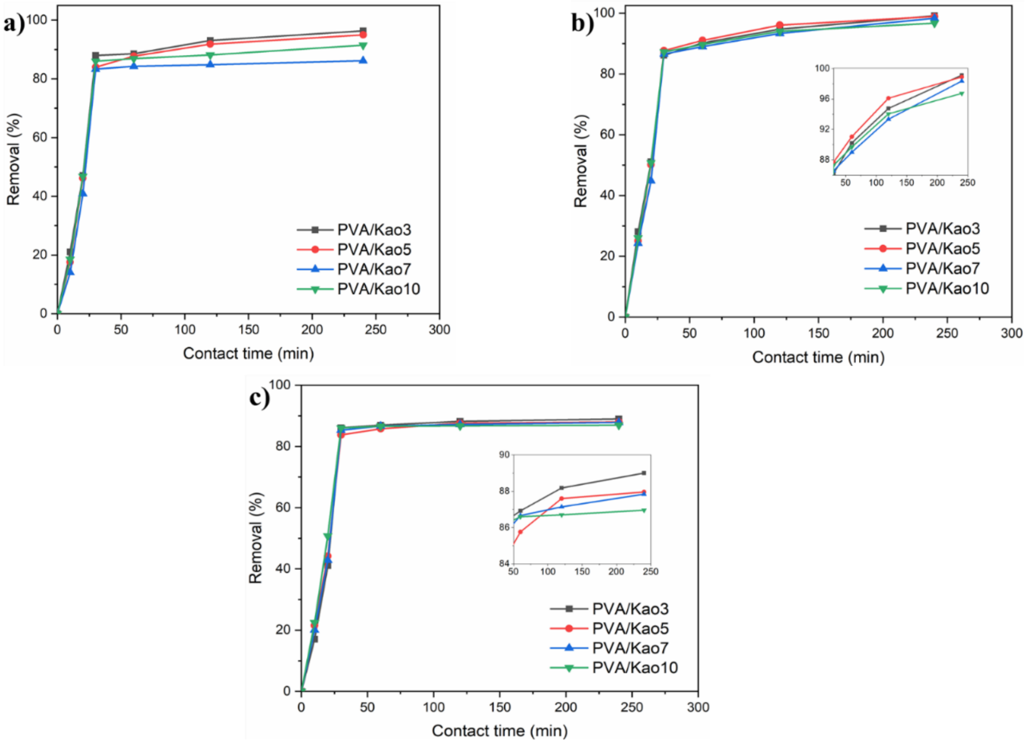

Fig. 6: Adsorption of copper using PVA/Kaolin samples at pH a) 4, b) 7, and c) 9.

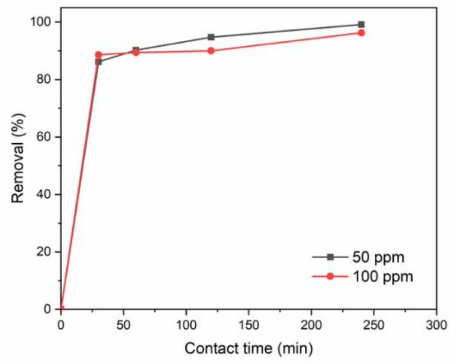

Fig. 7: Removal of copper using PVA/Kao3 at pH 7.

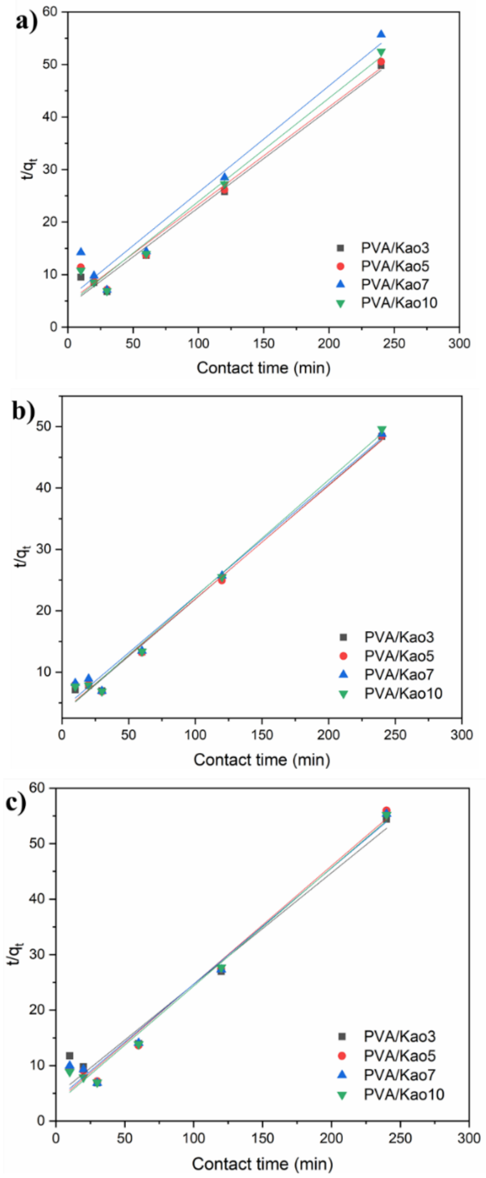

Fig. 8: Pseudo-second-order kinetic fitting of copper removal using PVA/Kaolin samples at pH a) 4, b) 7, and c) 9.

Where t is the adsorption time, k is the pseudo-second-order rate constant, q_e and q_t are the amount of copper adsorbed at equilibrium and certain time, t, respectively.

The adsorption mechanism is chemically rate-controlling; hence it favors the electrostatic interaction between copper and kaolin (Belachew & Hinsene 2019). The equilibrium adsorption capacity of the composite for the best sample is observed at around 5.379 mg g^{-1}, with a rate constant of 0.0105 g mg^{-1} min^{-1} (Table 1). The improvement can be made in the future to accelerate the adsorption process through crosslinking between the PVA and pretreated kaolin.

CONCLUSIONS

This study aims to fabricate a composite film made up of kaolin and PVA for the removal of copper ions from wastewater and aqueous solution. Thus, the experimental work includes the composite films fabricated with different kaolin loading varying between 3, 5, 7, and 10 wt% into the PVA solution. The loading of kaolin slightly increased the contact angle of the composite from 39.74° to 56.78°. The PZC of composite ranges from 6.3 to 7.9. The best adsorption performance was achieved by using 3 wt% of kaolin loading in PVA at pH 7 due to the surface of the composite being negatively charged, which improves the electrostatic attraction of copper on the surface of the composite. The pseudo-order kinetic fits the adsorption rate model, which shows that adsorption is governed by chemisorption.

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