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REMOVAL OF COPPER IONS FROM AQUEOUS SOLUTIONS USING POLY(VINYLBENZYL CHLORIDE)

(Penyingkiran Ion Kuprum dari Larutan Akueus Menggunakan Poli(vinilbenzil klorida))

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Abstract

Nowadays, contamination of copper (Cu(II)) has become one of the worst environmental problems. Due to its environmental resistance and persistence, the treatment of Cu(II) is crucial. Poly(vinylbenzyl chloride) (PVBC) was synthesised through reversible addition-fragmentation chain transfer (RAFT) polymerisation technique utilising monomer vinylbenzyl chloride (VBC), 4-cyanopentanoic acid dithiobenzoate (CPADB) as RAFT agent and 4,4′-Azobis (4-cyanopentanoic acid) (ACPA) as initiator. This study aims to synthesise PVBC and to test the ability of PVBC to remove Cu(II) ions from aqueous solution. In this study, PVBC was successfully synthesised when reacted for 24 h at 80 °C, and the ability of the PVBC to adsorb and remove Cu(II) ions was investigated. Important adsorption parameters such as adsorbate concentration, adsorption dosage, and contact time were studied. The maximum Cu(II) adsorption capacity (q_{max}) of PVBC was 263.15 mg/g with a copper removal rate of 95% under optimum initial concentration (160 mg/L), adsorbent dosage (14 mg), and contact time (180 min). The experimental results better fit into the Langmuir adsorption isotherm model than the Freundlich model, and the kinetics experiments were compared with the pseudo-second-order kinetic model. Polymer adsorption efficiency was above 90% after five cycles of adsorption and desorption, but the overall adsorption capability of PVBC for Cu(II) ions began to decrease after another five cycles from 80% to 54%. Given the outcomes acquired, it can be concluded that PVBC can be an efficient and potential adsorbent for the removal of Cu(II) ions from aqueous solution. The adsorption study showed that PVBC has an affinity to Cu(II) ions. The prepared PVBC is potentially useful for wastewater treatment applications.

Keywords: removal, copper(II), poly(vinylbenzyl chloride), isotherm, kinetic

Abstrak

Pada masa kini, pencemaran tembaga(II) (Cu(II)) telah menjadi salah satu masalah persekitaran yang paling teruk. Oleh kerana ketahanan persekitarannya, rawatan Cu(II) sangat penting. Poli(vinilbenzil klorida) (PVBC) disintesis melalui teknik pempolimeran pemindahan rantai penambahan-fragmentasi boleh dibalikkan (RAFT) yang menggunakan monomer vinilbenzil klorida (VBC), 4-sianopentanoik asid ditiobenzoat (CPADB) sebagai agen RAFT dan 4,4′-Azobis (asid 4-sianopentanoik) (ACPA) sebagai bahan pemula. Tujuan kajian ini adalah untuk mensintesis PVBC dan menguji kemampuan PVBC menyingkirkan ion Cu(II) dari larutan berair. Dalam kajian ini, PVBC berjaya disintesis selama 24 jam pada suhu 80 °C dan kemampuan PVBC untuk menjerap dan menyingkirkan ion Cu(II) telah dikaji. Parameter penjerapan penting seperti kepekatan adsorbat, dos penjerapan dan masa hubungan dikaji. Kapasiti penjerapan maksimum (q_{max}) Cu(II) PVBC adalah 263.15 mg/g dengan kadar penyingkiran tembaga 95% di bawah keadaan optimum kepekatan awal (160 mg/L), dos bahan penjerap (14 mg), dan masa hubungan (180 min). Data eksperimen lebih sesuai dengan model isoterm penjerapan Langmuir daripada model Freundlich dan kajian kinetik dihubungkan dengan model kinetik pseudo-jujukan kedua. Keupayaan penjerapan polimer melebihi tahap 90% setelah lima kitaran penjerapan tetapi keupayaan penjerapan jumlah PVBC untuk ion Cu(II) mula menurun setelah lima kitaran lain iaitu dari 80% hingga 54%. Daripada hasil yang diperolehi, dapat disimpulkan bahawa PVBC dapat menjadi bahan penjerap yang efektif dan berpotensi untuk menyingkirkan ion Cu(II) dari larutan berair. Kajian penjerapan menunjukkan bahawa PVBC mempunyai pertalian dengan ion Cu(II). PVBC yang disediakan terbukti berpotensi baik untuk aplikasi dalam rawatan air sisa.

Kata kunci: penyingkiran, kuprum(II), poli(vinilbenzil klorida), isoterma, kinetic, penggunaan semula

Introduction

One of the useful monomers that enable immediate post-polymerisation functionalisation via the chloride group is 4-vinylbenzyl chloride (VBC). This monomer can readily undergo nucleophilic substitution or be used as the initiating site in the atom transfer radical polymerisation [1]. Thus, VBC has been applied as a precursor to glycopolymer stars in various systems, photo- and pH-responsive nanoparticles, combs, nanofibers, triblock copolymers, and graft star polymers [2-6]. It has also been reported that copolymerisation of VBC by reversible addition-fragmentation chain transfer (RAFT) polymerisation is a convenient technique because side reactions can be avoided (such as C-Cl bond dissociation) [7, 8].

RAFT polymerisation was discovered and documented at CSIRO by Rizzardo and co-workers [9, 10], whereby it was based on the principle of degenerative chain transfer process [11]. The selection of the right chain transfer agent is one of the factors that makes RAFT polymerisation process efficient. RAFT agents are comprised of thiocarbonylthio compounds [12]. This particular characteristic drew substantial research focus on the technique from the time it was introduced two decades ago [13]. High-molecular-weight chains (approx. 20 to 100 kg/mol) are of interest for this study because the ability to produce high-molecular-weight chains from the polymer particle surface makes it possible to increase the number of functionalised benzyl chloride groups. In addition, having a sizeable significant polymer developed from particles allows for excellent control of the particles' effective diameter by merely adjusting the polymerisation conditions to determine the polymer size. This condition could not be done in low molecular weight chains, as their relative contribution to the particle diameter is negligible.

Contamination of groundwater sources with Cu(II) ions is a severe issue in several districts, particularly in small towns and villages. Additionally, due to their high toxicity, Cu(II) ions cause serious environmental issues for humans, animals, and plants [14]. Cu(II) ions do not have biodegradable properties like organic contaminants. Moreover, it tends to accumulate in living organisms with the potential of becoming toxic and carcinogenic. Cu(II) ions are of particular concern in industrial wastewater treatment. Therefore, toxic Cu(II) ions have to be minimised in the environment to avoid catastrophic effects on living organisms, including human beings [15-18]. Therefore, the removal of Cu(II) ions is a big challenge that needs to be overcome. Several methods have been employed to remove Cu(II) ions, such as ion exchange [19], membrane filtration [20], adsorption, and electrochemical treatment technologies [21]. Adsorption is the best option due to its low operation cost, flexibility, and minimal waste generation. Furthermore, the adsorption technology eliminates different types of inorganic cations. However, the adsorption efficiency is highly dependent on the types and characteristics of the adsorbents. To achieve optimum removal efficiency, the selection of appropriate materials for removing heavy metals is paramount. The methodology used in this study is beneficial compared to the conventional methods because it requires few chemicals for the polymerisation process besides eliminating flammable and toxic solvents such as dimethylformamide (DMF) and toluene.

This research investigates polymer behavior for the removal of Cu(II) from aqueous solutions using PVBC through adsorption. This study also focuses on RAFT polymerization in the synthesis of poly(vinylbenzyl chloride) (PVBC) at a particular temperature. The polymer is then used to study the ability to remove Cu(II) ions from aqueous solution via adsorption between the polymer and the Cu(II) ions.

Materials and Methods

Synthesis of poly(vinylbenzyl chloride)

In a typical polymerisation of VBC, the VBC monomer (1 mL, 7.03 mmol), ACPA (0.0025 g, 0.0089 mmol), and RAFT agent CPADB (0.0185 g, 0.066 mmol) were placed in a 100 mL two-necked round bottom flask and stirred until dissolved. The mixture had been degassed for 40 minutes under nitrogen. The polymerisation was achieved by placing the flask in a preheated oil bath at 80 °C for 5 hours to synthesise PVBC. Then the reaction mixture was cooled to room temperature and exposed to air to stop the polymerisation. The polymer solution from the flask was precipitated by adding it dropwise to the excess cold methanol in a centrifuge tube to remove unreacted VBC monomer and other impurities. The procedure was repeated with 10, 15, 20, and 24 hours reaction mixture to find the optimum time of PVBC synthesis. The PVBC obtained via polymerisation for 24 hours at 80 °C was precipitated in a centrifuge tube. The tube was sealed with aluminium foil with a few holes to avoid contamination and was left to dry for 24 hours. In the end, a solid pink PVBC was obtained.

Analysis of Cu(II) ions

The stock solution of Cu(II) ions at a concentration of 400 ppm were prepared via dissolving $CuSO_4.5H_2O$ (249.685 g/mol) in distilled water and topped up to 1000 mL in a volumetric flask. The desired concentration of the experimental solutions was prepared by diluting the stock solution with distilled water [22].

An ultraviolet (UV) absorption spectroscopy technique was used to determine the Cu(II) concentration in the aqueous solution, and because of its simple application, elevated sensitivity and economic efficiency [23]. In particular, the 2 mL matrix Na_2EDTA (0.025 M) as chromogenic reagent was introduced to the Cu(II) ion solution (2 mL). The solution of the desired Na_2EDTA concentrations was then mixed for 5 min to ensure a sufficient complexing response. An absorption peak was identified at 268 nm [22, 24, 25].

The Cu(II) concentrations were determined based on the standard calibration curve, which was plotted using different concentrations (20–200 ppm). The solutions were prepared from the stock solution (400 ppm). The different concentrations were mixed with Na2ETDA for the development of colour and then measured using UV-1800 UV-Vis spectrophotometer from Shimadzu in a 1 cm cuvette length for determining the absorbance at λ_{max} (268 nm) [22]. A standard calibration curve was determined by plotting the graph of absorbance against concentration.

Batch model studies

In this study, the batch model experiments were performed to investigate the effect of PVBC on adsorption of Cu(II) in aqueous solution and also the effect of concentration, adsorbent dosage, and contact time on the adsorption process. The Cu(II) concentration in the remaining solution (supernatant) was calculated. The adsorption ability of Cu(II) was determined as the Cu(II) ions adsorbed per gram of PVBC (mg/g) and calculated using Equation 1:

$$q_e \text{ (mg/g)} = (C_i - C_e)\, V/m \tag{1}$$

Equation 2 was used to determine the percentage of Cu(II) adsorbed on the adsorbent.

$$\text{Cu(II) removal \%} = (C_i - C_e)/C_i \times 100 \tag{2}$$

where C_i and C_e are the initial and final concentrations of Cu(II) in ppm, while m is the mass of PVBC in g and V is the volume (L) of the solution.

Isotherm and kinetic studies

To determine adsorption isotherms at optimum conditions, 14 mg PVBC was added to a solution of 5 mL Cu(II) of various initial concentrations (20-200 ppm). Then, adsorption of Cu(II) was characterised using the isothermic model of Langmuir and Freundlich. Adsorption kinetic experiments were also performed under optimum conditions at various contact time (30-300 minutes), and the Cu(II) adsorption was characterised using pseudo-first-order rate and pseudo-second-order rate. PVBC was isolated from the solution by filtration in all samples, and the residual concentrations of Cu(II) in the supernatant were determined.

Reusability test

Reusability of adsorbent was evaluated by repeated adsorption-desorption of copper metal ion and carried out in a batch system. Adsorbent (14 mg) was added to 50 mL of Cu(II) ions solution (160 ppm) at pH 4 in a 250 mL conical flask. The solution was stirred for 180 minutes. The adsorbent was removed from the solution and adsorbed Cu(II) ions was desorbed by stirring the adsorbent in 0.1 M HCl (10 mL), which efficiently removed the adsorbed Cu(II) ions. After thorough washing with distilled water, the adsorbent was reused for the subsequent adsorption-desorption cycle. The adsorption-desorption test of the adsorbent was repeated ten consecutive times.

Results and Discussion

Synthesis of poly(vinylbenzyl chloride)

PVBC was synthesised through reversible addition-fragmentation chain transfer (RAFT) polymerisation technique with the mole ratio of 100:1:0.1 for VBC:CPADB:ACPA at 80 °C for 5,10, 15, 20, and 24 hours, as shown in Figure 1. The PVBC synthesised was directly used for the optimisation and adsorption studies.

Effect of different Cu(II) concentration

The effect of PVBC on the adsorption process was determined using 5 mL copper sulphate pentahydrate ($CuSO_4.5H_2O$) solution of various concentrations (20-200 ppm). The experiment was conducted in different vials containing the Cu(II) solutions at different concentrations, determined at pH 4, whereby a fixed amount of PVBC was added to each vial and shaken at a specified time. The residual Cu(II) concentrations were analysed by a UV-Vis spectrophotometer. All experiments were conducted at room temperature, and the procedures were repeated in triplicates.

The effect of the initial adsorption concentration of metal ions on PVBC has a significant role in the metal ion adsorption process. Figure 2 shows that the initial concentration of Cu(II) solution adsorption on PVBC increases from 20 to 160 ppm with the removal efficiency from 63 to 87%. It was observed that at 160 ppm initial concentration percentage, removal was 87%, which was chosen as the optimum concentration of Cu(II) removal. At this point, all adsorption sites into the PVBC were saturated, as observed by the maximum interaction between the metal ions and the adsorbent binding sites at a lower concentration, resulting in a higher adsorption rate of 63% at the beginning [26]. In the case of a low initial concentration, relatively low adsorption was observed due to a reduced coefficient of diffusion and a reduced coefficient of mass transfer [27]. However, the percentage of removal efficiency decreases at higher concentrations at 180 ppm and 200 ppm. This could be due to saturated adsorption sites of the adsorbent [28]. In other words, all binding sites at a fixed dose of PVBC were already occupied. Therefore, higher Cu(II) concentrations did not lead to higher adsorption; instead, it started to decline [29].

Effect of different adsorbent dosage

Adsorption experiments were performed at ambient temperature with varying doses of PVBC, 160 rpm shaking speed, and without any changes in pH. Figure 3 shows that the adsorption efficiency of Cu(II) ions on the PVBC increased gradually from 47 to 91% along with the increase of adsorbent dose from 2 to 14 mg.

The increased adsorption dosages of PVBC increases the percentage removal of Cu(II) from 5 mL solution containing 160 ppm of Cu(II) ions, and the highest removal of Cu (II) was attained at the 14 mg of PVBC dose, which was defined as the optimum dosage of PVBC. However, no significant increase in the removal of Cu(II) ions was observed beyond the optimum dosage. The increase in the removal of adsorption with increased adsorbent dosage is consistent with the statement that all binding sites are entirely exposed to adsorption at the low adsorbent dosage, and the surface becomes saturated faster. It can be attributed to the increased adsorption surface area; thus, an increase in the number of active sites and the number of unsaturated sites. According to the values of these parameters, Cu(II) would have greater accessibility to the PVBC surface. This would contribute to a greater extent of the adsorption process. In addition, it was also noted that when the adsorbent dose was further increased to 20 mg, Cu(II) ion adsorption efficiency on the PVBC decreased. This effect is due to the saturated adsorption sites on the adsorbent [30]. Hence, the optimum PVBC dose is 14 mg.

Effect of different contact time

A series of adsorption experiments for contact times ranging from 30 to 300 min was performed to determine the contact time required to achieve the equilibrium, and the results are shown in Figure 4.

Figure 4 shows the effect of the contact time on PVBC adsorption of Cu(II) ions at ambient temperature, along with 14 mg of adsorbent dosage, 160 ppm of initial Cu(II) ion concentration, and solution pH of 4.0. After increasing the contact time from 30 to 180 minutes, it was observed that the Cu(II) percentage removal sharply increased from 58% to 95%. By increasing the contact time within 180 min, the adsorption gradually approached equilibrium around 210 min [28, 30, 31]. It is seen that the systems attained equilibrium after 180 minutes with maximum percentage Cu(II) removal of 95%. This is attributed to the increased adsorbent time to 300 minutes, whereby the percentage of Cu(II) removal efficiency showed a slight decrease, and it was observed that the adsorption efficiency of Cu(II) ions onto the composite was almost unchanged. The initial stage of rapid adsorption makes Cu(II) ions easily contact several accessible active sites on the PVBC surface. When the contact time increased further, the active sites available gradually decreased, and the adsorption rate will be equal to the adsorption rate in the equilibrium state [32, 33]. Consequently, the trend moved towards stabilization in adsorption. According to the previous debate, we have chosen 180 min as the optimum contact time (95%).

The adsorption ability of PVBC

The quantity of Cu(II) (mg) removed per unit of PVBC (g), q_e, and Cu (II) removal percentage were obtained from Equation 1 and Equation 2. The maximum removal ability (q_{max}) using PVBC after the optimised condition was 263.15 mg of Cu(II)/ g of PVBC with 95% of removal efficiency. The comparison of the removal ability of PVBC for Cu(II) ions with different adsorbents is presented in Table 4. However, the experimental data in Table 4 could not be directly compared due to the variations in systemic experimental conditions (concentration, pH, dosage, temperature, and contact time). It can be seen that the PVBC has potential as an adsorbent to remove Cu(II) from aqueous solutions up to 95% efficiency without any modification.

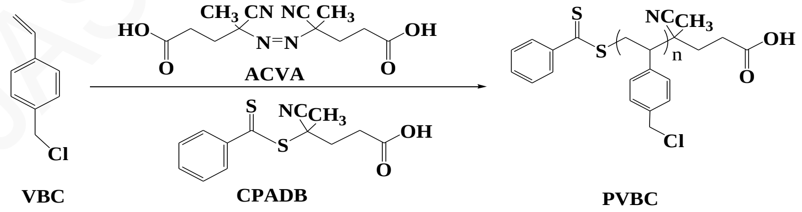

Figure 1. The RAFT polymerisation of PVBC.

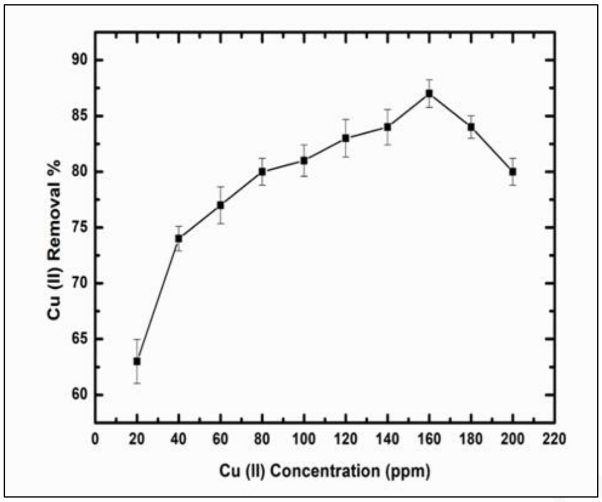

Figure 2. Removal efficiency of Cu(II) from aqueous solution using fixed amount of PVBC at different Cu(II) concentrations (ppm). Extraction conditions: 6 mg of adsorbent dose, temperature 22 °C, batch volume 5 mL, time 3 hours, and pH 4. Data are mean of three independent determinations ± standard deviation

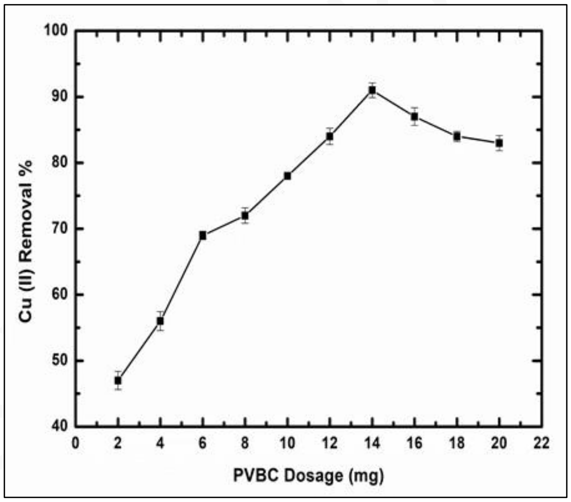

Figure 3. Removal efficiency of Cu(II) from aqueous solution using different amount of PVBC as adsorbent dosage (mg). Extraction conditions: Cu(II) concentration of 160 ppm, temperature 22 °C, batch volume 5 mL, time 3 hours, and pH 4. Data are mean of three independent determinations ± standard deviation

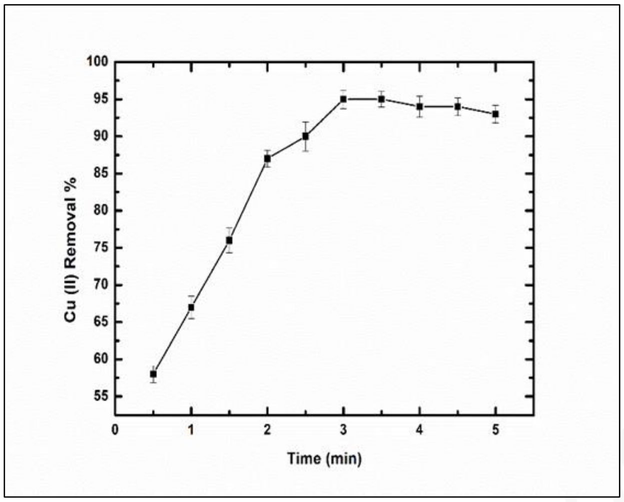

Figure 4. Removal efficiency of Cu(II) from aqueous solution at different contact time (min). Extraction conditions: 14 mg of adsorbent dose, Cu(II) concentration at 160 ppm, temperature 22 °C, batch volume 5 mL, time 3 hours, and pH 4. Data are mean of three independent determinations ± standard deviation

Adsorption kinetic study

To determine the adsorption rate of the Cu(II) ions studied at pH 4 and 22 ºC, the two most commonly used kinetic models in metal adsorption processes, namely pseudo-first-order and pseudo-second-order, were selected. The pseudo-first-order equation described in Equation 3 was used to analyse the experimental data obtained in the kinetic study [34, 35].

$$\log (qe - qt) = \log qe - K_1/2.303 * t \qquad (3)$$

where K_1 (min^{-1}) is the constants rate of pseudo-first-order. The (K_1) adsorption rate constant was achieved from the slope of plotting log (qe - qt) vs. t.

The linear plots of Log (qe - qt) vs. t of the Cu(II) ions are shown in Figure 5(A). The initial high metal uptake could be due to an increase in the number of binding sites available at the initial stage because there was an increased concentration gradient between the metal ions on the adsorbent and the metal ions in solution. The results showed that the coefficients of determination for the pseudo-first-order kinetic model were lower than 0.90. Therefore, the pseudo-first-order kinetic model cannot be used to describe the adsorption rate.

Pseudo-second-order kinetic model

The pseudo-second-order kinetic model has been successfully applied using different concentrations to many kinetic adsorption systems. The constant pseudo-second-order rate and determination coefficients were calculated using Equation 4 [34, 36].

$$t/qt = 1/(K_2*(qe)2) + 1/qe \; * \; t \qquad (4)$$

where K_2 (g/mg.min) is the constant rate of pseudo-second-order.

The pseudo-second-order kinetic model is valid if the plots of t/q_t vs. t give a linear relationship. The plot of t/q_t vs. time of the Cu(II) ions are shown in Figure 5(B).

The coefficients of determination for the linear plot was higher than 0.99 for Cu(II) ions. The applicability of the pseudo-second-order model indicated that chemisorption might be the rate-limiting step that governed these adsorption processes. When the experiment data fitted to the Equations 3 and Equation 4, the correlation coefficients (shown in Figure 5) indicated that the adsorption of Cu(II) on the PVBC were fitted well with Equation 4 (pseudo-second-order) rather than Equation 3 (pseudo-first-order) [33, 37].

Consequently, the mechanism of the adsorption of Cu(II) on PVBC was based on the pseudo-second-order model due to higher correlation coefficients (0.9967). The pseudo-second-order kinetic model assumes that the rate-limiting step may be chemical adsorption. In many cases, the pseudo-second-order model can be utilised to predict adsorption behaviour through the sharing of electrons between adsorbent and adsorbate. The results indicate that the adsorption perfectly correlated with the pseudo-second-order kinetic model. The pseudo-second-order rate constant (K_2) and coefficients of determination (R^2) are listed in Table 1.

Adsorption isotherm models

In this study, Langmuir and Freundlich models were used at pH 4 and 22 °C to describe the relationship between the adsorbed amount of Cu(II) ions on PVBC and its equilibrium concentration in solution. Langmuir isotherm is utilised to describe monolayer coverage utilising a kinetic method with the assumption of a single layer of adsorbed material forming a uniform surface at a constant temperature. The mathematical description of Equation 5 is [35]:

$$q_e = (q_{max}.\ bC_e)/(1+bC_e) \qquad (5)$$

The linear form of Langmuir is described in Equation 6:

$$1/q_e = (1/q_{max}b).1/C_e + 1/q_{max} \qquad (6)$$

where q_e is the concentration of Cu(II) on the adsorbent (mg/g) at equilibrium, q_{max} is the maximum achievable uptake by a system, b is the affinity between the adsorbate Cu(II) ions, and adsorbent PVBC and C_e is equilibrium solute concentrations in aqueous solution (mg/L).

The Freundlich isotherm model is not restricted to monolayer coverage, whereby a good fit of this model means there is no limit to the number of adsorbed molecules on the adsorbent (multilayer coverage). The Freundlich isotherm in Equation 7 was utilised to obtain maximum heterogeneous layer adsorption ability of the adsorbate [35].

$$q_e = K_F\ C_e^{\ (1/n)} \qquad (7)$$

The linear Freundlich Equation 8 is written as [34]:

$$\text{Log qe} = \text{Log KF} + 1/n \text{ log Ce} \qquad (8)$$

where K_F is the binding ability at the unit concentration (L/g) and n is the affinity between the adsorbent and adsorbate (adsorption intensity).

The Langmuir and Freundlich linearized models were fitted into the experimental data in Figure 6. The Langmuir isotherm plots of $1/q_e$ vs. $1/C_e$ for the adsorption of Cu(II) ions is shown in Figure 6(a) and the Freundlich isotherm plots of log q_e vs. log C_e for the adsorption of Cu(II) ions is shown in Figure 6(b).

Figure 7 shows a linearized Langmuir isotherm comparison of the experimental points with the expected values for Cu(II) adsorption on PVBC. It has been observed that the Langmuir isotherm equation linear expression can predict the experimental data.

The Langmuir constant, b can be expressed in terms of an equilibrium parameter known as a separation factor (R_L), based on which adsorption can be described as irreversible ($R_L = 0$), unfavourable ($R_L > 1$), favourable ($0 < R_L < 1$), and linear ($R_L = 1$) [34]. The R_L values for PVBC can be calculated from this Equation 9 [37, 38]:

$$R_L = 1/(1+bC_i) \qquad (9)$$

In our study, the values of R_L were between 0.9746 and 0.7936, as shown in Table 2, indicating favourable adsorption of Cu(II) on PVBC under optimised conditions. The Langmuir constants b and q_{max} that were calculated from the slop and intercept-Y of the plotted $1/q_e$ vs $1/C_e$ is comparable to the Freundlich constants for PVBC calculated from the slop and intercept-Y of the Log q_e vs. Log C_e plot, where the slope is (1/n) whereas the intercept-Y is (log K_F), as shown in Table 3. Table 3 lists the Freundlich constants n and K_F. Freundlich parameters (K_F and n) describe whether the adsorption nature is either favourable or unfavourable. The intercept is an indicator of adsorption ability, and the slope is an indicator of adsorption intensity. If the value of n =1, the adsorption is linear, if n < 1, it implies that the adsorption process is unfavourable and if n > 1, the adsorption is favourable. In another way, 1/n values give us whether isotherm is irreversible (1/n = 0), unfavourable (1/n > 1), or favourable (0 < 1/n < 1). The comparison of the two models indicated that both Langmuir and Freundlich models could be utilised to interpret the experimental data [39]. Based on the values of coefficients of determination (R^2) in Table 3, the Cu(II) adsorption was better explained by the Langmuir isotherm model, as it has higher R^2 values (0.9648). This result indicates that the adsorption of Cu(II) takes place on the PVBC surface at monolayer patterns. Therefore, the adsorption data in this study support the monolayer adsorption of Cu(II), which agrees with other studies [34, 35].

Reusability of the PVBC on Cu(II) solution

Reusability or recycling of adsorbent is one of the functional characteristics of adsorbents. To appraise the adsorbent's reusability, adsorption-desorption of Cu(II) were repeated ten times utilising metal ions concentration of 160 ppm and HCl (0.1 M, 10 mL) as efficient desorption solvent [29]. The adsorbent was thoroughly washed away with distilled water until the next process. It was observed that 95% of metal ions were adsorbed in the first cycle and the percentage of the following four adsorption cycles were still above 90% for Cu(II) removal: 95% in the 1st cycle; 94% in the 2nd cycle; 93% in the 3rd cycle; 92% in the 4th cycle; and 91% in the 5th cycle. The above process was repeated for five times. Figure 8 indicates that the total adsorption ability of PVBC for Cu(II) ions started to decrease from 80% to 54% for Cu(II) removal: 80% in the 6th cycle; 73% in the 7th cycle; 68% in the 8th cycle; 62% in the 9th cycle; and 54% in the 10th cycle. In these cases, reduction in adsorption efficiency has been attributed to the of PVBC weight after repeated from 14 mg to 8.6 mg, leading to a decrease in the number of adsorption sites on the adsorbent. The adsorbent indicates that the process could be repeatedly used for the removal of Cu(II), as shown in Figure 8.

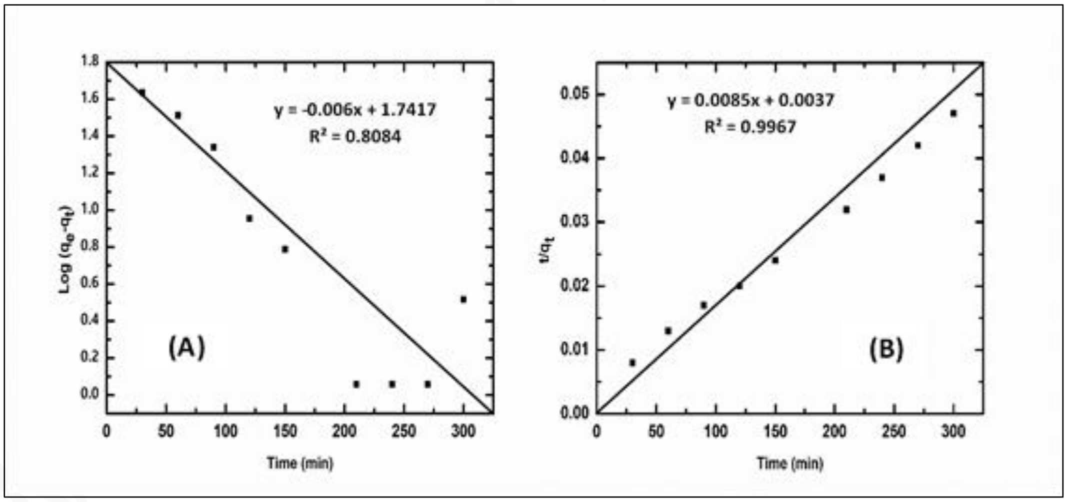

Figure 5. Adsorption Cu(II) fitting Pseudo-first-order model (A) and Pseudo-second-order model (B)

Table 1. Kinetic parameters for adsorption of Cu(II) onto PVBC

Model	Constant	Value
Pseudo-first order	q_e (mg/g)	55.17
	K_1 (min^{-1})	0.82
	R^2	0.8084
Pseudo-second order	q_e (mg/g)	117.65
	K_2(g/mg.min)	0.02
	R^2	0.9967

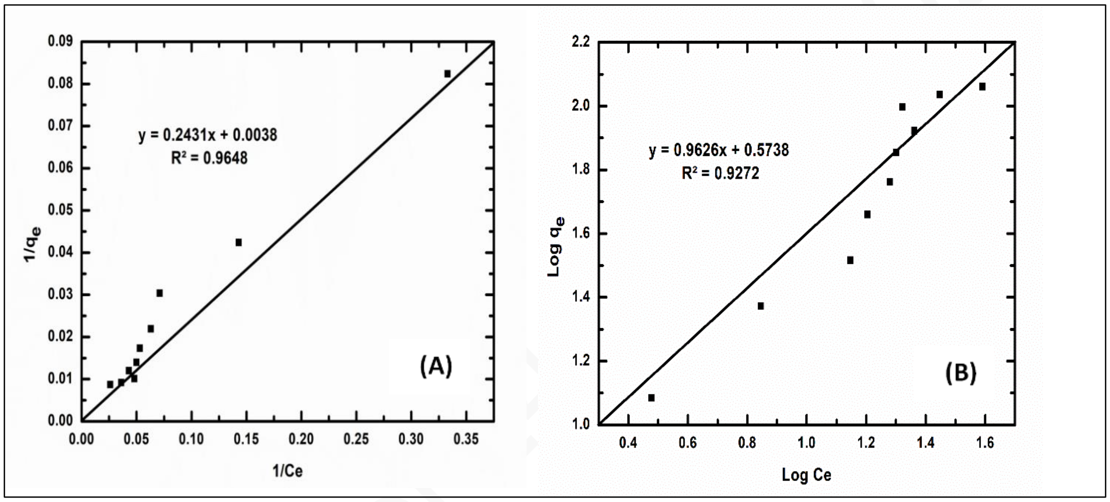

Figure 6. Adsorption Cu(II) fitting Langmuir (a) and Freundlich (b) models.

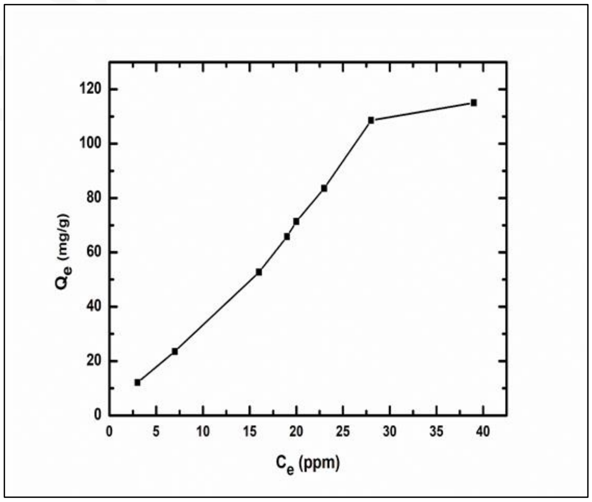

Figure 7. Adsorption isotherms of Cu(II) on PVBC: adsorbent dosage 14 mg, pH 4.0, temperature 22 °C, contact time 5 hours.

Table 2. R_L values for PVBC

Ci for Cu(II) ppm	R_L
20	0.9747
40	0.9506
60	0.9276
80	0.9058
100	0.8850
120	0.8651
140	0.8460
160	0.8278
180	0.8103
200	0.7937

Table 3. Isotherm model parameters for adsorption of Cu(II) onto PVBC

Model	Constant	Value
Langmuir	q_{max} (mg/g)	263.16
	b (L/g)	0.016
	R^2	0.9648
Freundlich	K_F (L/g)	3.75
	n	1.09
	1/n	0.96
	R^2	0.9272

Table 4. Comparison of adsorption capacities of Cu(II) ions with different adsorbents

Adsorbent	Technique	Cu(II) (mg/g)	Conc. (ppm)	pH	Reusability (% adsorption efficiency)	Ref.
PVBC-g-PSPMA2 microspheres	Adsorption process (Suspension polymerisation)	31.6	50	5	-	[40]
M10-PVBC-C beads	Adsorption process based on the use of chelating magnetic copolymer beads (Suspension polymerisation)	61.20	500	7	99.2	[41]
PVBC	Adsorption process (Bulk polymerisation)	263.15	160	4	95	This study

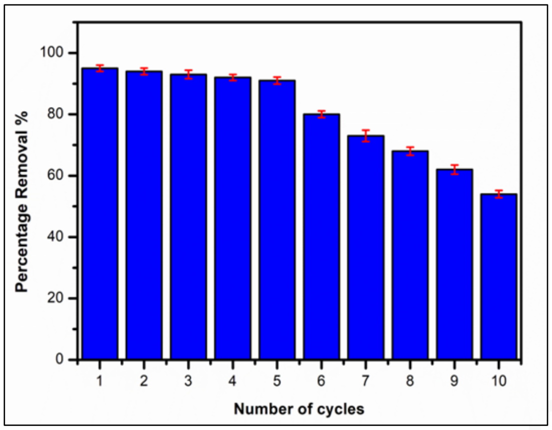

Figure 8. Adsorption-desorption cycles of the adsorbent. Extraction conditions: Cu(II) concentration, 160 ppm, adsorbent dose 14 mg, batch volume 50 mL, desorption solution, 0.1 M HCl (10 mL), contact time 180 minutes

Conclusion

In this study, we have provided a potential adsorbent for the removing Cu(II) from aqueous solutions. The advantage of using PVBC is a high adsorption capacity and environmentally friendly for the removal of Cu(II). In addition, the PVBC can be easily separated from the solution after adsorption. In the optimum points, the maximum removal of Cu(II) was 95%, and the maximum adsorption capacity obtained was 263.158 (mg/g) at 160 ppm Cu(II) concentration, 14 mg PVBC dosage, and pH 4 after 180 minutes of incubation. In addition, the adsorption data for Cu(II) adsorption had a good fit with Langmuir isotherm and pseudo-second-order kinetic model. To conclude, the results obtained confirm that PVBC was successfully prepared and can efficiently remove Cu(II) ion from aqueous solution.

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