

The Uptake of Copper(II) Ions by Chelating Schiff Base Derived from 4-Aminoantipyrine and 2-Methoxybenzaldehyde

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ABSTRACT

The Schiff base, 4-[(2-methoxybenzylidene)amino]-1,5-dimethyl-2-phenyl-1*H*-pyrrol-3(2*H*)-one (SB), was used for the first time to adsorb copper(II) ions in aqueous solution. Various parameters such as initial pH, agitation period and different initial concentration of copper(II) ions which influenced the adsorption capacity were investigated. The equilibrium adsorption data for copper(II) ions were fitted to Langmuir, Freundlich and Dubinin-Radushkevich isotherm models. The maximum monolayer adsorption capacity of SB as obtained from Langmuir isotherm was 5.64 mg/g. Kinetic data correlated well with the pseudo second-order kinetic model indicating that chemical adsorption was the rate limiting step.

Keywords: Schiff Base; Adsorption; Copper(II) Ions; Isotherm; Kinetics

1. Introduction

Heavy metal ions are the most harmful of the elemental pollutants and are of particular concern because of their toxicities to humans. The human body cannot metabolize heavy metals and it displays bioaccumulation properties causing various diseases and disorders. Metal ions in the environment can accumulate and are biomagnified along the food chain. Therefore, their toxic effects are more pronounced in human. There are many possible sources of these heavy metal ions. These include wastes from metal plating operations, mining operations, tanneries, fertilizer and textiles industries [1,2]. Copper is one of the most useful metals due to its low toxicity, corrosion resistant, workability and electrical conductivity. Copper has antibacterial properties and has a biological role in sustaining life. However, accumulation of copper in human body can cause adverse effect on human health such as stomach and intestinal cancer, liver and also kidney damage [3]. The presences of copper are mainly found in effluents from electroplating and brass manufacturing industries and also in the Cu-based agrichemicals run off from agricultural lands [4]. Many conventional techniques such as ion exchange, reverse osmosis, membrane filtration, precipitation-neutralization etc. have been used to remove heavy metal ions from aqueous solution [5,6]. However, these methods involved high operation cost,

generated secondary toxic sludge and were incompetent for the removal of heavy metal ions at low concentration [7]. Alternatively, adsorption onto solid substrate materials is considered as the most suitable process for the removal of heavy metal ions from solution of high and low concentrations.

Over the years, many studies have been conducted on the removal of heavy metal ions from aqueous solution by using adsorbents such as activated carbon, chitosan beads, silica, ion exchange resins and also chelating agents. Chelating agents have been widely employed as adsorbent because it has moderate coordination sites like nitrogen which shows great affinity towards metal ions [8]. One of the important chelating agents receiving an increased interest recently due to the presences of defined chelating groups is Schiff bases. Schiff bases are obtained through the condensation of aldehydes with amines and contain multidentate coordination sites such as O- and N-donor atoms which have high bonding affinity towards many heavy metal ions [6,8,9].

In this study, the efficiency of 4-[(2-methoxybenzylidene)amino]-1,5-dimethyl-2-phenyl-1*H*-pyrrol-3(2*H*)-one (written as SB) synthesized from 4-aminoantipyrine and 2-methoxybenzaldehyde was evaluated for the first time in the removal of copper(II) ions from aqueous solution. Crucial parameters that affected the removal of copper(II) ions, such as initial pH, contact time and different initial copper(II) concentration were investigated.

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2. Materials and Methods

2.1. Materials

The starting materials such as 4-aminoantipyrine and 2-methoxybenzaldehyde used in this research were purchased from Fluka. All the reagents used were of analytical-reagent grade and were used without further purification. Distilled water was used throughout this research.

2.2. Synthesis of

4-[(2-Methoxybenzylidene)amino]-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-one (SB)

The Schiff base, 4-[(2-methoxybenzylidene)amino]-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-one (SB) was prepared by adding 4-aminoantipyrine (10 mmol, 2.03 g) into 2-methoxybenzaldehyde (10 mmol, 1.36 g) solution that was dissolved in 20 mL of ethanol in the presence of one drop of glacial acetic acid. The mixture was refluxed for 2 hours. The resulting mixture was cooled to room temperature and the resulting precipitate was filtered, washed repeatedly with distilled water and recrystallized from ethanol. The Schiff base (SB) was isolated as a yellow crystalline solid. The structure of SB was shown in **Figure 1**.

FTIR (KBr pellet): ν 3051, 2933, 2833, 1642, 1609, 1593, 1508 cm^{-1} . Calc. for $\text{C}_{19}\text{H}_{19}\text{N}_3\text{O}_2$: C, 71.01; H, 5.96; N, 13.08. Found: C, 71.20; H, 5.77; N, 12.80.

2.3. Characterization of the SB

The types of functional groups existing on SB were confirmed by a PerkinElmer Fourier transform infrared (FTIR) System 2000 Model spectrophotometer. Meanwhile, the surface morphology of SB before and after adsorption of copper(II) ions was observed using a Leica Cambridge S360 scanning electron microscope (SEM) coupled with energy dispersive X-ray spectroscopy (EDX).

2.4. Batch Adsorption Experiments

Stock solution of 1000 mg/L of copper(II) ions was prepared using the analytical-reagent grade copper(II) nitrate salt. The stock solution was diluted accordingly to prepare different concentration of copper(II) ions. The

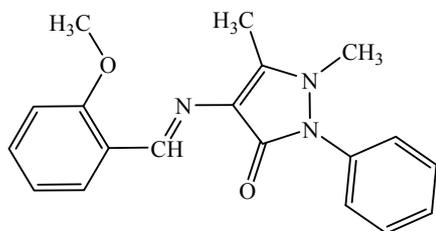


Figure 1. The structure of 4-[(2-methoxybenzylidene)amino]-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-one (SB).

batch adsorption experiments were conducted in 250 mL Erlenmeyer flasks with 50 mL of standard solution and equilibrated using a shaker. The amount of SB used throughout this research was 0.1 g. Each experiment was carried out in duplicates. All filtrates were analysed using atomic absorption spectrometer (AAAnalyst 200 AA, PerkinElmer, USA) at a wavelength of 324.75 nm for copper(II) ions.

The effect of pH on the adsorption of copper(II) ions was studied in a pH range of 1.5 - 7.0. The pH of the 10 mg/L of copper(II) ions was adjusted to different pH using appropriate concentration of HCl and NaOH solutions and equilibrated for 3 h. The effect of agitation time was also studied at different time interval ranging from 5 - 240 min at the optimum pH. The isotherm study was conducted under the optimum condition by varying the initial concentration of copper(II) ions from 5 to 30 mg/L. The amount of adsorption at equilibrium was calculated using the following equation:

$$\text{Adsorption capacity } (q_e) = \left(\frac{C_o - C_e}{W} \right) V \quad (1)$$

where C_o is the initial concentration of copper(II) ions (mg/L), C_e is the final concentration of copper(II) ions (mg/L), V is the volume of copper(II) ions solution (L) and W is the weight of SB (g) used.

3. Results and Discussion

3.1. FTIR of the SB

The FTIR spectrum of SB was shown in **Figure 2**. The peaks at 1642 and 1508 cm^{-1} were attributed to the C=O group (conjugated) and the C=N bonds, respectively. The present of imine group, C=N confirmed that a Schiff base was formed from the reaction between 4-aminoantipyrine and 2-methoxybenzaldehyde. The peaks found at 1609 and 1593 cm^{-1} were due to the C=C bonds in the benzene rings of SB. The peaks at 2933 and 2833 cm^{-1} were attributed to the C-H stretching of the methoxy group. Meanwhile the =C-H stretching was evident at 3051 cm^{-1} . The medium broad peak at 3431 cm^{-1} could be due to the present of water molecule on the SB because of its hygroscopic nature.

3.2. Adsorption Studies

3.2.1. Effect of Initial pH

The pH of metal solution is the most important parameter governing metal adsorption. This is due to the fact that pH of the metal solution affects the solubility of metal ions and the surface charge of the adsorbent. In most cases, the metal uptake increased at higher pH when the surface charge of the adsorbent is opposite to that of the metal cation. At this point, the attraction force between the adsorbent and the metal cation will increase. **Figure 3**

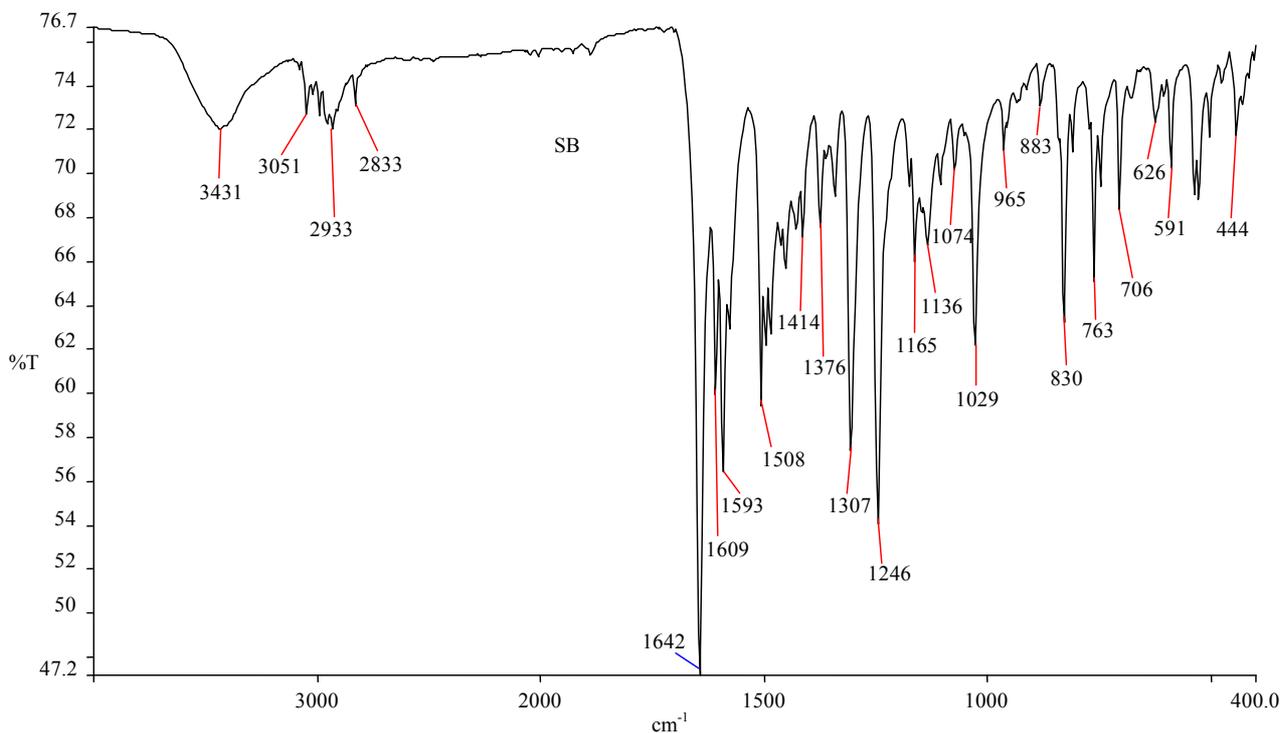


Figure 2. FTIR spectrum of SB.

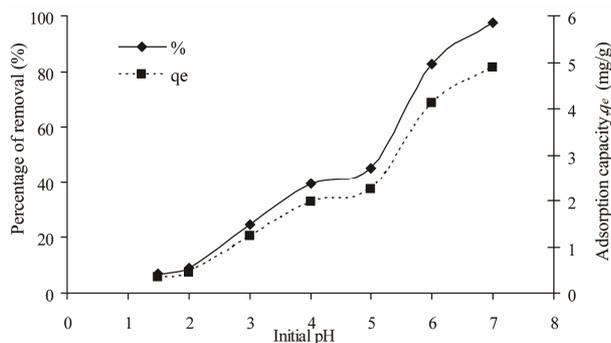


Figure 3. Effect of initial pH on removal of copper(II) ions by SB.

shows the effect of pH on the removal of copper(II) ions by SB. At low pH, the uptake of copper(II) ions was low because the functional groups (O-CH₃ and C=N) on the adsorbent surface were protonated giving rise to positively charged adsorption sites. The electrostatic repulsion between the positively charged SB and the copper(II) ions together with the competition from the proton (H⁺) for the active adsorption sites will contribute to the low adsorption percentage. Furthermore, dissolution of SB was observed at acidic pH of 2 to 4. However, as the pH of the solution increased the adsorption percentage increased as well, whereby at pH 6, 82.66% of copper(II) ions was being adsorbed. At higher pH, the functional groups of the adsorbent were deprotonated creating the negatively charged surface that will attract the copper(II)

ions. Less amount of protons in the solution also reduced the competition between copper(II) ions and the protons for the active adsorption sites. In this study, pH 6 was chosen as the optimum adsorption pH. Although at pH 7, the percentage of removal was much higher, it was not considered as the optimum pH because at higher pH, copper(II) ions will form the insoluble Cu(OH)₂ precipitate.

3.2.2. Effect of Contact Time

The uptake rate of copper(II) ions onto SB was investigated as it represented the amount of time required before the adsorption process becomes constant and equilibrium was reached. As shown in **Figure 4**, for the first 90 min, the uptake rate was high and it decreased gradually until it reached equilibrium at 180 min with an adsorption percentage of 83.18%. The high uptake rate observed at initial stage could be due to the adsorption of copper(II) ions onto the external surface of the adsorbent. Meanwhile, the slower uptake rate observed after 90 min is due to the pore diffusion and the quick exhaustion of the available adsorption sites. The adsorption data were then analyzed with pseudo first- and pseudo second-order kinetic models.

3.2.3. Adsorption Kinetics

The adsorption kinetics of metal ions is important for designing the adsorption system and is required for determining the optimum operating conditions for a full-scale batch process [10]. Many adsorption kinetic models

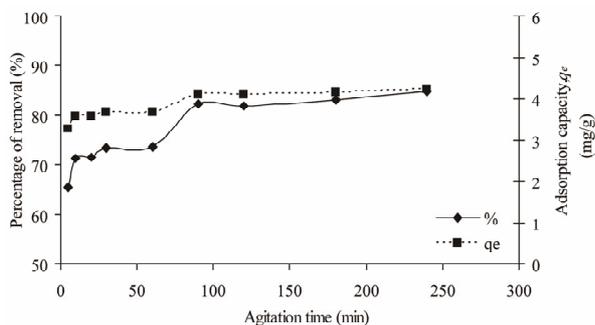


Figure 4. Effect of agitation time on the removal of copper(II) ions by SB.

have been applied to understand the adsorption kinetics and the rate-limiting step. Among all, pseudo first- and pseudo second-order models are the most commonly used to study the adsorption kinetics of heavy metal ions [11]. The pseudo first-order kinetic model is given in its linear form as:

$$\log(q_e - q_t) = \log q_e - \frac{K_1 t}{2.303} \quad (2)$$

where q_e is the amount of copper(II) ions adsorbed at equilibrium (mg/g), q_t is amount of copper(II) ions adsorbed at time t (mg/g) and K_1 is the pseudo first-order kinetic constant (1/min). Linear plot of $\log(q_e - q_t)$ against t for the adsorption of copper(II) ions onto SB was shown in **Figure 5**. In many cases, the pseudo first-order kinetic model does not fit well to the whole range of contact time. It would only be applicable over the initial stage of the adsorption process [12]

The pseudo second-order kinetic model is based on the assumption that the rate-limiting step in the adsorption of heavy metal ions is chemisorption involving the valence force through the sharing or exchange of electrons between the adsorbate and the adsorbent [2,13-15]. This kinetic model is represented as:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

where q_e and q_t are the amount of copper(II) ions adsorbed at equilibrium and time t (mg/g), respectively and K_2 is the pseudo second-order kinetic constant (g/mg·min). **Figure 5** showed the linear plots of t/q_t against t .

The pseudo second-order kinetic model gave higher correlation ($R^2 = 0.9991$) than the pseudo first-order kinetic model ($R^2 = 0.8953$). Furthermore, the calculated equilibrium adsorption capacity based on pseudo second-order (4.27 mg/g) was in agreement with the experimental data (4.16 mg/g). Hence, the pseudo second-order is more appropriate to represent the adsorption data of copper(II) ions onto SB. The poor fit observed for pseudo first-order kinetic model could be due to a time lag caused by a boundary layer or the external resistance

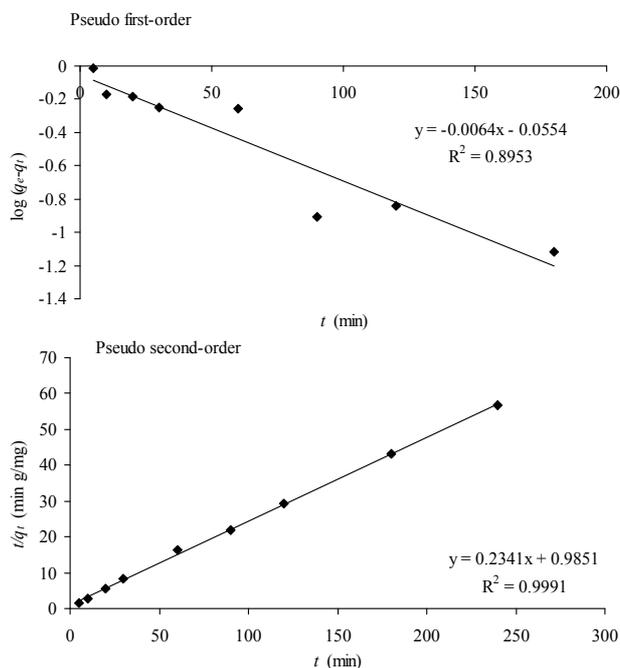


Figure 5. Pseudo first- and pseudo second-order plots for the removal of copper(II) ions with SB.

controlling at the beginning of the adsorption process [16].

3.2.4. Isotherm Studies

The equilibrium adsorption isotherm is essential to be studied as it describes the interactive behavior between the solutes and the adsorbent. Different initial concentration of copper(II) ions ranging from 5 - 30 mg/L was used to study the effectiveness of SB to remove trace amount of copper(II) ions. As shown in **Figure 6**, the adsorption capacity increased with an increase in the initial concentration of copper(II) ions at optimum adsorption pH and agitation time. The adsorption capacity reached equilibrium once the active adsorption sites were saturated at the initial concentration of 25 mg/L of copper(II) ions.

The adsorption equilibrium data were fitted with different isotherm models mainly Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherm in order to evaluate the adsorption phenomenon. In this study, non-linear method was used to evaluate the fitness of the isotherm models to the experimental data. The non-linear method is a better way to obtain the isotherm parameters compared to the linear least-square method [17]. The plots based on Langmuir, Freundlich and D-R isotherms were shown in **Figures 7 and 8**, respectively, while the isotherm constants were tabulated in **Table 1**.

3.2.4.1. Langmuir Isotherm

Langmuir isotherm relates the coverage of molecules on a solid surface to the concentration of a medium above

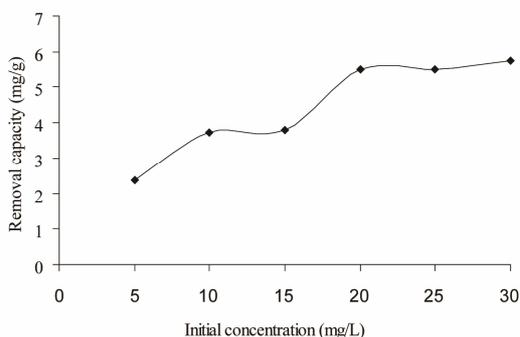


Figure 6. Effect of initial concentration of copper(II) ions on the adsorption capacity of SB.

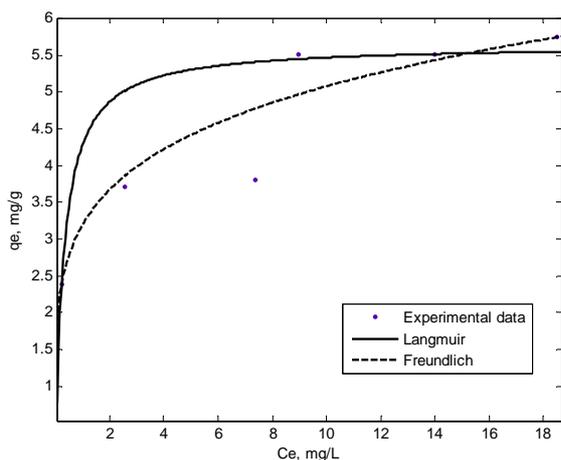


Figure 7. Langmuir and Freundlich isotherms for the adsorption of copper(II) ions onto SB.

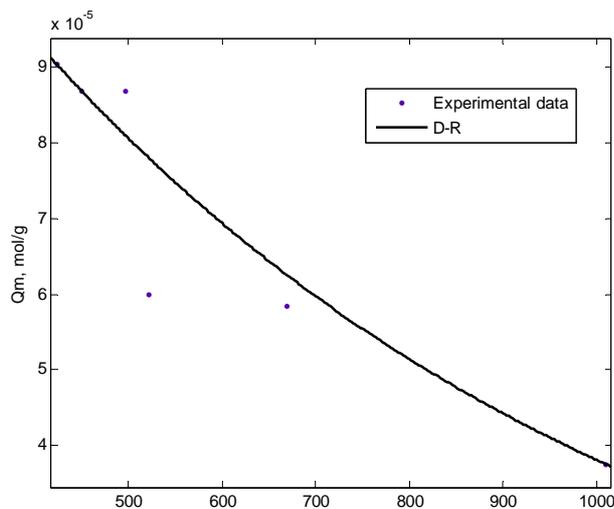


Figure 8. D-R isotherm for the adsorption of copper(II) ions onto SB.

the solid surface at a fixed concentration [11]. It describes monolayer adsorption and is based on the assumption that all the adsorption sites are energetically

Table 1. Isotherm and kinetic constants of different models for the adsorption of copper(II) ions onto SB.

Isotherm models			Kinetic models		
Langmuir	K_L	3.127	Pseudo first-order	K_t	0.0147
	V_m	5.64		q_e (theor.)	0.88
	r	0.9129		r	0.8953
Freundlich	K_F	3.192	Pseudo second-order	K_2	0.0557
	$1/n$	0.2013		q_e (theor.)	4.27
	r	0.9729		r	0.9991
	D-R	Q_m		6.9860×10^{-5}	q_e (exp.)
	K	0.3305			
	E	1.2299			
	r	0.9692			

identical and adsorption takes place on a structurally homogenous adsorbent [2]. This model can be represented as:

$$q_e = \frac{V_m K_L C_e}{1 + K_L C_e} \tag{4}$$

where C_e is the equilibrium concentration (mg/L), q_e is the amount of copper(II) ions adsorbed at equilibrium (mg/g), V_m is the monolayer adsorption capacity (mg/g) and K_L is the Langmuir equilibrium constant (L/mg). Based on **Figure 7**, the steep initial slope observed for the Langmuir plot reflected high K_L value (3.127 L/mg) indicating that the adsorbent has high affinity for copper(II) ions [18,19] with a monolayer adsorption capacity of 5.64 mg/g.

3.2.4.2. Freundlich Isotherm

Freundlich isotherm is an empirical equation used for the adsorption on heterogeneous surfaces or the surface adsorption sites of varied affinities [20]. It describes monomolecular layer coverage of adsorbent by the solutes [21]. Freundlich isotherm is given as:

$$q_e = K_F C_e^{1/n} \tag{5}$$

where q_e is the amount adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration (mg/L), K_F is the adsorption capacity (mg/g) and $1/n$ is the adsorption intensity. Adsorption is said to be favorable when the Freundlich constant $1/n$ is between 0.1 and 1 and represented a heterogeneous surface structure of the adsorbent [22,23]. Meanwhile, smaller value of $1/n$ indicates stronger interaction between the adsorbent and the heavy metal ions, while $1/n$ equal to 1 implies linear adsorption leading to identical adsorption energies for all sites [11]. As

shown in **Table 1**, adsorption of copper(II) ions onto SB has a $1/n$ value of 0.2013 with K_F equal to 3.192 mg/g. This showed that SB had a strong interaction with copper(II) ions which makes SB a favourable adsorbent for copper(II) ions.

3.2.4.3. Dubinin-Radushkevich (D-R) Isotherm

D-R isotherm, apart from being analogue of Langmuir isotherm, is a more general model than Langmuir isotherm as it does not assume homogenous surface or constant sorption potential [24]. D-R isotherm was derived as the overall adsorption isotherm for the adsorption onto heterogenous solid surface [20]. The D-R isotherm equation is expressed as:

$$Q = Q_m \exp(-K\varepsilon^2) \quad (6)$$

where, Q is the amount adsorbed at equilibrium (mol/g), Q_m is the maximum adsorption capacity (mol/g), K is the D-R constant (mol/kJ) which is related to the adsorption energy. The Polanyi potential (ε) is given as:

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (7)$$

where R is the gas constant in kJ/mol K and T is the temperature in Kelvin. The mean energy of adsorption, E is used to estimate the type of adsorption process and can be calculated by the following equation:

$$E = \frac{1}{\sqrt{2K}} \quad (8)$$

The adsorption process can be explained by an ion exchange process if the value of E is between 8 and 16 kJ/mol [2,18]. Meanwhile, E values lower than 8 kJ/mol correspond to physical adsorption (physisorption) [25,26]. The E value for the adsorption of copper(II) ions onto SB was calculated as 1.2299 kJ/mol indicating the involvement of physisorption.

3.3. Adsorption Mechanism

The adsorption of solute on any sorbent can happen either through physical bonding, ion exchange, complexation, chelation or a combination of any of these interactions [11]. The adsorbent used in the present study is a Schiff base which has the $-OCH_3$ and $C=N$ functional groups as the active sites to interact with copper(II) ions. At the optimum pH, the oxygen and nitrogen atoms on these active sites behave as the electron donors and can form complex with the copper(II) ions as shown in **Figure 9**. This process can be classified as chemisorption which involves the sharing of electrons between the adsorbate and the adsorbent.

The removal of copper(II) ions by SB, however, was not solely governed by chemisorption. The mean adsorp-

tion energy, E calculated from the D-R isotherm suggested that physical adsorption might have taken place as well. This was proven based on the SEM-EDX analysis carried out on SB before and after the adsorption of copper(II) ions. The SEM-EDX micrographs were shown in **Figure 10**. The SEM image for SB before the adsorption of copper(II) ions (**Figure 10(a)**) shows an even and smooth surface morphology. Many small particles which clustered on the surface of SB were also found. Based on the EDX analysis, the presences of carbon, hydrogen and nitrogen were detected. The gold peaks (Au) found in the spectra were due to the gold purposely settled to increase electrical conductive of the sample. After the adsorption of copper(II) ions (**Figure 10(b)**) surface morphology of SB changed drastically. The surface was found to be very uneven and many small coarser particles were formed on the surface. The EDX spectra showed the presences of copper on the surface of SB especially on these smaller particles. These observation proved that copper(II) ions were deposited on the surface of the adsorbent by means of physical adsorption. Physical adsorption occurs through the existences of van der Waals forces between the adsorbent and the adsorbate.

4. Conclusion

Schiff base derived from 4-aminoantipyrine and 2-methoxybenzaldehyde can act as a potential adsorbent to remove copper(II) ions from the aqueous solution. Present study showed that SB has a monolayer adsorption capacity of 5.64 mg/g for copper(II) ions. Chemisorption of copper(II) ions could be occurred through the interaction of copper(II) ions with the methoxy and imine groups on SB. Copper(II) ions also can be removed via physical adsorption. The kinetic studies showed that the removal of copper(II) ions by SB followed the pseudo second-order kinetic reaction.

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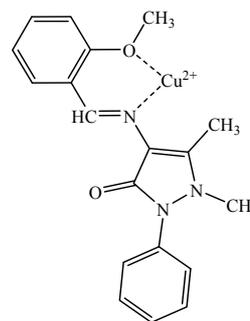
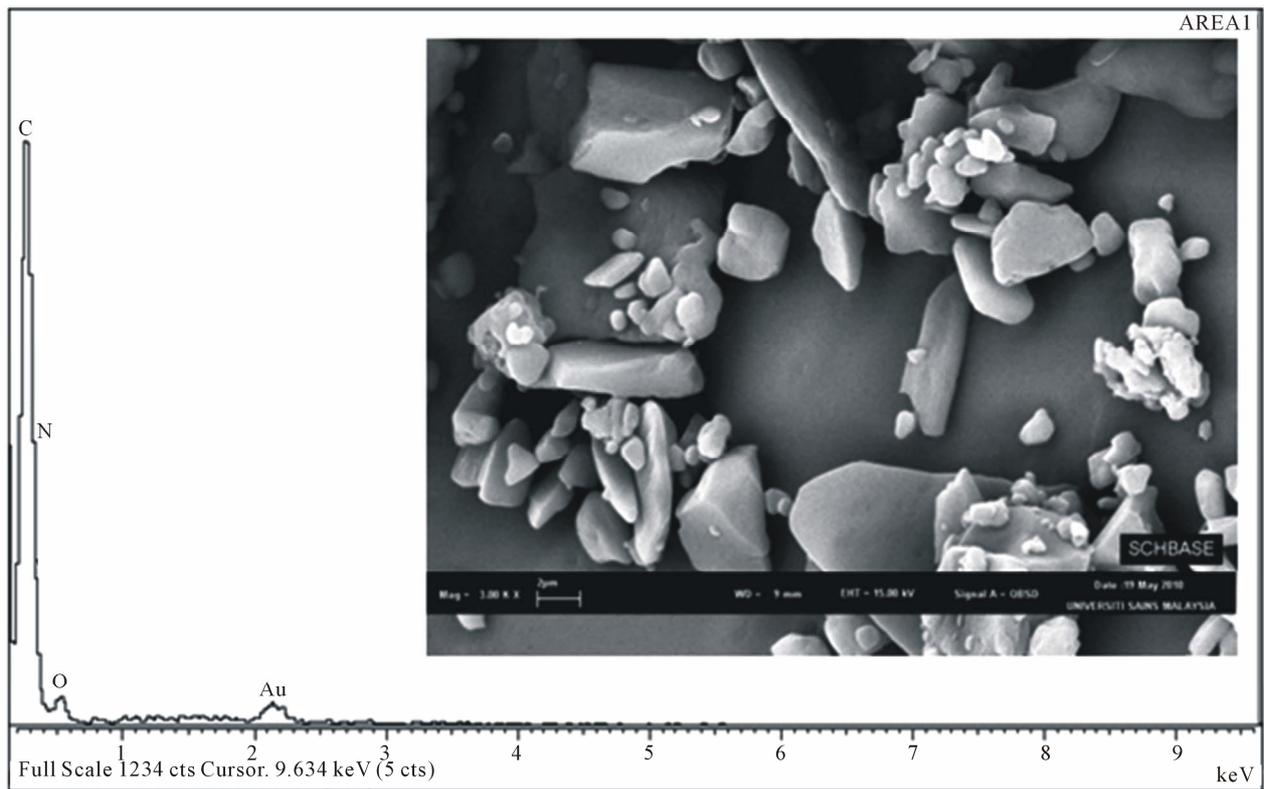
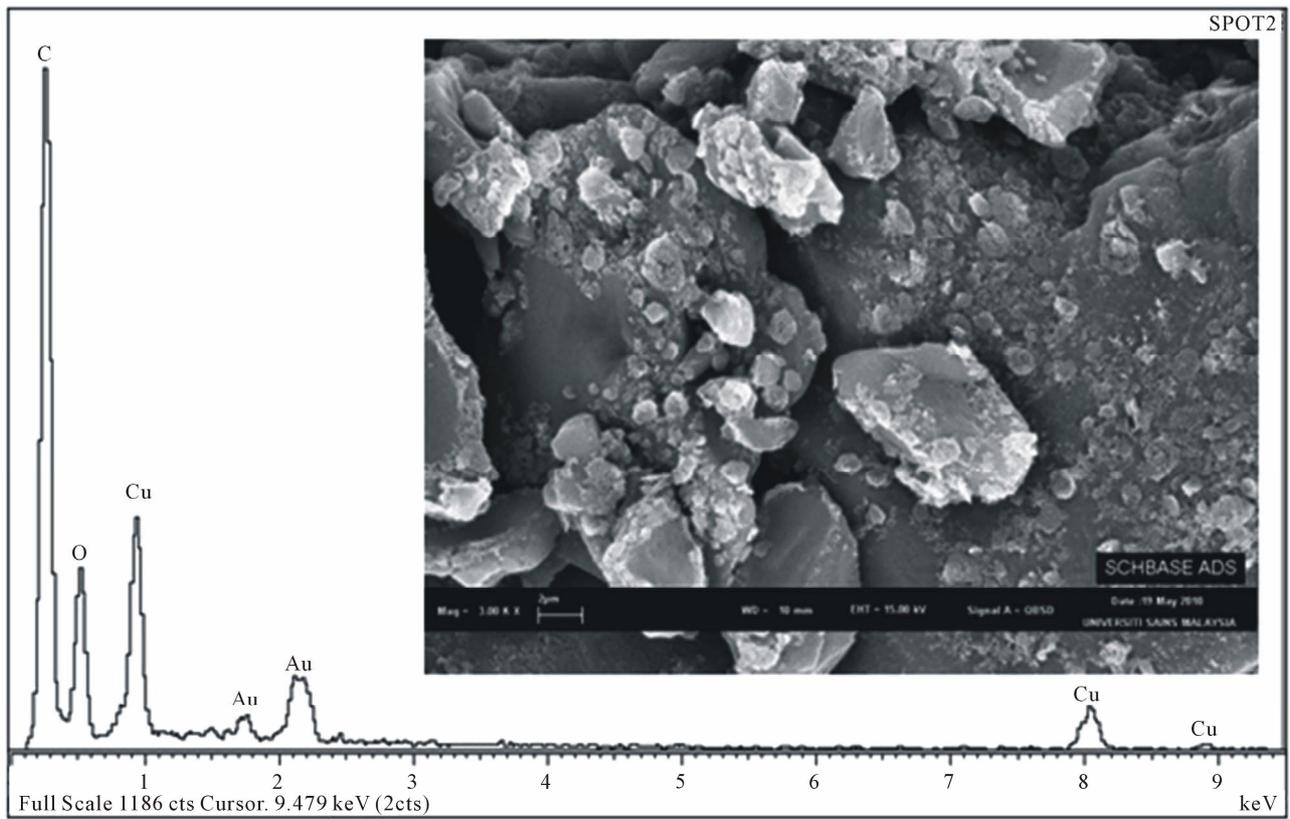


Figure 9. Proposed mechanism for the adsorption of copper(II) ions onto SB.



(a)



(b)

Figure 10. SEM-EDX spectra of SB (a) before and (b) after the adsorption of copper(II) ions.

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