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Dried activated sludge as an appropriate biosorbent for removal of copper (II) ions



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Abstract Removal of Cu (II) from aqueous solution by dried activated sludge (DAS) was investigated. Batch process for the biosorption of Cu (II) ions was performed to determine equilibrium and adsorption characteristics of DAS. Obtained results by scanning electron microscope showed DAS pretreated with 1% H₂O₂ was porous and also it had effective removal for Cu (II) ions from aqueous solutions. Effects of contact time, temperature, pH and DAS dosage on the biosorption of Cu (II) were studied. The maximum biosorption of Cu (II) at temperature of 20 °C and pH of 5 was obtained (85%) with the DAS dosage of 3.5 g/L, Cu (II) ion concentration of 100 mg/L and 4 h contact time. Also removal efficiency of Cu (II) decreased with increasing temperature. Langmuir, Freundlich and Dubinin–Radushkevich (D–R) models were employed to study biosorption isotherms for removal of Cu (II). Weber–Morris, pseudo first order and pseudo second order models were applied to describe the biosorption kinetics.

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1. Introduction

Chemical industries release heavy metals as toxic pollutants into the environment. Copper (II) is one of the most common

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heavy metal ions in industrial effluents. Intake of copper causes mucosal, irritation, hepatic and capillary damage (Ajmal et al., 1998; Yao et al., 2010). Currently, treatment processes are oxidation–reduction, membrane filtration–osmosis, ion exchange, precipitation, adsorption and biosorption (Fu and Wang, 2011; Igwe and Abia, 2009; Ko et al., 2000; Malakootian et al., 2009). Biosorption is one of the most promising processes for removal of heavy metals from municipal and industrial wastewater (Akar and Tunali, 2006; Mona et al., 2011). Biosorption of heavy metals has advantages such as low costs, metal recovery, regeneration of biosorbent and high efficiency in detoxifying very dilute effluents (Mo and Lian, 2011; Volesky, 2001; Waseem et al., 2014).

Biosorbents are potential inexpensive alternative to conventional adsorbents. In biosorption, both living and dead microbial cells are able to absorb heavy metal ions (Choi et al., 2009;

Filipović-Kovačević et al., 2000). Since living cells require addition of nutrients, the BOD and COD of the wastewater often are increased by using living cells (Rezaei et al., 2011). Dead cells have been gaining advantage because of toxic ions that do not affect on stabilized biomass. Besides, dead cells require less maintenance and also are effortlessly regenerated (Das et al., 2008; Khosravan and Lashkari, 2011).

Activated sludge is an effective biomaterial for biosorption or bioleaching of the metal ions such as Cd (II), Zn (II), Pb (II) and Cu (II) from wastewater. The removal of heavy metals from wastewater using activated sludge is highly efficient and has low installation and operation and maintenance costs (Buyukgungor and Gurel, 2009; Gavrilescu, 2004; Hussein et al., 2005). Activated sludge is a biosorbent with different functional groups such as carboxylic acid, carboxyl and amine groups (Gulnaz et al., 2006). It is composed of both live and dead microbial fractions. Many reports have shown that aldehyde, carboxyl, sulfhydryl, phosphoryl, hydroxyl, amine organic and acidic functional groups in biomass are the most important functional groups that could eliminate metal ions from aqueous solutions (Arief et al., 2008; Marandi, 2011; Zhang and Banks, 2006). The formation of functional groups in biomass may enhance with the pretreatment method such as heating, autoclaving, acidic treatment and alkali treatment (Pereira, 2001; Shroff and Vaidya, 2011).

The aim of the present research was to investigate biosorption of Cu (II) ions by dried activated sludge (DAS). Effects of contact time, pH, temperature and DAS dosage on biosorption of Cu (II) ions were studied. Langmuir, Freundlich and Dubinin–Radushkevich (D–R) were applied to obtain biosorption isotherms. Also biosorption kinetics was described by Weber–Morris, pseudo first order and pseudo second order models.

2. Materials and methods

2.1. Preparation of the biosorbent and stock solution

The activated sludge used in this study was collected from pulp and paper wastewater treatment plant (Mazandaran Pulp and Paper plant, Iran). Initially activated sludge was suspended in 500 ml of 1% H₂O₂ solution in a beaker with a magnetic stirrer (VELP, SCIENTIFICA, Italy) for 12 h at 25 °C. The suspension was then centrifuged (HERMLE, Germany) at 5000 rpm for 8 min. The resulted cake was washed with deionized water until the pH of the solution decreased to 7. The cake was dried in oven (Binder, Germany) at 65 °C for 48 h. The dried biomass was grinded and sieved with mesh No. 35 into particle size smaller than 0.5 mm. Copper stock solution with concentration of 100 ppm was prepared using analytical grade of CuSO₄·5H₂O (Merck, Darmstadt, Germany). The stock solution was diluted with double distilled water to obtain desired solutions.

2.2. Batch experiments

Biosorption of Cu (II) onto DAS was carried out by batch experiments. Biosorption experiments were performed in 250 ml Erlenmeyer flasks containing 100 ml of aqueous solution with an initial concentration of 100 ppm Cu (II). For optimization of contact time, pH and adsorbent dosage, batch

experiments were carried out at 20 °C in incubator shaker (Excella E24, New Brunswick Scientific, Edison, NJ) at 120 rpm. Batch experiments were performed with contact time 0.5 to 4 h, pH 2–6, adsorbent dosage 1.5–3.5 g/L and temperature range from 20 to 50 °C. The required pH of aqueous solution was adjusted by adding 0.2 M HCl and 0.1 M NaOH. The pH of the solution was measured using a pH meter (HANA 211, Romania) model glass-electrode. After that, the biosorption kinetics and isotherm studies were carried out under optimized condition of pH, contact time and adsorbent dosage. All experiments were carried out twice. Data reported in this study were the means of the duplicate experimental results. Treated samples were filtered through a paper filter.

2.3. Analytical methods

In order to remove solid particles, the samples were centrifuged at 10000 rpm for 8 min and then filtered. The concentration of Cu (II) in the samples was determined using an atomic absorption spectrometer (ATI Unicam 929 AA, England) at 324.8 nm wavelength according to procedure reported in standard methods (American Public Health Association (APHA), 2005). The removal efficiency and the amount of metal adsorbed per unit mass of the adsorbent were calculated as $100 \times (C_i - C_f)/C_i$ and $(C_i - C_f) \times V/m$ (mg/g), respectively; where C_i and C_f (mg/L) are the initial and final concentrations of Cu (II) ions, V (L) is the volume of the solution and m is the amount of adsorbent (g).

The specific surface area and the porosity of the DAS were determined by BET adsorption isotherm of nitrogen gas in a micromeritics porosimeter ASAP 2010 V2.00 A (Micromeritics Instrument Co., USA). The percentage of carbon, nitrogen and hydrogen in the DAS was analyzed with an element analyzer (Heraeus CHNO, USA) and acetanilide was used as the standard. Also the ash content of DAS was determined with the analysis method according to ASTM D2866-94. In order to investigate on surface morphology of DAS, the sample was dried and gold coated with a sputtering coater (Emitech K575X, England). The morphology of DAS was studied by Scanning Electron Microscope (VEGA\TESCAN, Czech Republic).

3. Results and discussion

3.1. Properties of DAS

Biosorption capacity and specific surface area of DAS were increased with pretreatment with H₂O₂. The Characteristics of DAS used in this work are summarized in Table 1. The

Table 1 Characteristics of the DAS treated by H₂O₂.

| Parameter | Values |
|-----------------------|------------------------|
| Size range | < 0.50 mm |
| Bulk density | 0.88 g/cm ³ |
| Porosity | 45% |
| Specific surface area | 183 m ² /g |
| Ash | 18% |
| C | 42% |
| N | 6.7% |
| H | 3.5% |

activated sludge was suspended in a 1% H_2O_2 solution for 12 h. The pretreated activated sludge showed better performance for the copper sorption (see Fig. 2). This result may be explained that some functional groups on the surface of DAS can be oxidized and activated by H_2O_2 (Pamukoglu and Kargi, 2006). In order to investigate the surface morphology of the DAS, scanning electron microscopy (SEM) image was taken. Fig. 1 shows the pore structure of the DAS which it can be resulted from pretreatment of DAS by H_2O_2 . According to SEM image, the DAS as an adsorbent was sufficiently porous and can be used for adsorption of Cu (II) ions.

3.2. Effect of contact time

The equilibrium contact time is an important parameter for adsorption process. In order to determine the effect of contact time, biosorption was performed for 4 h. Fig. 2 demonstrates contact time effects on biosorption of Cu (II) onto treated and untreated DAS. For untreated Das, removal efficiency reached to 76% after 4.5 h. For Das treated with H_2O_2 , removal efficiency rapidly increased during the initial adsorption stage and reached to 83.5% when contact time was 3 h. Then the removal efficiency gradually increased with contact time and equilibrium was reached after 4 h. At equilibrium, removal efficiency was 85% and then it was constant. At initial stage, adsorption of Cu (II) onto monolayer surface of DAS may explain the rapid increase in removal efficiency. After that the monolayer surface was saturated, the Cu (II) ions were gradually adsorbed into the inner part of DAS with diffusion; therefore lower biosorption rate was obtained.

3.3. Effect of pH

Biosorption of Cu (II) at temperature of 20 °C was carried out with DAS dosage of 3.5 g/L, Cu (II) ion concentration of 100 mg/L and contact time of 4 h. Since at pH higher than 6 hydrate structures of the Cu (II) ions formed and the metal ions precipitate in the solution, effect of pH was investigated in the pH range from 2 to 6. Fig. 3 shows the effect of pH value

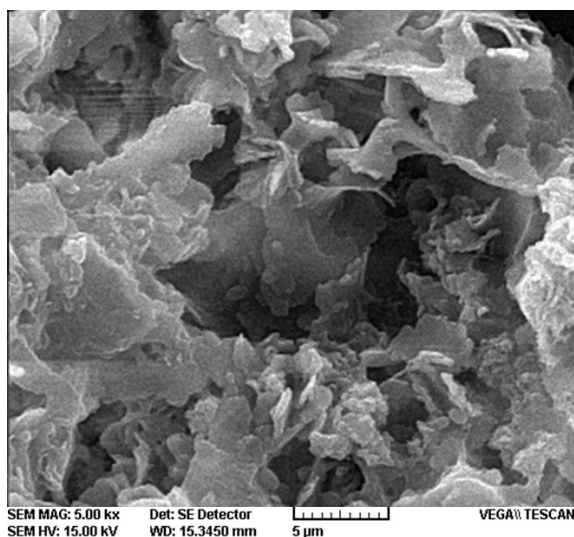


Figure 1 Scanning electron microscopy image of the DAS with magnification of 5000.

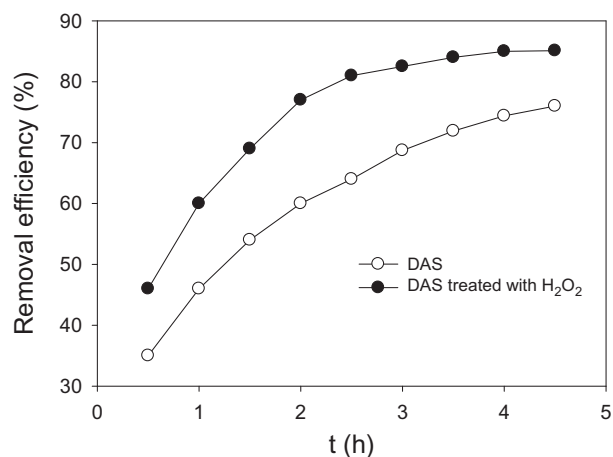


Figure 2 The effect of contact time on the biosorption.

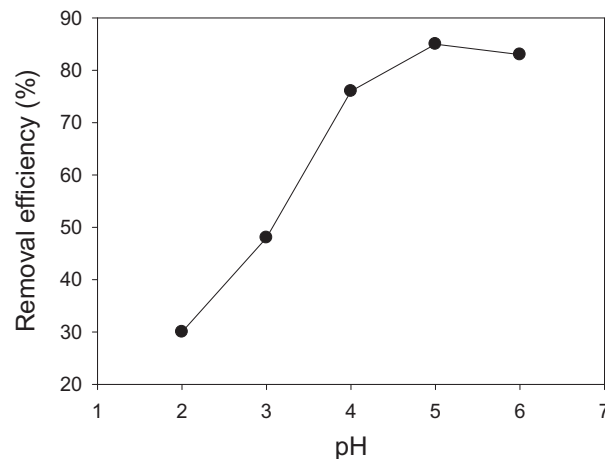


Figure 3 Effect of pH on the biosorption.

on biosorption of Cu (II) onto DAS. Removal efficiency of Cu (II) increased with an increase in pH solution, reached at a maximum value of 85% at pH 5 and then slightly decreased and reached to 83%. In acidic solution, H^+ ions compete with Cu (II) for the adsorption site, which impedes biosorption of Cu (II) by DAS.

3.4. Effect of DAS dosage and temperature

Effect of DAS dosage on adsorption isotherm for removal of Cu (II) at four different temperatures was also investigated and obtained results are presented. Fig. 4 shows the removal efficiency of Cu (II) at DAS dosage of 1–3.5 g/L and temperature of 20–50 °C. Removal efficiency increased with an increase in DAS dosage; meanwhile as the temperature was increased, the removal efficiency for the same dosage of DAS decreased. It is obvious that desorption rate increased as the temperature was increased, which implies that the adsorption affinity decreased. In order to evaluate adsorption isotherm, Langmuir and Freundlich models were fitted to experimental data.

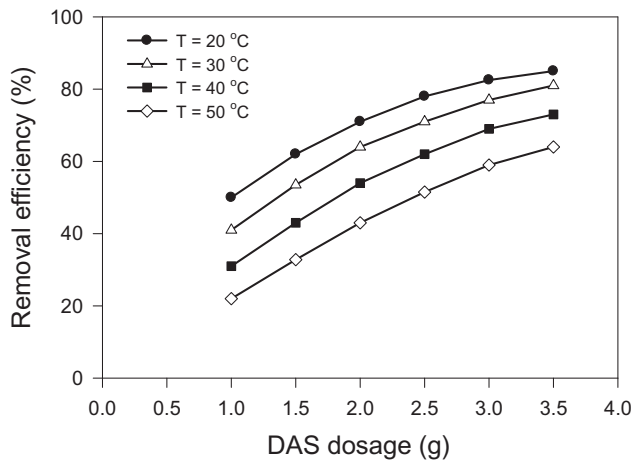


Figure 4 The effect of DAS dosage and temperature on the biosorption.

3.5. Biosorption isotherms

The Langmuir model is valid for monolayer adsorption containing finite number of identical biosorption sites. In this case interaction between adsorbate particles is negligible. The Langmuir model is given by the following equation (Langmuir, 1918):

$$q_e = \frac{(q_m K_L C_e)}{(1 + K_L C_e)} \quad (1)$$

where C_e (mg/L) is the equilibrium concentration of the solution, q_m (mg/g) is the maximum amount of metal ions required to form monolayer, K (L/mg) is the adsorption equilibrium constant related to the sorption energy between the adsorbate and adsorbent and q_e (mg/g) is the amount of metal adsorbed per specific amount of adsorbent. In order to conveniently determine Langmuir constants, Eq. (1) can be rearranged to a linear form as follows (Mo and Lian, 2011):

$$\frac{C_e}{q_e} = \frac{1}{(K_L q_m)} + \frac{C_e}{q_m} \quad (2)$$

The equilibrium data were analyzed using the linearized form of Langmuir adsorption isotherm Eq. (2). Langmuir constants, K_L and monolayer biosorption capacity, q_m were calculated from the slope and intercept of the plot C_e/q_e versus C_e (Fig. 5). The maximum copper sorption capacity of DAS was obtained (91 mg/g) at 20 °C. The q_m was one and a half times higher than that was obtained (62.5 mg/g) by Benaissa and Elouchdi (2011). The Langmuir isotherm constants are shown in Table 2.

The Freundlich isotherm model is employed to describe heterogeneous surfaces that represents the binding sites are not equivalent and/or independent. This model considers repulsive interactions between adsorbed solute particles (Freundlich, 1906; Sinha et al., 2012). Freundlich equation is given as follows:

$$q_e = K_F (C_e)^{(1/n)} \quad (3)$$

where n is the adsorption intensity and K_F is the adsorption capacity (mg/g)(L/mg) $^{1/n}$. Freundlich equation can be linearized in logarithmic form for the convenience of plotting and determining Freundlich isotherm parameters (Eq. (4)):

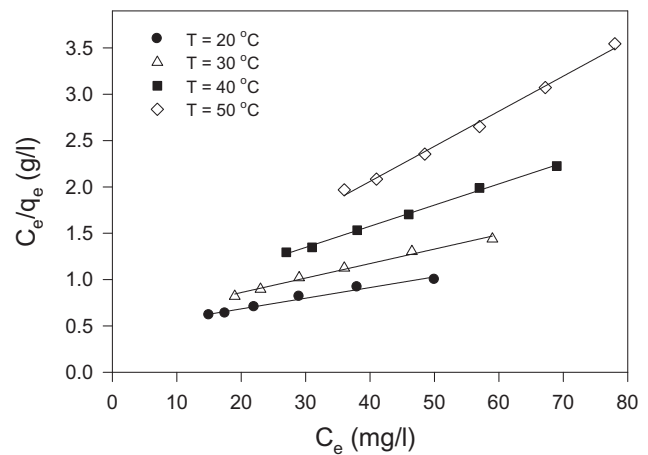


Figure 5 Langmuir isotherm model for the biosorption of Cu (II) ions onto DAS.

Table 2 Langmuir isotherm model parameters for biosorption of Cu (II) ions onto DAS.

| Temperature (°C) | Langmuir isotherm constants | | |
|------------------|-----------------------------|--------------|-------|
| | q_m (mg/g) | K_L (L/mg) | R^2 |
| 20 | 91 | 0.024 | 0.975 |
| 30 | 67 | 0.027 | 0.989 |
| 40 | 45 | 0.033 | 0.997 |
| 50 | 27 | 0.068 | 0.994 |

$$\log(q_e) = \log(K_F) + \left(\frac{1}{n}\right) \log C_e \quad (4)$$

As shown in Fig. 6, the plot of $\log q_e$ versus $\log C_e$ was fitted linearly for Freundlich isotherm model. Freundlich isotherm parameters, K_F and $1/n$ were calculated from the slope and intercept of linear plots of $\log q_e$ and $\log C_e$. The Freundlich parameters for adsorption of Cu (II) ions on DAS at different temperatures are summarized in Table 3.

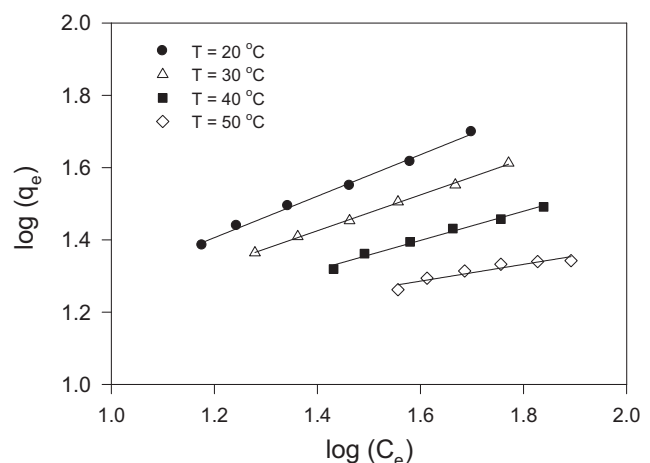


Figure 6 Freundlich isotherm model for the biosorption of Cu (II) ions onto DAS.

The D–R isotherm model was employed to determine the nature of the biosorption process. Linearization of this model is presented in Eq. (5) (Dubinin et al., 1947):

$$\ln(Q_e) = \ln(Q_m) - \beta \varepsilon^2 \quad (5)$$

where Q_m (mol/g) is the monolayer capacity, and β (mol²/J²) is the activity coefficient related to biosorption energy, Q_e (mol/g) is the amount of copper ions adsorbed per unit mass of the adsorbent and ε is the Polanyi potential given as follows:

$$\varepsilon = RT \ln \left[1 + \left(\frac{1}{C_e} \right) \right] \quad (6)$$

The mean free energy E (J/mol) of biosorption for the transfer of adsorbate from the infinity to the adsorbent surface is given as follows:

$$E = \frac{1}{\sqrt{2\beta}} \quad (7)$$

the E values below 8 kJ/mol indicate, physisorption mechanism is the dominant mechanism of adsorption, and the values between 8 and 16 kJ/mol show the chemisorption mechanism of adsorption (Sari and Tuzen, 2008). A representative plot of D–R isotherm model is shown in Fig. 7. The D–R isotherm parameters are summarized in Table 4. Obtained results based on E values indicated that chemisorption is the dominant mechanism of biosorption.

3.6. Kinetics models

Kinetics models of biosorption were investigated by Weber–Morris, pseudo-first-order and pseudo-second-order models. With the purpose of kinetic study of Cu (II) ions biosorption on DAS, variation in the concentration of adsorbate on biosorbent with mixing time was described by the following equation (Weber and Morris, 1963):

$$q_t = R_{id}(t)^{(1/2)} + C \quad (8)$$

where R_{id} (h^{-1/2}) is the rate constant for the intra-particle diffusion and C (mg/g) is the intercept constant of the plot that is related to the boundary layer thickness, q_t (mg/g) is the adsorbed concentration of Cu (II) ions with respect to the time t . The Weber–Morris model represents multi linearity which indicates that adsorption may occur in two or more steps. As shown in Fig. 8a, in the first stage, the sharp slope of the line was attributed to the diffusion of Cu (II) ions through the solution to the external surface of the adsorbent. In the second stage, the low slope of the line was caused by a low diffusion rate of Cu (II) adsorption onto internal pore surface of DAS.

The intra-particle diffusion rate constants were calculated from the slope of the linear plots. The Weber–Morris constants

Table 3 Freundlich isotherm model parameters for biosorption of Cu (II) ions onto DAS.

| Temperature (°C) | Freundlich isotherm parameters | | |
|------------------|--------------------------------|-------|-------|
| | n | K_F | R^2 |
| 20 | 1.74 | 5 | 0.995 |
| 30 | 2.02 | 5.37 | 0.998 |
| 40 | 2.48 | 5.65 | 0.986 |
| 50 | 4.3 | 8.20 | 0.896 |

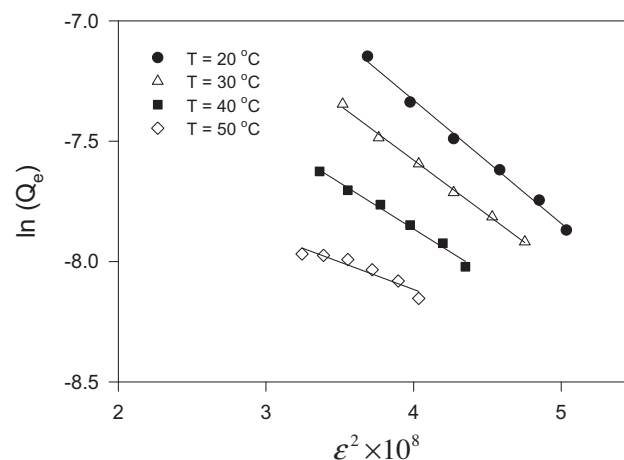


Figure 7 D–R isotherm model for the biosorption of Cu (II) ions onto DAS.

Table 4 D–R isotherm model parameters for biosorption of Cu (II) ions onto DAS.

| Temperature (°C) | D–R isotherm parameters | | | |
|------------------|---|--------------|-------|--------------|
| | β (mol ² /J ²) | Q_m (mg/g) | R^2 | E (kJ/mol) |
| 20 | 5.12×10^{-9} | 149 | 0.994 | 9.88 |
| 30 | 4.55×10^{-9} | 103 | 0.997 | 10.48 |
| 40 | 3.84×10^{-9} | 65 | 0.989 | 11.41 |
| 50 | 2.28×10^{-9} | 41 | 0.905 | 14.80 |

(R_{id} , C) for the first and second stages were $R_{id} = 11.8 \text{ h}^{-1/2}$, $C = 5.09 \text{ mg/g}$ and $R_{id} = 2.39 \text{ h}^{-1/2}$, $C = 19.59 \text{ mg/g}$, respectively.

Also the kinetic modeling of Cu (II) adsorption onto DAS was studied by two common models which are pseudo-first-order and pseudo-second-order kinetic equations. Lagergren pseudo-first-order rate is given as follows (Lagergren, 1989; Zhou et al., 2007):

$$\log(q_e - q_t) = \log q_e - \frac{k \cdot t}{2.303} \quad (9)$$

where k (h⁻¹) is the first order rate constant and q_e (mg/g) is the sorbed concentration at equilibrium. As shown in Fig. 8b, the linear plot of $\log(q_e - q_t)$ versus time t (h) demonstrates the applicability of the pseudo-second-order model for Cu (II) adsorption onto DAS. The pseudo-first-order rate constant and the correlation coefficient were $k = 0.671 \text{ h}^{-1}$ and $R^2 = 0.96$, respectively.

The kinetic data for Cu (II) ions adsorption onto DAS was subjected to pseudo-second-order model given by the following equation (Ho and McKay, 1999; Wang and Guo, 2011):

$$\frac{t}{q_t} = \frac{1}{Kq_e^2} + \frac{t}{q_e} \quad (10)$$

where K (g/mg h) is the second order rate constant and q_e (mg/g) is the adsorbed concentration at equilibrium. The pseudo-second-order rate constant was from the slope and intercept of the line drawn based on obtained experimental data (Fig. 8c). The rate constant and correlation coefficient were $K = 0.058 \text{ g/mg h}$ and $R^2 = 0.99$, respectively.

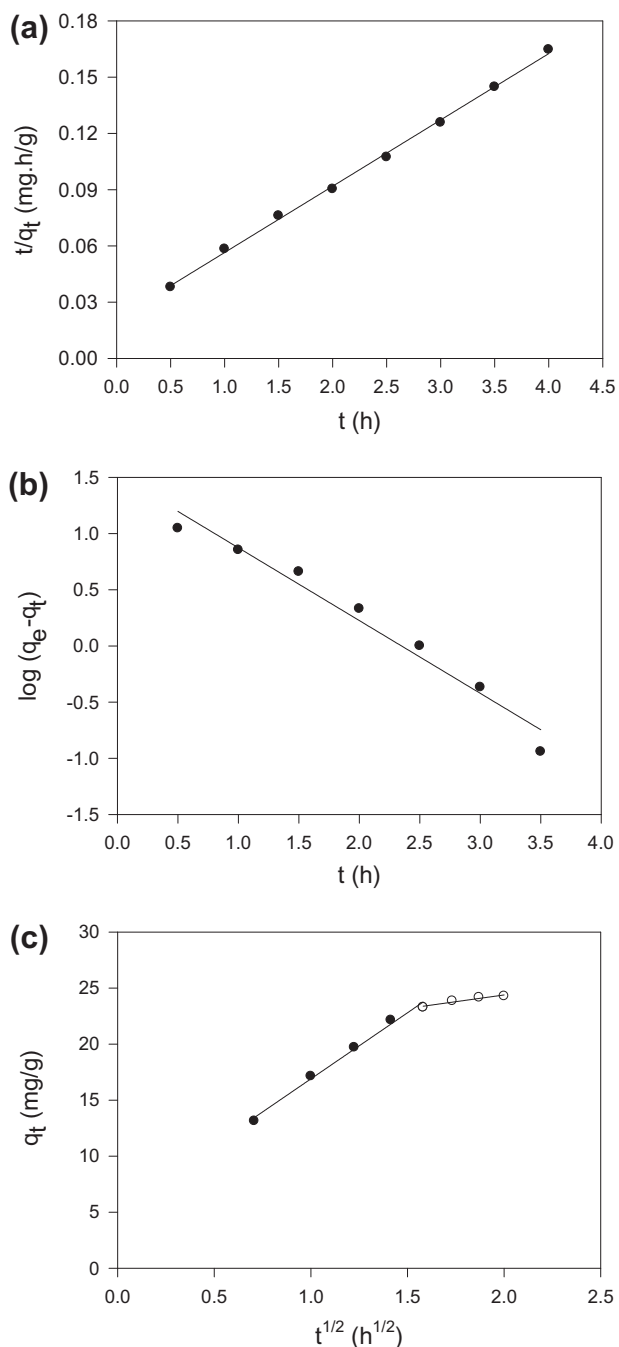


Figure 8 Kinetic models for the biosorption of Cu (II) ions onto DAS, (a) Weber–Morris, (b) pseudo-first-order and (c) pseudo-second-order.

4. Conclusions

In this research, the DAS showed effective removal of Cu (II) from synthetic aqueous solutions. Langmuir, Freundlich and D–R isotherm models were well fitted to experimental data. Biosorption kinetics was studied by Weber–Morris, pseudo second order and pseudo second order models. The Maximum removal efficiency of Cu (II) was 85% at temperature of 20 °C and pH of 5; this result was obtained with the Cu (II) initial

concentration of 100 mg/L, DAS dosage of 3.5 g/L and contact time of 4 h. Also it was found that the increase of temperature had a negative impact on biosorption of Cu (II) onto DAS.

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