Treatment of wastewater by ion exchange resin using a pulsating disc

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ABSTRACT

The rate of removal of the copper ion (Cu^{2+}) from synthetic wastewater was studied using an ion exchange resin and pulsation technique. Variables examined were initial concentration of (Cu^{2+}), a ratio of the mass of resin to solution liquid volume, frequency, amplitude, and geometry of the disc responsible for the pulsation motion. The results were presented mathematically by using the dimensionless analysis and the mass transfer correlation was obtained also Langmuir and Freundlich adsorption isotherms were examined where the date fits Freundlich adsorption isotherms more than Langmuir adsorption isotherms. It is concluded that the percentage of (Cu^{2+}) removal decreases as the initial concentration of (Cu^{2+}) presented increases and increases with the contact time, frequency (rpm), amplitudes, and mass of resin per unit volume of solution.

$Sh = 0.0949\,Sc^{0.33}\,Re^{0.7428}$

The present data for the conditions: $1,273 < Sc < 1,352$ and $23,400 < Re < 130,565$.

Keywords: Adsorption; Ion exchange resin; Industrial wastewater; Heavy metal; Copper ion; Mass transfer; Pulsation

1. Introduction

Freshwater makes up about 3% of earth's water and is the source of virtually all drinking waters, agriculture, and manufacturing purposes so it is a source of life. Most of this water comes from reservoirs, rivers, streams, and lakes; and these sources are vulnerable to pollution [1].

Nowadays many industrial bodies get rid of their toxic wastes in these sources which threaten not only human beings but also all living organisms. The exposure chronically of a huge dose of heavy metals in mankind results in various complications in systems such as nervous, respiratory, renal, hepatic, and reproductive. Metals are also caused allergies and contacting for long-term with such metals or their compounds have been proven carcinogenic. Most of the heavy metals are toxic and carcinogenic and is a symbol of serious intimidation to the human race and the fauna

and flora of the receiving water bodies as they are persistent and non-biodegradable [2]. Industrial sources: example chemical fertilizers, petroleum products, oil refineries, metal finishing and plating, semiconductor manufacturing, and textile dyes. Most of the industries like textiles, varieties of these factories are situated near the lake and discharge their effluents directly into it. Some statistics show waste disposal amounts: Fuel and power industries generate 2.4 million tons of heavy metals annually. Waste disposal adds 0.72 million tons/y. The metal industry adds 0.39 million tons/y. Other manufacturing contributes 0.24 million tons/y [3]. The most dangerous waste that has a fatal effect on all organisms are heavy metals and the most commonly encountered toxic heavy metals in wastewater are silver, lead, mercury, cadmium, chromium, copper, nickel, zinc, and arsenic [4,5].

Many heavy metals are essential trace elements for humans, animals, and plants in small amounts, but in larger

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amounts causes acute and chronic toxicity, linked to learning disabilities, cancers, and even death. Heavy metals have inhibitory effects on the biological treatment process at the wastewater treatment plants. They are elements having atomic weights between 63.5 and 200.6, and a specific gravity greater than 5.0 [6,7].

Among different techniques used for removal of high concentrations of heavy metals, precipitation–filtration, ion exchange, reverse osmosis, oxidation–reduction, solvent extraction, as well as membrane separation [3]. Ion-exchange processes have been widely used to remove heavy metals from wastewater due to their many advantages, such as high treatment capacity, high removal efficiency, and fast kinetics [8,9].

The aim of the present work is to remove copper ion from wastewater using ion exchange resin, introducing pulsation technique instead of stirring to enhance copper removal due to vibration motion that would increase the turbulence that will affect the rate of the reaction and gives a better mass transfer. The apparatus used is made from plexiglass where insulated stainless steel rod is fitted with a fixed disc at its end to produce oscillations in the solution.

2. Experimental part

2.1. Set-up and materials used

The apparatus used in the experimental work is shown in Fig. 1. It consisted mainly of more than 5 L plexi-glass vessels. 3 discs with diameter 10 cm each were used alternately in the experimental work, one of them is solid and the other two are perforated with different diameters (2 and 4 mm), they also have the same distance between the consecutive pores. The disc was connected to a shaft of 0.5 cm diameter which was connected to a variable speed dc motor of 0.5 hp. Motor rotation speed was controlled by means of a variac and was measured by an optical tachometer.

2.2. Cation exchange resin

A strong cation exchange resin, macroporous Mono-Plus SP 112 (Laxness energizing chemistry) in the sodium form was used in the present work. Before using the resin, it was treated with a solution of sodium hydroxide. The treatment step was carried out by immersing the resin in sodium hydroxide solution of 1.5 M concentration for 45 min to ensure that all the resin is in the sodium form, and the following steps were carried out to complete the pretreatment step [7]. The resin was washed with distilled water three times to remove excess OH⁻ group. The following processes were carried out on the resin respectively:

• Immersing the resin in 2 M HCl solution for 45 min to replace all sodium ions by hydrogen ions.
• ashing with distilled water three times to remove excess Cl⁻ ions.
• Drying at ambient temperature for 2 d.
• Drying in a drying oven at 60°C for 20 min.

3. Procedures

Before each run, the cylindrical plexiglass container and the disc, were washed with tap water than distilled water and after that they must be dried. Before each run 2 L of freshly prepared copper sulfate solution of the required copper ion concentration were placed into the cylindrical vessel. The initial copper ion concentrations used in the
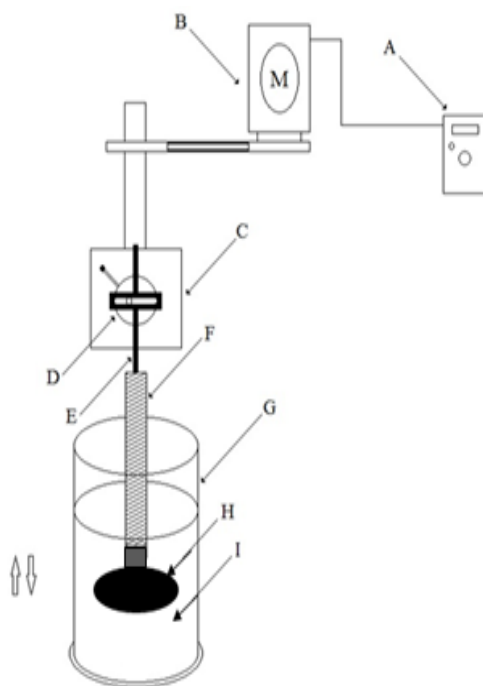
A: Inverter
B: electrical motor
C: mechanical vibrator
D: Rotating disc
E: Crank shaft
F: Stainless steel shaft
G: Plexi-glass cylinder
H: Plexi-glass disc
I: Copper sulphate solution

Fig. 1. The experimental setup.

experiments were 200, 300, 400, and 500 ppm. The amount of pretreated resin placed into the cylindrical plexiglass apparatus, were 1, 1.5, and 2 g/L of solution. The disc which was connected to stainless steel shaft was completely immersed in the solution. The pulsation frequency was adjusted by the variac and was measured by an optical tachometer. The pulsation speeds used were 100, 150, 200, 250, and 300 rpm. The amplitudes of the device were adjusted at 2, 2.8, and 3.6 cm. Kinetics of the ion exchange reaction was followed by withdrawing 5 ml sample from the vessel every 3 and 5 min. The samples were analyzed for the remaining copper ion concentration by iodometric titration [10,11].

Experimental work was carried out at 25°C. Density and viscosity of the solution used were determined using a density bottle and an Ostwald viscometer respectively [12]. The diffusivity of copper ion in solution was obtained from the literature and was corrected for the change in temperature using the Stokes–Einstein [13].

$$\frac{D\mu}{T} = \text{constant} \tag{1}$$

4. Results and discussion

4.1. Mass transfer analysis and correlation

There are two mass transfer mechanisms that exist in ion-exchange reactions, one of them occurs outside the resin by the action of the liquid layer encircling the particle, the other one is inside the particle. By applying the pulsation technique one of these diffusions will be the rate-controlling step [14].

For a batch reactor, assuming pseudo-first-order reaction, the rate of copper ion elimination by the action of ion-exchange resin is given by the following relations [15].

$$\left(\frac{dC}{dt}\right) = \frac{KAC}{V} \tag{2}$$

When integration is applied at $t = 0$, $C = C_0$ and at $t = t$, $C = C$.
Thus:

$$\ln\left(\frac{C_0}{C}\right) = \left(\frac{KA}{V}\right)t \tag{3}$$

$$A = \frac{(6W)}{\rho d_p} \tag{4}$$

A is the area of the resin which has a spherical shape.

Eq. (3) can be well explained and displayed in Fig. 2 which shows a typical plot of $\ln(C_0/C)$ vs. time by using different frequencies (rpm). This suggests that the reaction is a first-order diffusion-controlled reaction.

A plot of $\ln(C_0/C)$ vs. time gives a straight line of slope (KA/V). The mass transfer coefficient of copper ion removal by the resin was obtained from the slope under different operating conditions that are, resin = 4 g, metal concentration = 200 ppm, and amplitude = 3.6 cm.

Fig. 3 shows the effect of frequency on the rate constant K at different amplitudes where 4 g of resin and 300 ppm copper ion initial concentration were used. The results show that the mass transfer rate is enhanced with
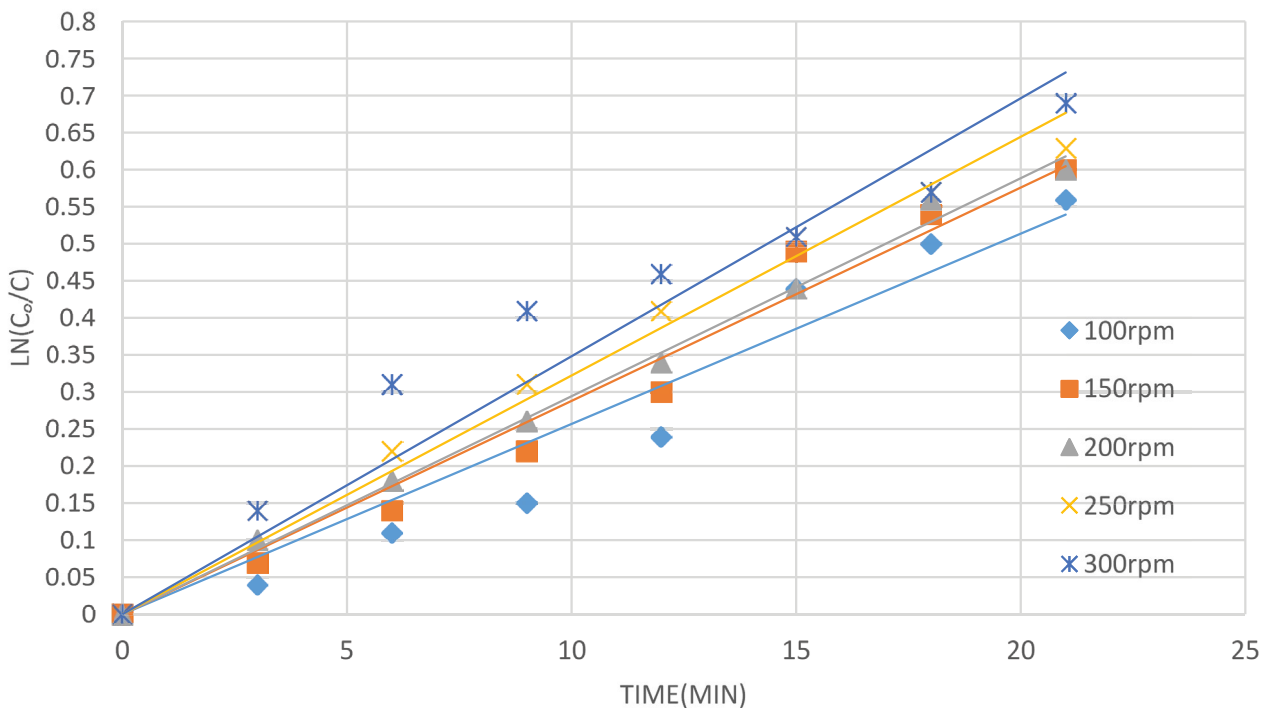

Fig. 2. Plot $\ln(C_0/C)$ vs. time at different pulsation frequencies.

increasing frequency and amplitude which is responsible for the turbulence in the medium.

Fig. 4 shows the effect of frequency on the rate constant K at different doses of resin in g/L of solution using 300 ppm copper ion initial concentration and 2 cm amplitude. Where the mass transfer rate is increased with increasing the frequency and the resin concentration which possesses active sites that is responsible for the ion exchange.

Fig. 5 shows that the percent of copper ion removal increases with increasing the frequency and decreasing the initial concentration of copper ion with the same resin amount due to the decrease of active sites in the resin as 4 g resin were used under the influence of 3.6 cm amplitude.

The increase in the rate of copper ion removal with increasing vibration intensity suggests that the liquid phase diffusion of a copper ion across the diffusion layer surrounding each particle (Fig. 6) is the rate-determining step given the fact that interparticle diffusion is not sensitive to pulsation and that follows the same concept as the stirring mechanism [15].

The data were correlated in terms of the dimensionless group's Re, Sh, and Sc usually used in correlating forced convection mass transfer data.

$$\text{Re} = \frac{\rho v_i d_e}{\mu} = \rho 2\pi a f \frac{d_e}{\mu} \tag{5}$$

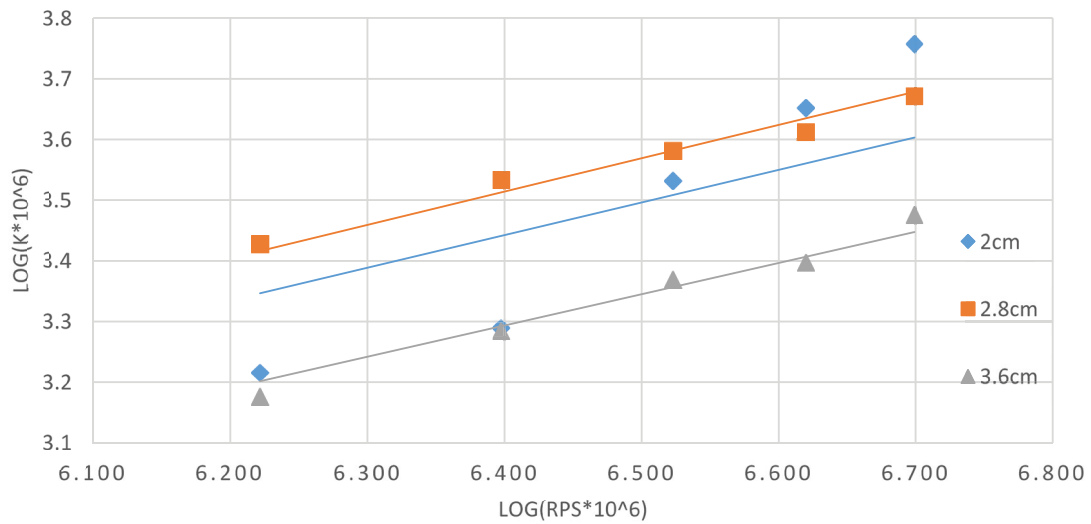$$\text{Sh} = \frac{K d_e}{D} \tag{6}$$

Fig. 3. Effect of pulsation frequency and amplitudes on the value of the mass transfer coefficient.
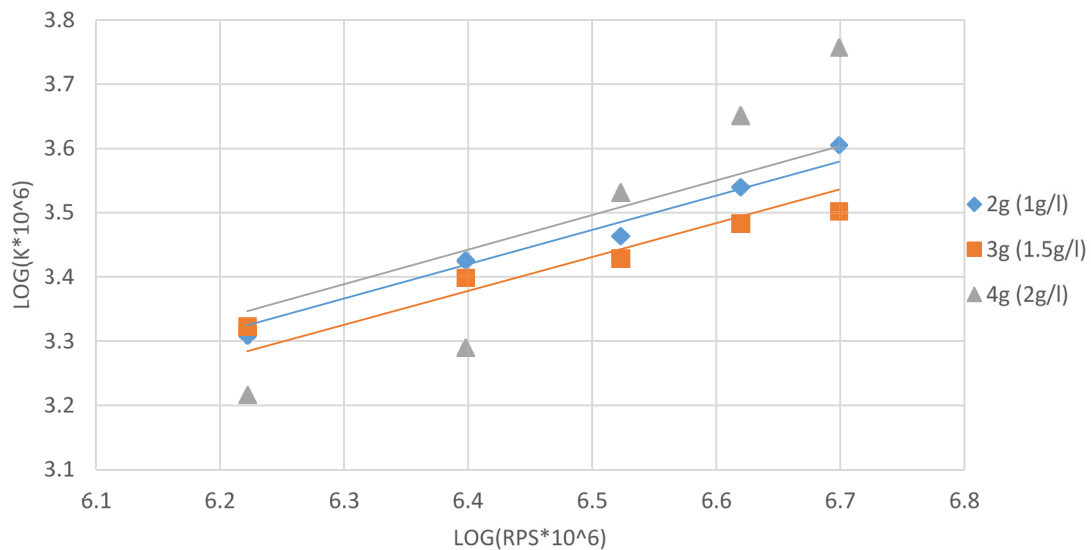

Fig. 4. Effect of pulsation frequency and resin amount on the value of the mass transfer coefficient.

$$Sc = \frac{\mu}{\rho D} \tag{7}$$

Fig. 6 shows the relation between log(Re) vs. log(Sh) at different Sc numbers.

The data fit Eq. (8)

$$Sh \, \alpha \, Re^{0.7428} \tag{8}$$

Fig. 7 shows that the present data for the conditions: 1,273 < Sc < 1,352 and 23,400 < Re < 130,565.

The previous data fit the overall mass transfer Eq. (9):

$$Sh = 0.0949 \times Sc^{0.33} \, Re^{0.7685} \tag{9}$$

4.2. Factors affecting the removal of copper ion

4.2.1. Effect of the initial concentration of copper ion

Fig. 5 shows the effect of initial copper ion concentrations on the percentage removal of copper ion. The data shows that the percentage removal of copper ion increases as the initial copper ion concentration decreases from 400 to 200 ppm. This result may be explained by the fact that for a given amount of resin, as the initial concentration of copper ion increases, the number of active sites of the resin available for copper ion adsorption will be decreased and any extra amount will not be attached to free sites [16].

4.2.2. Effect of the amount of resin

Fig. 8 shows the effect of the resin concentration in g/L on the percentage removal of Cu^{2+}. The data show that as the solid/liquid ration increases, the percentage of Cu^{2+} removal increases with time for the same initial Cu^{2+} concentration 300 ppm due to the number of active sites available in the resin that is ready for exchanging ions as explained previously [17].

Fig. 4 also showed the effect of frequency on mass transfer. It is clear that mass transfer is enhanced by the increasing the amount of resin which confirms the previous conclusion.
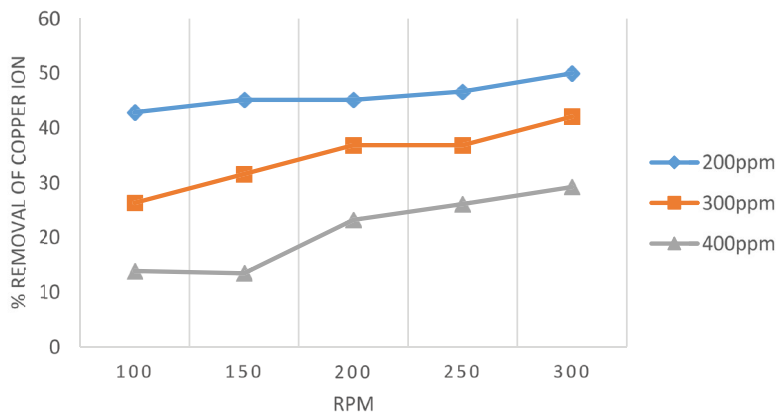

Fig. 5. Percentage removal of copper ions vs. frequency (rpm) with different initial copper ions concentrations.
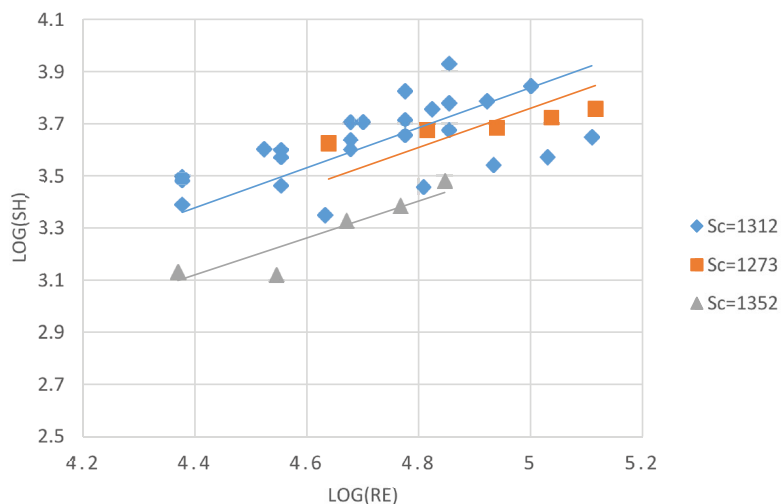

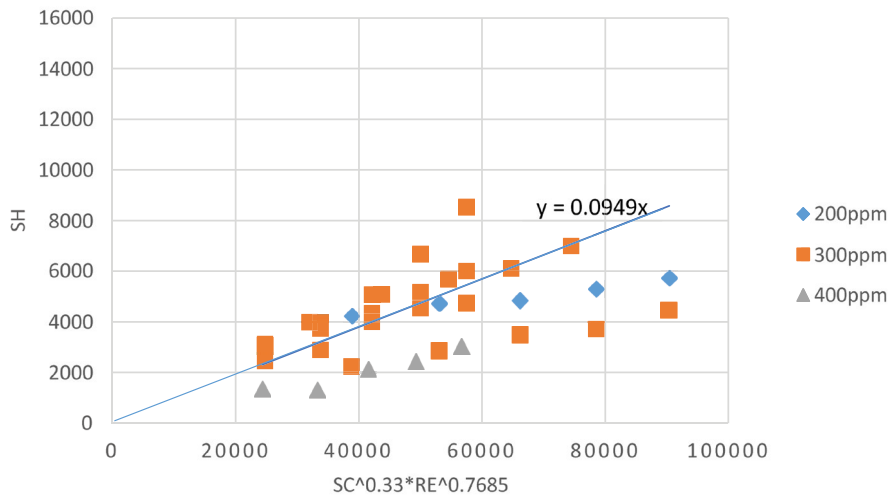Fig. 6. Plot of logSh vs. logRe at different Sc values.

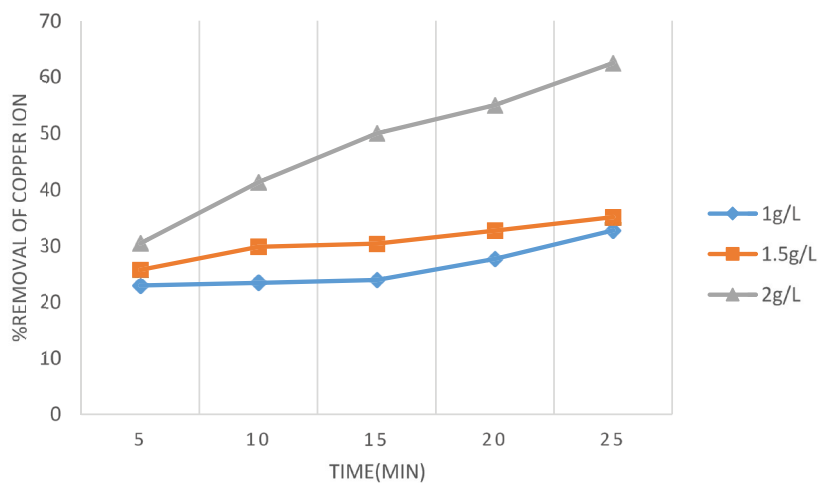Fig. 7. Overall mass transfer correlation at different Sc values.

Fig. 8. % removal of copper ion vs. time at different solid to liquid ratio.

4.2.3. Effect of contact time

Figs. 2 and 8 show the effect of time on the percentage uptake of copper ions at different initial copper ions concentrations and different doses of resin in gram. The data show that the percent of copper ion removed increases with increasing contact time also it depends on the initial copper ion concentration. The higher the initial copper ion concentration, the more the percent of copper ion removal.

4.2.4. Effect of amplitude

Fig. 9 shows the effect of changing the amplitudes at initial copper ions concentration 300 ppm, 2 g/L resin in the solution and different frequencies which implies the optimum amplitude at which the mass transfer rate is enhanced and this occurs with the condition a = 2.8 cm, the amplitude is an important criteria that affect the vibration intensity ($v_i = 2\pi f a$).

As noticed first when the amplitude is increased the mass transfer rate increased then after a further increase in amplitude the mass transfer rate decreased, maybe the reason is the intensity of the turbulence is not much high in case of high amplitude.

4.2.5. Effect of frequency

From Figs. 2, 3, 4, 5, and 9 it is so clear the dependence of the diffusion mass transfer and the % removal of copper ion on the frequency (rpm or rps), the vibration and oscillation propagate in the medium enhances the mass transfer of copper ion and letting the exchange and adsorption occur on the resin.

4.2.6. Effect of disc geometry

Table 1 shows the effect of disc geometry (one solid and two other perforated discs) that was studied and
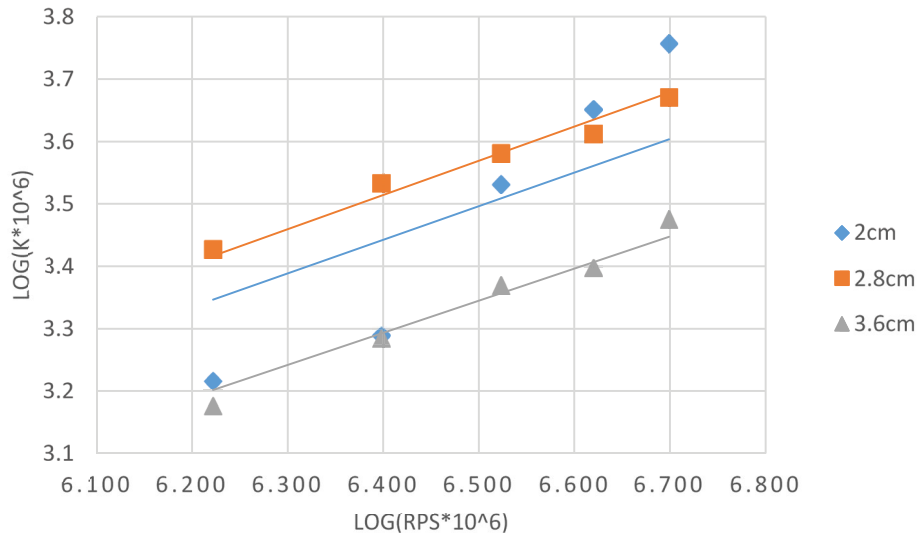
Fig. 9. Effect of pulsation frequency and amplitudes on the value of the mass transfer coefficient.
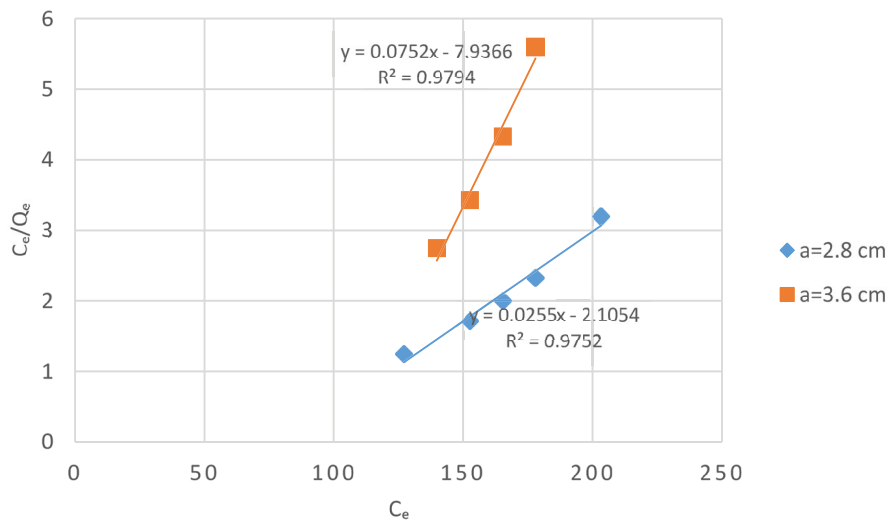

Fig. 10. Langmuir adsorption isotherm at copper ion initial concentration 300 ppm and 2 g/L resin concentration.

compared at the same initial copper ion concentration 200 ppm. The experiment with the least percent of copper ion removal was in the case of a perforated disc that owns large perforation. Obviously the result favors the solid disc than the perforated and this is due to the better turbulence that occurred in case of a solid disc that enhances the diffusion and ion exchange.

4.2.7. Isotherm studies

The adsorption equilibrium relates q to C. The equilibrium is a function of the temperature. Therefore, the adsorption equilibrium relationship at a given temperature is typically referred to as adsorption isotherm.

The adsorption capacity after reaching equilibrium, q_e (mg/g), was calculated using the Eq. (10) [18,19].

$$q_e = \frac{(C_0 - C_e)V}{W}$$ (10)

where C_0 and C_e (mg/L) are the initial and equilibrium concentrations of copper ions; V is the volume of the solution (L); W is the mass of dry adsorbent (g).

It is important to evaluate the most appropriate isotherm which fits the present data to optimize the design of a sorption system. It has been found that for most of the cases of importance in wastewater treatment the function $q = f(C)$ takes the form of one of the following isotherms:

Langmuir and Freundlich isotherm models that were used to describe the adsorption equilibrium. Experimental isotherm data were conducted at an equilibrium time for a different amounts of resin per liter of solution, different

Table 1
Compares different moving discs from the perspective of copper ion removal

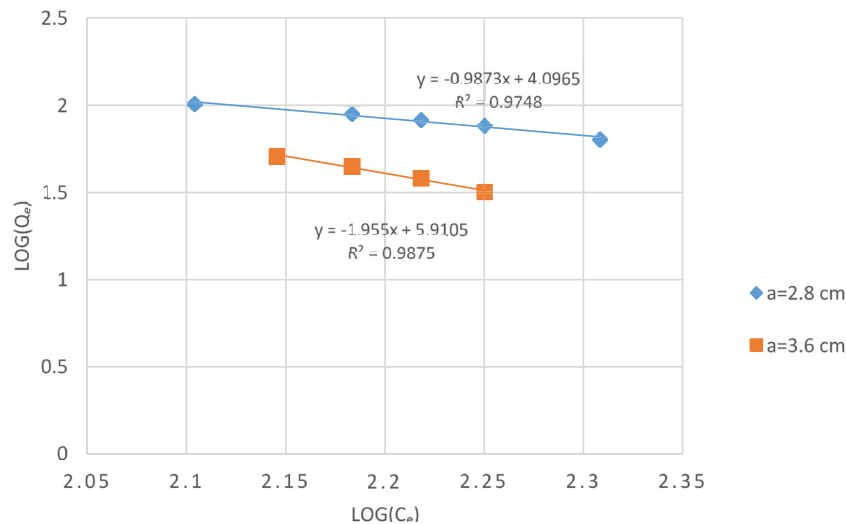| Type of disc	% of Cu^{2+} removal range at 200 ppm
10 cm diameter solid disc	43%–50%
10 cm diameter perforated disc (2 mm hole diameter)	24%–53%
10 cm diameter perforated disc (4 mm hole diameter)	8%–33%

Fig. 11. Freundlich adsorption isotherm at a copper initial concentration of 300 ppm and 2 g/L resin concentration.

initial concentration of copper ion, different amplitudes, and frequencies.

Comparing the two isotherms, the Langmuir isotherm has a theoretical justification. The Freundlich isotherm represents an empirical model· The Langmuir isotherm assumes reversible adsorption and desorption of the adsorbate molecules. No assumption is made for the Freundlich isotherm· The Langmuir isotherm typically represents well data for single components. The Freundlich isotherm can be used also for mixtures of compounds.

4.2.7.1. Langmuir isotherm

This model is shown in Fig. 10 is established upon the assumption that all sites have the same affinity for the adsorbate, it is represented by the following relation,

$$\frac{C_e}{q_e} = \frac{1}{(K_L Q_m)} + C_e Q_m \tag{11}$$

After applying the previous relation on the present work it gives $K_L = -0.022$ L/mg and $Q_m = 26.26$ mg/g; Q_m: maximum copper adsorbed, K_L: Langmuir isotherm constant. Where these values are average values for the experiments that follow this model.

4.2.7.2. Freundlich isotherm

The Freundlich isotherm (Fig. 11) is based on the equilibrium between surfaces. This isotherm is concluded from the

assumption that the adsorption sites are distributed exponentially with respect to the heat of adsorption. The logarithmic linear form of Freundlich isotherm may be represented as follows:

$$\log q_e = \log K_F + \left(\frac{1}{n_F}\right)\log C_e \tag{12}$$

K_F and $1/n_F$ are the Freundlich constants indicating the capacity and intensity,
where $1/n_F = -0.99$ and $K_F = 12{,}488.2$ L/g, where these values are average values for the experiments that follow this model.

Figs. 10 and 11 show that Langmuir adsorption isotherm gives better data fitting than Freundlich isotherm (as shown by the high value of R^2).

5. Conclusion

The present results have shown that a pulsator reactor with ion exchange resin medium is a useful technique for the removal of heavy metals from wastewater.

Copper ion removal by the ion exchange resin by vibrating technique was found to take place through diffusion-controlled first-order reaction. The mass transfer data were correlated by the following dimensionless equation:

$$Sh = 0.0949\ Sc^{0.33}\ Re^{0.7428}$$

This equation could be used to design a batch reactor.

As ion exchange is similar to adsorption isotherms models were studied, the present work shows that the data fit the Freundlich isotherm better than the Langmuir isotherm, other isotherms models should be studied.

Comparing the vibrating solid discs vs. the perforated discs which were displayed in the current experimental work, the solid disc favors the area in addition to turbulence action and the perforated disc favors the turbulence action, obviously the area companied by turbulence perspective was the dominant factor.

The copper ion removal efficiency is highest when the system is working at 2.8 cm amplitude, using the solid disc as the moving part, increasing the amount of resin, increasing the frequency intensity and contact time and decreases with increasing initial copper ion concentration.

Symbols

a	—	Amplitude, cm
C_0	—	Initial concentration of copper ion, ppm
C_e	—	Concentration of copper ion at equilibrium, ppm
C	—	Concentration of copper ion at any time, ppm
d_e	—	Equivalent diameter, cm
d_p	—	Particle average diameter, cm
f	—	Frequency, 1/s
D	—	Diffusivity, cm^2/s
K	—	Rate constant of adsorption, cm/s
K_F	—	Freundlich isotherm adsorption coefficient, L/g
K_L	—	Langmuir isotherm parameter, L/mg
n_F	—	Freundlich isotherm constant, –
N	—	Rotation speed, rps
Q_m	—	Langmuir isotherm parameter, mg/g
q_e	—	Equilibrium mass adsorbed heavy metal per unit resin, mg/g
Re	—	Reynolds number, dimensionless
Sh	—	Sherwood number, dimensionless
Sc	—	Schmidt number, dimensionless
t	—	Time, min
T	—	Absolute temperature, K
v_i	—	Vibration intensity, cm/s
V	—	Volume of the solution, cm^3
W	—	Dry weight of the ion-exchange resin, g
ρ	—	Density of the solution, g/cm^3
μ	—	Viscosity of the solution, g/cm s
δ	—	Diffusion layer thickness, cm

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