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Adsorption of Cu^{2+} Ion from Aqueous Solution by Clam Shell Powder

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Abstract

Seashell has become one of the most significant aquaculture wastes. In this work clam shell derived from local market was used as adsorbent for removal of Cu^{2+} heavy metal ion from aqueous solution at different temperature and initial solution pH of 5. The shell was characterized using XRD, SEM and FTIR spectroscopy. The Langmuir and Freundlich adsorption isotherms models were found to be useful for describing the equilibrium adsorption system. The monolayer saturation capacities calculated according to the Langmuir adsorption isotherm were given to be 6.37-13.58 meq g^{-1} at 20-40 °C. The adsorption kinetics showed that the adsorption process can be well described with the pseudo-first order model.

Key word: $Cu2^{+}$ ion adsorption, aqueous solution, clam shell powder, XRD, SEM and FTIR spectroscopy

1. Introduction

The release of toxic substances to the water system from industrial and different human activities such as mining, metal processing, pharmaceuticals, pesticides, organic chemicals, rubber and plastics, etc. may cause serious effects to the environment and human health. It is because the toxic substances have a tendency to accumulate in the soil, sea water, fresh water and sediments due to their high dispersion from where they enter into the food chain [1].

Rapid industrialization has led to increased disposal of heavy metals into the environment. The tremendous increase in the use of the heavy metals over the past few decades has inevitably resulted in an increased flux of metallic substances in the aquatic environment. The heavy metals are special because of their persistency in the environment. At least 20 metals are classified as toxic, and half of these are emitted into the environment in quantities that pose risks to human health [2]. The ability of a water system to support aquatic life as well as its suitability for other uses, however, depends on many trace elements.

Heavy metal pollution of wastewater is a common environmental hazards, one of such heavy metal of concern is copper. It is present in the wastewater of several industries, such as metal cleaning and plating baths, refineries, paper and pulp, fertilizer, and wood preservatives [3].

In order to have a pollution-free environment, the toxic heavy metals should be removed from wastewater before its disposal. A number of technologies have been developed over the years to remove heavy metals from industrial wastewater [4-6]. Different technologies include coagulation/flocculation [7,8], precipitation, ion-exchange, electrochemical processes and membrane technology have been studied. All the chemical methods have proved to be much costlier and less efficient than the biosorpti--on process [9]. In addition, chemical methods increase the pollution load on the environment. Biosorption, is a biological method of environmental control that can be an alternative to conventional wastewater treatment facilities. Natural biopolymers are industrially attractive because of their capability of lowering transition metal-ion concentrations to parts per billion concentrations [10]. Very few researches have been carried out to study the clam shell as sorbent [11-15]. In this work an investigation was carried out to evaluate the effectiveness of employing a clam shell for the adsorption removal of Cu^{2+} from wastewater. The experimental batch kinetic and isotherm studies were carried out to determine the adsorption capacities.

2. Materials and methods

2.1 Materials

All chemicals used were of analytical grade and used without further purification. Copper chloride (99 %) was used for the preparation of stock standard solutions of Cu (II) was purchased from Aldrich. Its chemical formula and molecular weight are ($CuCl_2.2H_2O$) and 170.54 g mol^{-1}, respectively. Clam shell samples, was obtained from local market (Cairo city, Egypt). The samples were first cleaned with boiling distilled water for two hours to remove fresh remnants attached to the shells, and then dried in oven at 100^0 C for 30 min. The dried shells were graded with mill to prepare powder particles. The shell powders were thus sieved to three different mesh number ranges of 0.841 mm, 0.420 mm and 0.037 mm, according to USA standard sieve designation. The resulting shell powders were stored in the desiccator prior to the physical and adsorption characterizations.

2.2 Characterization of clam shell powder

2.2.1 Determination of calcium content of clam shell

To carry out the elemental analysis of the used clam shell, EDTA titration was performed to identify percentage of calcium in clam shell [16]. To determine the calcium content of used clam shell, the fine powder was dissolved in 0.6 M HCl and the pH adjusted to10 by ammonium buffer solution. Finally, the resulted solution was titrated by EDTA (0.05N).

2.2.2 X-ray diffraction (XRD)

X-ray diffraction (XRD) patterns of the shell were performed in order to identify the crystalline spaces present at room temperature on X- ray diffraction (D/Max2500 VB2+/Pc, Rigaku Company, Tokya, Japan), with area detector operating at voltage of 40 kV and a current of 50 mA using CuKα radiation (wavelength λ=0.153nm) .The X- ray diffraction analysis was carried out in the scanning angle (2θ) range 5-90^0 at scanning speed of 1^0 min^{-1}.

2.2.3 Scanning electron microscope (SEM) and XPS

In order to elucidate surface morphology of the resulting shell powders, the powder texture was observed by the scanning electron microscope (SEM). The surface morphologies of the samples were examined using an S-3000N (Hitachi High-technologies Co., Tokyo, Japan) SEM apparatus operated at a 15 kV accelerating potential. Prior to the observation, the surface of the sample was coated with a thin, electric conductive gold film. The XPS was also reported.

2.2.4 Fourier transform infrared (FT-IR)

Fourier transform infrared spectroscopy (FTIR) was performed to identify the chemical structure of the clam shell. FTIR spectra of the sample was measured with JASCO, Nicolet IS-10 (made in Japan) spectrophotometer which used the KBr disc in measurement and the IR absorption band was adjusted by the baseline at wavelengths in the range for 4000 to 400 cm^{-1},with increments of 500 cm^{-1} and resolution of 4 cm^{-1} .

2.2.5 Determination of Point of zero charge

The pH drift test of clam shell was carried out as follows: 50 ml of 0.01 M NaCl solution was placed in titration vessel (298K). Nitrogen was bubbled through the solution to stabilize the pH by preventing the dissolution of CO2. The pH was adjusted in the range from 3 to 10 by addition of 0.1M HCl or 0.1M NaOH solutions. The clam shell (0.15g) was added to the solution and after 2h the final pH was measured and plotted against the initial pH. As reported elsewhere, [17, 18] the pH at which the curve crossed the line pH initial = pH final was taken as the point of zero charge, pH_{pzc}.

2.3 Adsorption studies

2.3.1 Effect of pH on Cu (II) Adsorption

The effect of pH on the adsorption of Cu (II) was studied by mixing 0.05 g of adsorbent with 25 ml of copper solution of 500 mg/L at different pH value (2 – 5) under room temperature. The pH was adjusted with 0.005 M HCl solution and measured by pH meter (Cyperscan 500^{pH}, USA). Agitation was made at a constant stirring speed of 500 rpm for overnight. The solid was separated from the solution with the aid of centrifuge at 5000 rpm. The Cu^{2+} concentration was measured using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES).

2.4 Equilibrium Studies of Cu (II) Adsorption

To study the adsorption isotherm, a series of solutions containing different initial concentrations of Cu(II) ions (in the range of 200 – 900 mg/L) was prepared and employed for the batch adsorption studies at room temperature. The solid was separated from the solution with the aid of centrifuge at 5000 rpm. The Cu^{2+} concentration was measured using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), and the amount of adsorption at equilibrium, qe (mg/g) was calculated [1] by the following equation (1):

$$q_e = \frac{[(C]_o - C_e)V}{W} \quad (1)$$

where C_o and C_e (mg/L) are the liquid-phase concentration of copper at initial and equilibrium, respectively, V (L) is the volume of the solution and W (g) is the mass of dry adsorbent used (clam shell). The adsorption efficiency of Cu (II) can be calculated [1] by the following equation (2)

$$\text{adsorption percentage} = \frac{[(C]_o - C_e)x\,100}{C_o} \quad (2)$$

2.5 Kinetics Studies of Cu (II) Adsorption

The kinetics studies of Cu (II) adsorption were carried out by batch adsorption technique [13]. The duration time intervals up to 180 min were investigated .The solid was separated from the solution with the aid of centrifuge at 5000 rpm. The Cu^{2+} concentration was measured using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) and the amount of adsorption at time t, q_t (mg/g) was calculated [1] by the following equation (3)

$$q_t = \frac{[(C]_o - C_t)V}{W} \quad (3)$$

Where C_t (mg/L) is the liquid-phase concentrations of Cu (II) solutions at any time, t.

2.6 Effect of contact time on Cu (II) Adsorption

The copper of 500 mg/L was kept in contact with clam shell powder at room temperature for different time intervals. The effect of contact time investigated were 5, 15, 30, 45, 60, 75, 90, 120,150 and 180 min at pH5.

2.7 Effect of concentration on Cu (II) Adsorption

Initial copper concentrations of 300, 500, 700 and 900 mg /L were performed at pH5 for 180 min.

2.8 Effect of particle sizes on Cu (II) Adsorption

The grounded powder of used biosorbent was graded with standard sieves to three particle sizes (0.841 -0.420 -0.037 mm). Biosorbent (0.05g) from each graded size were added to six beakers of 25 ml copper chloride solution of 500 mg/L at pH5 for different intervals (5, 15, 30, 45, 60, 75, 90, 120,150 and 180 min) . The solid was separated from the solution with the aid of centrifuge at 5000 rpm. The Cu^{2+} concentration was measured using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES).

2.9 Effect of temperature on Cu (II) Adsorption

The effect of temperature on the adsorption of Cu^{2+} on clam shell was studied at different temperature (20-40^0) at pH5, particle size of 0.037 mm and concentration of copper 500 mg/L. The solid was separated from the solution with the aid of centrifuge at 5000 rpm. The Cu^{2+} concentration was measured using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES).

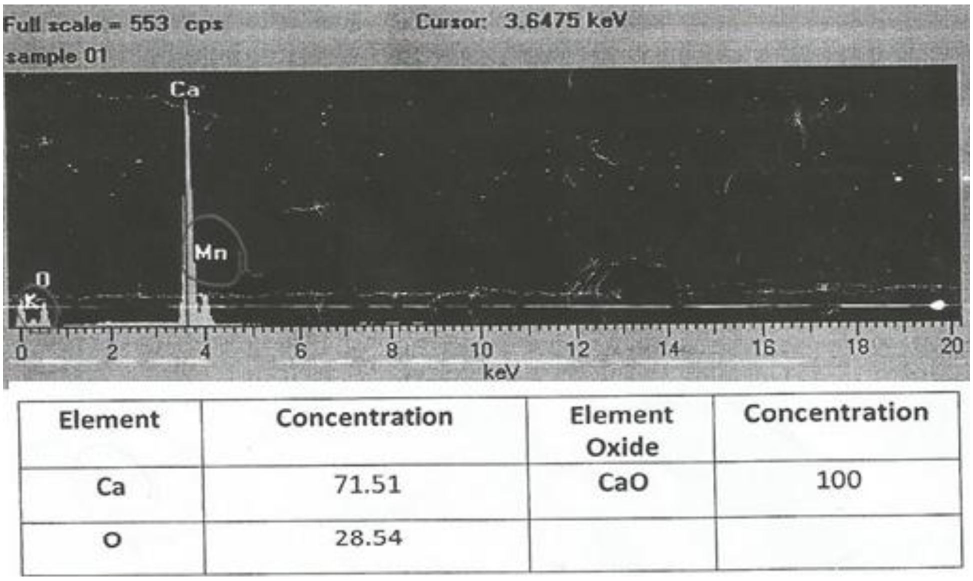
3. Result and discussion

3.1 Characterization of clam shell powder

3.1.1 Determination percentage of calcium content of clam shell

Table (1) Elemental analysis of clam shell.

Element	Ca^{2+}	CO^{3+}		Total percentage
		C	O	
% of element in shell	59	8.2	32.8	100



Element	Concentration	Element Oxide	Concentration
Ca	71.51	CaO	100
O	28.54		

Fig (1) XPS chart of the used clam shell As shown from Table (1) and XPS Fig (1) both analysis reveal that the content of calcium was in range 59-70%.

3.1.2 X-ray diffraction analysis of clam shell

Powder XRD patterns for clam shell over 2Θ range 6-80^0 are shown in Fig (2). The pattern reveals complete agreement of clam shell powder with aragonite calcium carbonate. All planes concerning the $CaCO_3$ were indexed on the basis of aragonite orthorhombic system. The main planes in the XRD pattern of $CaCO_3$ were assigned to the planes of 111, 121, 102, 112, 220, 040, 202 and 113 respectively. However the lattice parameters a,b,c are given to be 4.94, 7.94 and 5.72 respectively [19]. The particles size was calculated using Scherrer equation and given to be 33 nm.

$$(= K\lambda/(B\cos\theta) \tag{4}$$

Where:

τ: is the main particle size

K : scherrer factor (0.9)

λ : X-ray wave length

B : is the line broadening at half the maximum intensity (FWHM) in radiation

θ : is the Bragg angle

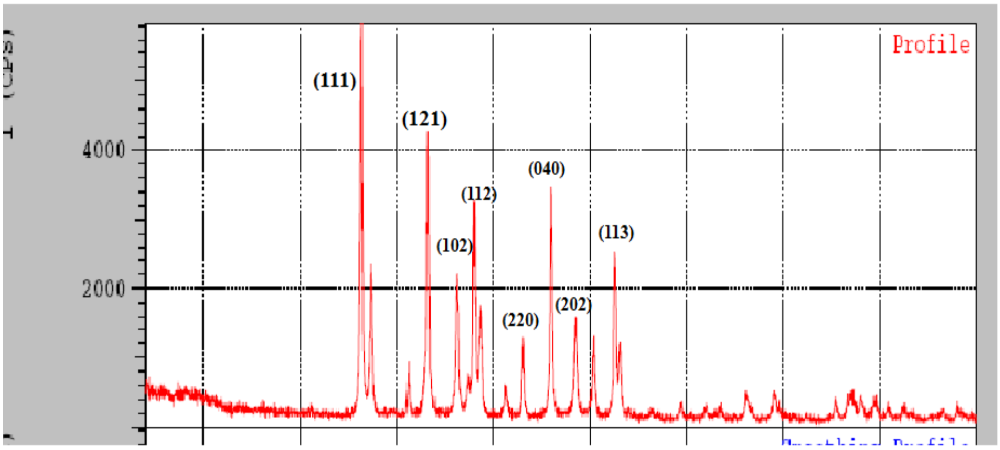


Fig (2) X-ray diffraction for clam shel

3.1.3 Scanning electron microscope (SEM)

The textural structure of clam shell under investigation can be observed from SEM photograph with the magnification of 10000, shown in Fig (3,4) which show a large distribution of particle size. It is also not indicate well-defined pore structure, however; this rough surface structure may provide the required surface for ion removal process [20, 21].

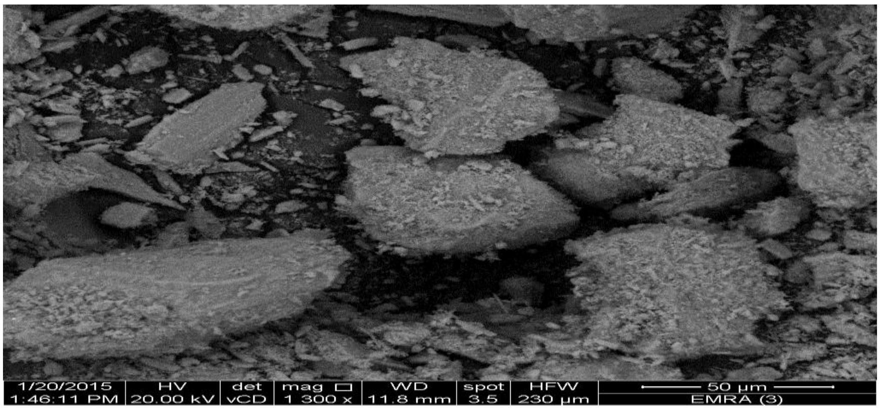


Fig (3) SEM micrograph for clam shell

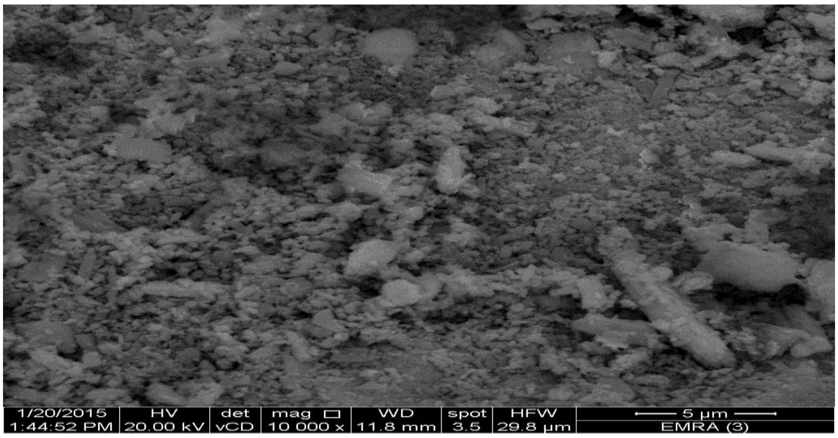


Fig (4) SEM micrograph for clam shell

3.1.4 FTIR spectroscopic analysis

FTIR spectroscopic analysis of clam shells under investigation was performed using KBr disk. To determine adsorption functional groups.FTIR spectra were measured for adsorbent samples before and after adsorption Fig (5). The vibrational bands between 500 and 1500 cm^{-1} were assigned the C-O stretching of $CaCO_3$. For the sample after adsorption, all the peaks had substantially exist as those in raw sample ,however, the small difference of these bands may be due to the physical adsorption of Cu^{2+} ions onto the clam shell [13].

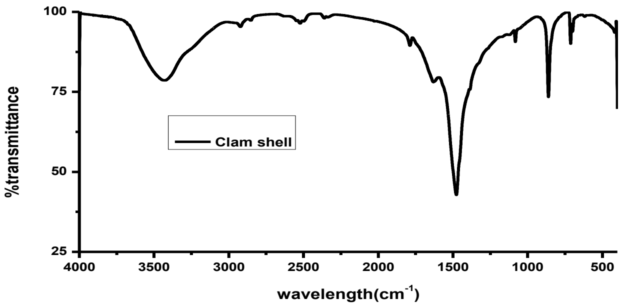


Fig (5) FTIR spectra for clam shell with copper

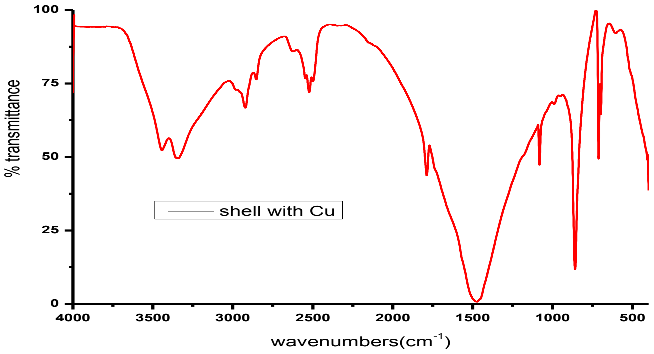


Fig (6) FTIR spectra for clam shell

3.1.5 Point of zero charge

Fig (7) shows the pH drift test for clam shell. The pH of point of zero charge, pH_{pzc}, corresponds to that at which the curve crosses the straight line that fits the points $Initial_{pH}$=$Final_{pH}$. The clam shell studied has a pH_{pzc} equal to 7.8; therefore its surface has a basic character.

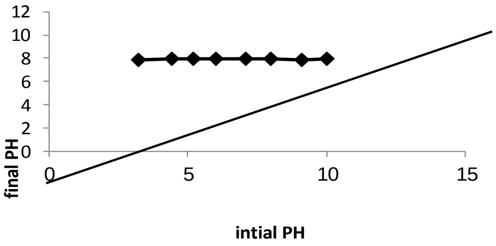


Fig (7) point of zero charge

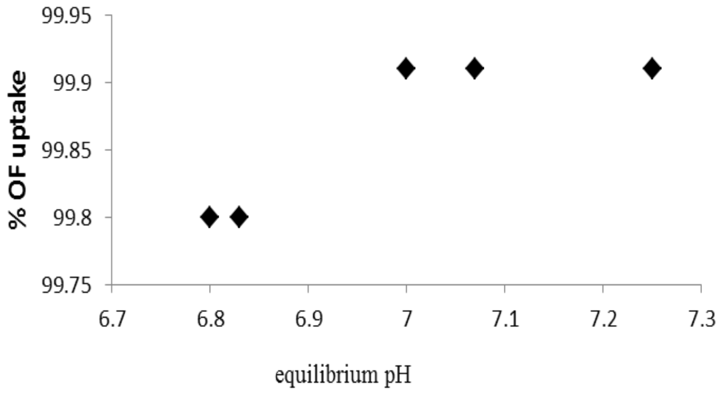


Fig (8) Effect of pH on the uptake of copper.

3.2 Effect of acidic stability of clam shell

In preliminary experiment the clam shell acid solubility was studied and the most stable pH was found to be around 5. However, the shell starts to dissolved at pH 3.3. Accordingly, all further experiments were carried out at pH 5, Table (2).

Table (2) The acidic stability of clam shell

Sample	Weight of Ca (dissolved)	% of Ca (dissolved)	Initial PH	Final pH
H_2O + shell	-	-	5.4	5.51
1ml HCl + shell	$2x10^{-3}$	1	3.27	7.01
3ml HCl + shell	$3.4x10^{-3}$	1.7	2.80	6.56
5ml HCl + shell	$4.66x10^{-3}$	2.33	2.55	3.77
7ml HCl + shell	$7.4x10^{-3}$	3.7	2.38	3.61
9ml HCl + shell	0.011	5.33	2.29	2.98

3.3 Effect of pH

The effect of pH was carried out at initial pH range from 3.3 and 5. As shown in Fig (8) the adsorption of copper was increase by increasing the initial pH up to 5. Higher pH was avoided due to the precipitation effect.

3.4 Effect of particle size

The particle size studied was in the range of 0.037-0.6305 mm. The removal of copper was found to be increase with decrease of particle size and range from 64.5-160 mmol/g. This can be attributed to the increase of surface area due to the decrease in particle size [15].

3.5 Total capacity

Total capacity of the clam shell under investigation was carried out by repeated equilibrium of 0.05 g solid with 500mg/L copper till no further uptake can be detected. The total capacity was found to be 20.31 mmol/g

$$\text{total } capacity = \frac{\%\text{ of uptake x ppm}}{\text{wt(g)}} \text{ x } \boldsymbol{M}.\boldsymbol{wt}$$

3.6 Effect of temperature

Fig (9) Shows the effect of the temperature on the adsorption of copper on the clam shell. It is obvious that as the temperature increase the adsorption increase up to the equilibrium state. This is due to the increasing of kinetic energy of Cu^{2+} and the nature of endothermic adsorption process of Cu^{2+} on clam shell.

3.7Kinetics of adsorption

Kinetics of adsorption process was studied using the pseudo-first order Lagergren equation [22, 23] and a pseudo- second order rate equation [24, 25] represented by Eqs (5, 6), respectively.

$$\boldsymbol{Ln}(Q_e - Q_t) = \ln Q_e - K_1 t \qquad (5)$$

$$\frac{t}{Qt} = \left({}^{1}\!/_{K_2 {Q_e}^2}\right) + \left(\frac{1}{Q_e}\right) t \qquad (6)$$

Where Qt is the amount (mg g^{-1}) of metal ion adsorbed at time t , Qe is the adsorption capacity (mg g^{-1}) at equilibrium , $K_1$and K_2 are the rate constants (min^{-1}) of pseudo-first order and pseudo-second order models, respectively. Fig (10,11) present the best fitted adsorbates using the pseudo-first and second order kinetics models, respectively. Table (3) lists the resulting parameters calculated using both models.

In the pseudo-first order, the rate constant K_1 increase as temperature increase and reached maximum 2.47 x 10^{-2} min^{-1} at 40 ^{0}C,however, the adsorption rate constant followed the order 20<30<40 ^{0}C .

The pseudo –second order model (R^2 0.930-0.989) did not quit fit the kinetics as well as those obtained using the pseudo- first order kinetics model where the high linearity of the plots of $\boldsymbol{Ln}(Q_e - Q_t)$ versus t (R^2 = 0.995-0.998) confirmed the pseudo-first order nature of the process.

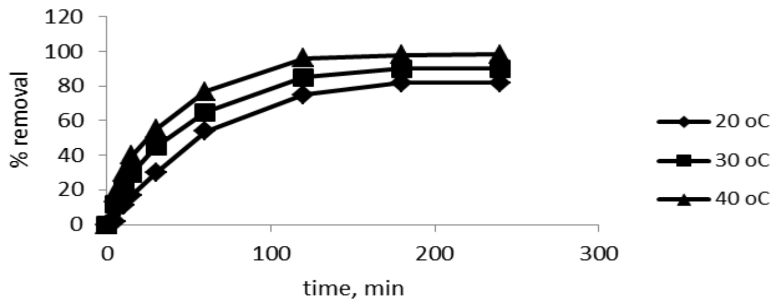


Fig 9. Effect of temperature on the adsorption of copper on clam shell at pH5 and 400 particle size.

Table (3) Kinetic parameters for the adsorption of Cu^{2+} onto clam shell

Temperature	pseudo-first -order		pseudo-second -order			
	$K_1(min^{-1})$	R^2	$Q_e(mg\ g^{-1})$	$K_2(g\ mg^{-1}\ min^{-1})$	$h\ (mgg^{-1}min^{-1})$	R^2
20	1.20×10^{-2}	0.998	10.13	2.09×10^{-3}	0.215	0.930
30	1.65×10^{-2}	0.998	10.50	2.983×10^{-3}	0.329	0.978
40	2.47×10^{-2}	0.995	10.83	4.44×10^{-3}	0.521	0.989

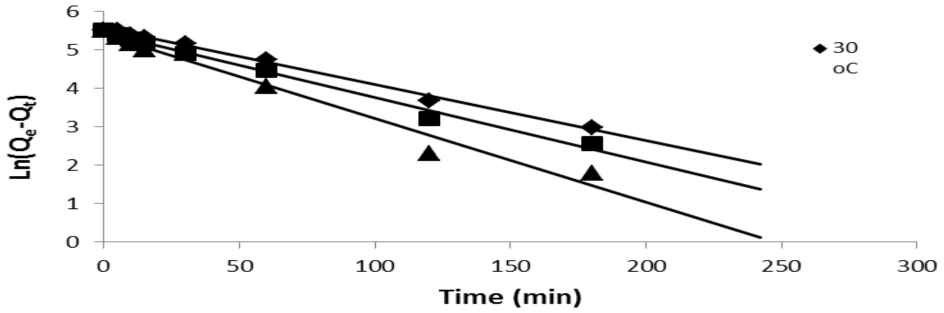


Fig (10) Plots of the pseudo-first-order lagergren equation for the adsorption of copper onto clam shell at various temperature

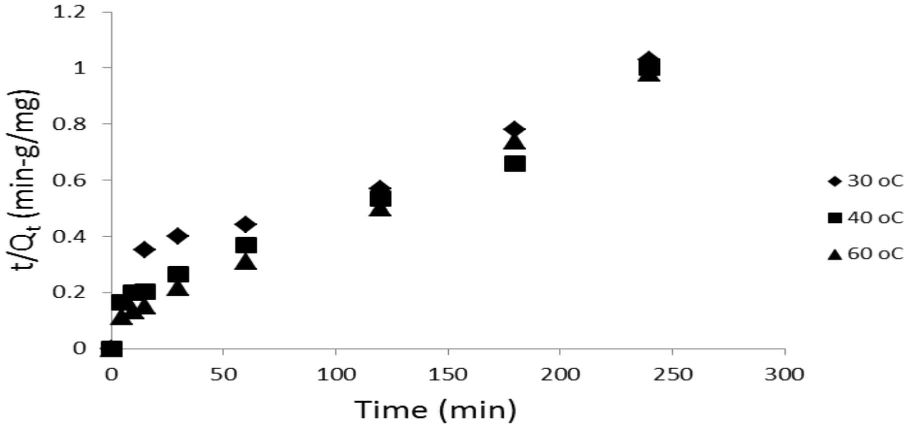


Fig (11) Plots of the pseudo second order kinetics of the adsorption of copper on clam shell at various temperature.

3.8 Adsorption isotherm

Langmuir and Freundlich models were used to analyze the adsorption of copper onto clam shells at different temperature.

3.8.1 Langmuir isotherm

The Langmuir isotherm is the most commonly monolayer adsorbed to solid surface. The linear form of the equation [13] can be represented as follows:

$$C/W = C/M + 1/am \qquad (7)$$

Where, C is the equilibrium concentration, W is the amount of sorbed per gram sorbent, M is the monolayer saturation capacity and a is a constant related to the heat of adsorption.

When C/W is plotted against C, a straight line has a slope of $1/M$ and an intercept at $1/am$ is obtained. The calculated Langmuir constants were given in Table (4) .The values of R^2 are in the range of 0.996- 0.994 revealing that the Langmuir isotherm fit the adsorption process. The calculated adsorption capacities of monolayer adsorption show higher value comparing to other adsorbents [26, 27].

3.8.2 Freundlich isotherm

The Freundlish isotherm is most frequently used to describe the adsorption of organic or inorganic species from aqueous solution. The Logarithmic form representing Freundlich isotherm [13] can be represented as follows:

$$\log W = K + 1/n \log C \qquad (8)$$

where W and C as mentioned above K, n are Freundlich constants related to adsorption capacity and adsorption intensity.

When log W is plotted against $\log C$, a straight line having a slope of $1/n$ and an intercept of $\log W$ is obtained. Table (4) lists the Freundlich constants for adsorption of Cu^{2+} on the clam shell. The values of R^2 all fall in the range of 0.998–

0.977, these adsorption events appear to follow the Freundlich isotherm quite well. However, the value of n was greater than 1, revealing that adsorption was a favorable process.

Table (4) Langmuir and Freundlich constants for adsorption of copper onto clam shell

temperature	Langmuir			Freundlich		
	q(mg/g)	b	R^2	n	K_f	R^2
20	6.37	0.26	0.996	2.4	1.73	0.981
30	5.92	4.34	0.994	1.11	3.78	0.998
40	13.58	11.97	0.996	2.6	27.24	0.977

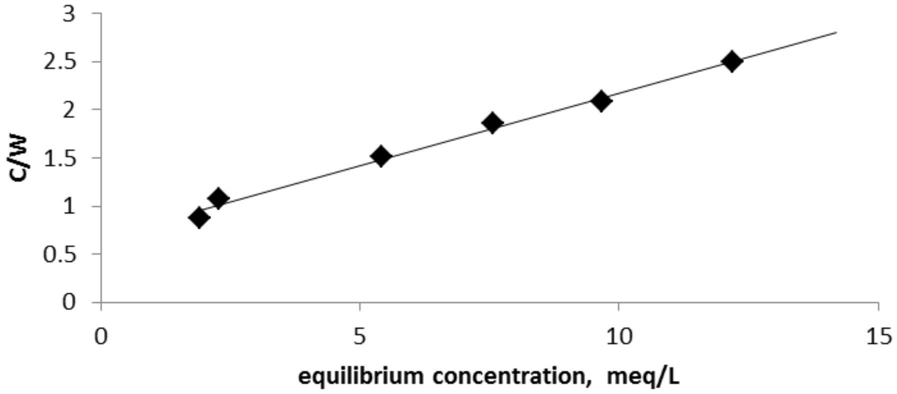


Fig (12) Langmuir adsorption isotherm for copper to clam shell at 20 °C.

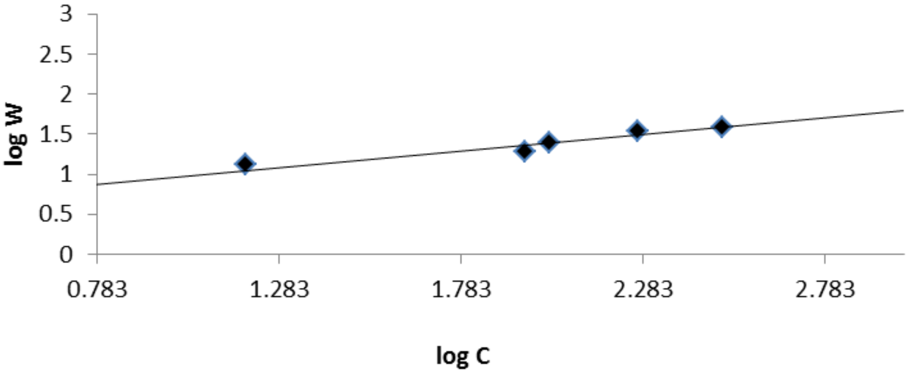


Fig (13) Freundlich adsorption isotherm for copper to clam shell at 20 °C.

3. Conclusion

It is clear that the clam shell is effectual and viable as sorbents for copper removal from aqueous solution. The different operational parameters observed during the process of investigations reveal that the pH, temperature, and contact time of the clam shell govern the overall process of adsorption. The batch studies clearly suggest that clam shell exhibit high adsorption at low particle size. The results obtained are well fitted in the linear forms of Freundlich and Langmuir adsorption isotherms. The calculated values of different parameters clearly indicate that the ongoing adsorption process is feasible, spontaneous and endothermic in nature. The kinetic evaluation suggests that the process is following the pseudo-first order.

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