Removal of Copper Ions onto Walnut Shells by Using Batch and Continuous Fluidized Bed

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ABSTRACT

An agricultural waste (walnut shell) was undertaken to remove Cu(II) from aqueous solutions in batch and continuous fluidized bed processes. Walnut shell was found to be effective in batch reaching 75.55% at 20℃ and 200 rpm, when pH of the solution adjusted to 7. The equilibrium was achieved after 6 h of contacting time. The maximum uptake was 11.94mg/g. The isotherm models indicated that the highest determination coefficient belongs to Langmuir model. Cu (II) uptake process in kinetic rate model followed the pseudo-second-order with determination coefficient of 0.9972. More than 95% of the Cu(II) were adsorbed on the walnut shells within 6 h at optimum agitation speed of 800 rpm. The main functional groups responsible for biosorption of Cu(II) onto walnut shell were hydroxyl, carbonyl, carboxylate, carboxylic acids, alcohols groups, and aromatic compounds. In continuous system, fluidized bed column at 20℃, and pH 7 was carried out to study the effects of various parameters like (flow rate, bed depth, and initial concentration). The time of breakthrough was 97 min when the initial concentration (C_o= 20mg/l), bed depth (L=10cm), and flowrate (Q=10l/h).

KEYWORDS: **Biosorption, Cu(II), Walnut Shell, , Fluidized Beds, Kinetics models, rate constant, functional groups.**

ازالة ايونات النحاس بواسطة قشور الجوز باستخدام مفاعلات الدفع المتقطع والمستمر

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الخلاصة

تعتبر العناصر الثقيلة في الماء واحدة من اهم المشاكل البيئية. حيث انها تعتبر ملوثات غير قابلة للتحلل بايولوجيا ولها تأثيرات خطيرة على الصحة والبيئة .ان عملية ازالة هذه الملوثات من الممكن انجازها بنجاح باستخدام مواد رخيصة. في هذا البحث تمت اختيار دراسة ازالة ايونات النحاس والذي هو احد العناصر الثقيلة التي تنتج من مختلف الصناعات بعملية الامتزاز وذلك باستخدام فضلات زراعية وهي قشور الجوز بطريقتي الدفع المتقطع والمستمر. .ان كلفة عملية الازالة منخفضة بسبب رخص المادة المستخدمة (قشور الجوز) وتوفرها بكميات كبيرة. تمت دراسة تأثير سرعة الخلط ، كمية المادة المازه، زمن الخلط بالإضافة الى تأثير الدالة الحامضية pH للمادة الممتزه بثبوت درجة الحرارة (20℃) وحجم الدقائق المازه (1mm) في ازالة ايونات النحاس لتحديد ظروف التشغيل الامثل. في نظام الدفع المتقطع، تم ايجاد ان افضل كفاءة قشور الجوز لإزالة الايونات النحاس تصل الى 75.55% في درجة حرارة 20℃ وبسرعة

خلط 200 rpm وقيمة الدالة الحامضية pH مساويه الى 7 وزمن الخلط مساوي الى 6 ساعات وكانت اعلى سعة الامتزاز مساويه الى 11.94 mg/g. تم اجراء تجارب (Equilibrium Isotherm) وتم تحليل النتائج باستخدام اربعة موديلات رياضيه ووجد ان موديل Langmuirهو افضل موديل رياضي يمثل نتائج العملية. تم اجراء تجارب(Kinetic) واستخدمت النتائج لتحليل تأثير الطبقة المحيطة بدقائق المادة المازه . وكان هناك تطابق جيد بين النتائج العملية والنظرية المستحصله من موديل الامتزاز في تجارب ال Kinetic عند استخدام موديل التفاعل الحركي من الدرجة الثانية Pseudo Second Order Kinetic حيث ان اكثر من 95% من ايونات النحاس تم امتزازها خلال 6 ساعات و باستخدام سرعة مثلى مقدارها 800rpm. تم استخدام نظامين في تجارب الدفع والمستمر لتحري ازالة ايونات النحاس باستخدام قشور الجوز في عمودي الامتزاز الثابت والمتميع بدرجة حرارة 20 °C و pH 7. وتمت دراسة تأثيرات كل من معدل الجريان ،تركيز الملوث الابتدائي وارتفاع الحشوة لكلا النظامين. ان منحنيات الاختراق (Breakthrough Curves) تدل على ان زيادة تركيز الملوث الابتدائي ومعدل الجريان يؤدي الى سرعة حصول الامتزاز والوصول الى نقطة الاختراقBreak Point ، بينما يستغرق الوصول الى نقطة الاختراق زمن اطول في حالة زيادة ارتفاع الحشوة. وتم التوصل الى ان عمود الامتزاز المتميع هو افضل من اداء عامود الامتزاز الثابت حتى في زيادة التركيز الابتدائي ومعدل الجريان وهذا يعزى الى وجود (Dead Zone) بين الدقائق المازه في العمود المستمر.

الكلمات الرئيسية : الامتزاز، ايونات النحاس، قشور الجوز، عمود الامتزاز، موديل الحركي، ثابت معدل السرعة، مجاميع فعالة

1. INTRODUCTION

A tremendous increase in the use of heavy metals over the past few decades has inevitably resulted in an increased flux of metallic substances in the environment. Heavy metals get distinguished from other toxic pollutants due to their non-biodegradability. Consequently, increased concentration of heavy metals in the environment can cause phyto-toxicity, bio-concentration and biomagnification by organisms (Ayyappan et al., 2005).

Copper ions have been identified as a pollutant of concern by the U.S. Environmental Protection Agency (EPA) because of its widespread occurrence and toxic impact in the environment (chouyyok et al., 2010). High concentration of copper (above 3.0 mg/l) in water may lead to accumulate in liver and lenticular nucleus of brain. Excess copper ions in human body have a serious health threats such as cellular or organ damage and Wilson’s disease. Similarly, copper is extremely toxic to aquatic biota. and can accumulate in the environment and food chain, especially in fish (finefrock et al., 2003; Hindo et al., 2009; Quinn et al., 2009).

The world health organization (WHO) recommended a maximum acceptable concentration of Cu (II) in drinking water of 1.5 mg/l. Therefore, it is essential that potable waters should be given some treatment to remove copper before domestic supply (Sarkar, 1984; Rao, 1992).

Biosorption is one of the easiest, safest and most cost-effective methods because it is widely used in effluent treatment processes .In recent years, the biosorption process has been studied extensively using biomass as biosorbent for heavy metals removal. Unlike physical and chemical treatments, biosorption does not entail high operational costs and many potential sources of suitable biological materials are cheaply and readily available. Compared with the other processes, biosorption of metal ions onto insoluble is compounds as biosorbent is the most effective and widely used method (Costly and Wallis, 2001; Zhou et al., 2004).

Choice of an adsorbent is the starting point in the development of an adsorption unit. Several adsorbents can be used to treat industrial wastewater. The most widely used adsorbent for industrial applications is activated carbon. The application of activated carbon for wastewater treatment is not feasible due to its high price and cost associated with the regeneration as a result of high degree of losses in real process. Therefore, it will be much logical and cost effective to use the abundant agricultural and industrial wastes as adsorbents since they are already posing disposal problems. More studies have been carried out on the feasibility of using agricultural adsorbents such as sawdust (Ismadji et al., 2005), rice husk (Kumar and Bandyopadhyay, 2006), and walnut shell (Altun and pehlivan, 2007).

The aim of the present research is to investigate the Cu(II) biosorption in batch and continuous fluidized bed process using walnut shell as a biosorbent, as well as the effect of different influent Cu(II) concentrations, flow rates, and bed depths on the performance of fluidized bed.

2. BATCH MODELS

2.1 Biosorption Isotherms Model

The analysis of the isotherm data by fitting them to different isotherm models is an important step to find a suitable model that can be used for design purpose. The biosorption capacity of this system was investigated with Langmuir, Freundlich, Toth, and Khan biosorption isotherm models.

2.2 Kinetic Models

There are various kinetic models have been used for evaluating the rate constant for biosorption of Cu(II) onto walnut shell. The pseudo-first order was widely used for the adsorption of liquid/solid system. The linear form generally expressed as the following (Lagergren, 1989):

$$\ln(q_e - q_t) = \ln q_e - k_l t \qquad (1)$$

Where q_e(mg/g) and q_t(mg/g) are the adsorption amount at equilibrium and at time t (min), respectively. k_l (min^{-1}) is the rate constant. While the pseudo-second order mode based on the assumption that the adsorption occurs only on localized sites and involves no interactions between adsorbed pollutants. The liner form can be written as follows (Sulaymon et al., 2010):

$$\frac{1}{q_t} = \frac{1}{k_2\, q_e^2}\frac{1}{t} + \frac{1}{q_e} \qquad (2)$$

Where k_2 (g/mg. min) is the rate constant of adsorption. In the intra-particle diffusion model the kinetic data were analyzed by an intra-particle diffusion model to elucidate the diffusion mechanism (Weber and Morris, 1963):

$$q_t = k_{id}\, t^{1/2} + C \qquad (3)$$

Where k_{id} (mg/g. min) is the intra-particle diffusion rate constant and C (mg/g) a constant that gives idea about the thickness of the boundary layer. According to this model, if the plot of q_t versus $t^{1/2}$ gives a straight line, then the adsorption process is controlled by inter-particle diffusion, while, if the data exhibit multi-linear plots, then two or more steps influence the adsorption process.

Finally the Elovich kinetic model is widely used to describe the kinetics of chemical adsorptions, which can be described as follows (Cheung and Mckay, 2003):

$$q_t = \frac{1}{b}\ln a\bar{b} + \frac{1}{b}\ln t \qquad (4)$$

Where a (mg/g.sec) and $\bar{b}$ (g/mg) are parameters of the equation. The parameter a is regarded as the initial rate and parameter $\bar{b}$ is related to the extent of surface coverage and activation energy for chemical adsorptions.

3 MATERIAL AND METHODS

3.1 Materials

Adsorbate

A stock solution of copper ions with desired concentration was prepared by using $Cu(NO_3)_2$ $3H_2O$ (Hannover- Q/YLB-2005-07, Germany). Copper nitrate salt was dissolved in distilled water.

Adsorbent

Walnut shells were collected from local markets and local natural resources in the north of Iraq (sulaimania). They were washed with distilled water to remove fine particles and then dried in an oven (Type BBDE; S/N 20-601148, Korea) at 105°C for 24 hours, after which, the dried walnut shells were cracked and grinded with agate mortar (Type BB1A, Masch.Nr.4323, Germany). The product was passed through sieve US mesh No. 18 to obtain particle size (1mm) and then the walnut shell is kept for use. The physical properties of walnut shell was measured at Oil Research and Development Center, Ministry of Petroleum, Baghdad, Iraq and are listed in Table 1.

Table (1): Physical properties of walnut shell

Properties	Walnut Shell
Color	Light brown
Appearance	Granular or Powder
Odors	Odorless
Solubility	Insoluble in Water
Specific Surface Area(m^2/g)	1.042
Porosity	0.43
Apparent Density (g/cm^3)	0.7416
Actual Density(g/cm^3)	1.2669
Pore Size (Å)	13.0683
Max. Moisture Content (%)	11
Specific Gravity	1.2-1.35
Durability	Excellent
Elasticity	Excellent
Hardness(Mohs)	3

3.2 Methods

About 100 ml of Copper ions solution were placed into ten 250 ml volumetric flasks with 40mg/l concentration of Cu (II) solution, and pH 7. The amount of biosorbents were added starting from 0.05-1.0g into the volumetric flasks. The flasks were then placed in a thermostatic shaker (Type SI-600R, Korea) and agitated continuously with 200 rpm for 6 h (optimum contact time) at 20℃. The two phases under investigation were separated using whatman filters No. 42 and the supernatant was collected for copper ions analysis using Atomic Absorption Spectrophotometer (Type GBc sensAA; PN/ 01-0960-00, India).The adsorbed amount was then calculated using the following equation (Yang et al, 2006):

$$q_e = \frac{V_L(C_o - C_e)}{W_o} \qquad (5)$$

The biosorption efficiency (η) was calculated by the difference of the initial and equilibrium concentration of Cu(II) according to the following equation:

$$\eta = \frac{(C_o - C_e)}{C_o} \times 100 \qquad (6)$$

The external mass transfer coefficient was estimated using the following steps (Alexandar and Zayas, 1989):

- Estimating the optimum agitating speed for batch adsorber to reach 95% removal.
- Estimating the mass transfer coefficient (k_2) in batch process at optimum agitation speed using pseudo-second order model.

The mass transfer coefficient was obtained by using 2 l Pyrex beaker fitted with a variable speed mixer. The beaker was filled with 1 l of a known concentration solution and agitation started before adding the walnut shell. At time zero, the accurate mass of walnut shell was added. Samples were collected and filtered through a whatman filter No.42. The filtrates are analyzed using Spectrophotometer. The necessary mass of walnut shell to reach equilibrium related concentration of C/C_o equal 0.05, was calculated by using the following equation:

$$W_o = \frac{V_L\left(C_o - C_e\right)(1 + b\,C_e)}{(q_m b\,C_e)} \qquad (7)$$

The fluidized experiments was carried out in a glass column of 50mm inside diameter and 1000 mm height. A schematic diagram of the experimental apparatus is shown in figure (1). The walnut shell was placed in a biosorption column for the desired bed depth. The Cu(II) solution with the desired concentration was prepared in the feed container, using distilled water. The prepared solution was adjusted to pH 7. The solution was circulated via the centrifugal pump to achieve homogeneous solution. The Cu(II) solution was pumped to the biosorption column through the a flowmeter at the desired flow rate. Samples were collected from the exit at appropriate time intervals. The concentration of Cu(II) in these samples were analysed using spectrophotometer. The breakthrough curves were obtained by plotting related effluent concentration (C_e/C_o) against time.

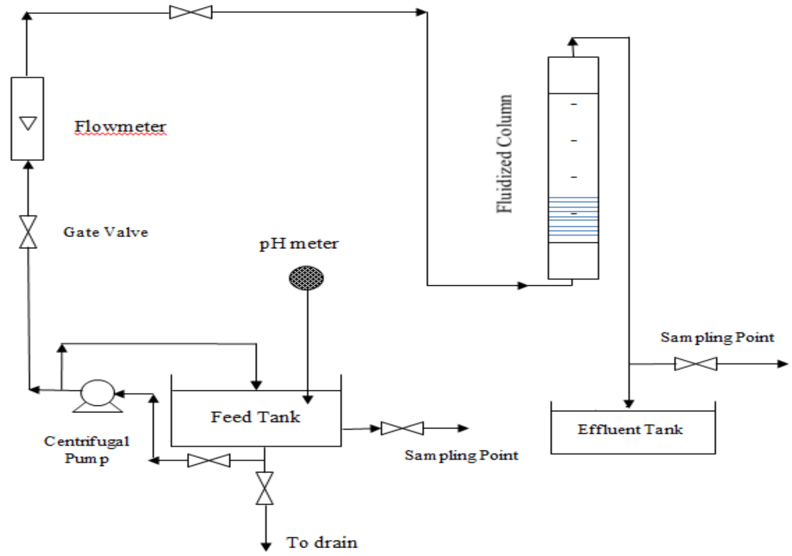


Figure (1): Schematic representation of experimental equipment

3.3. Fourier-Transform Infrared Analysis (FT-IR)

The FT-IR spectra of walnut shell before and after copper ions biosorption was examined to identify the functional groups which are responsible for metal uptake and frequency changes of the functional groups in the biosorbent. In order to have a sample of walnut shell after the copper ions biosorption on its surface, the following experiment was carried out:

One gram of dry (walnut shell) was contacted with 100 ml of 40 mg/l of Cu(II) concentration in a volumetric flask. The Cu(II) solution was adjusted to pH value of 7. The sample was left on a shaker for 6 h at agitation speed of 200 rpm and then, the sample was filtered through Whatman No. 42 filter Paper. The supernatant was discarded and the biosorbent of walnut shell on filter paper was left to dry. Dried sample was collected and analyzed by FTIR spectrophotometer (Type IRPRESTIGE-2; Shimadzu 8000, Japan).

4 RESULTS AND DISCUSSION

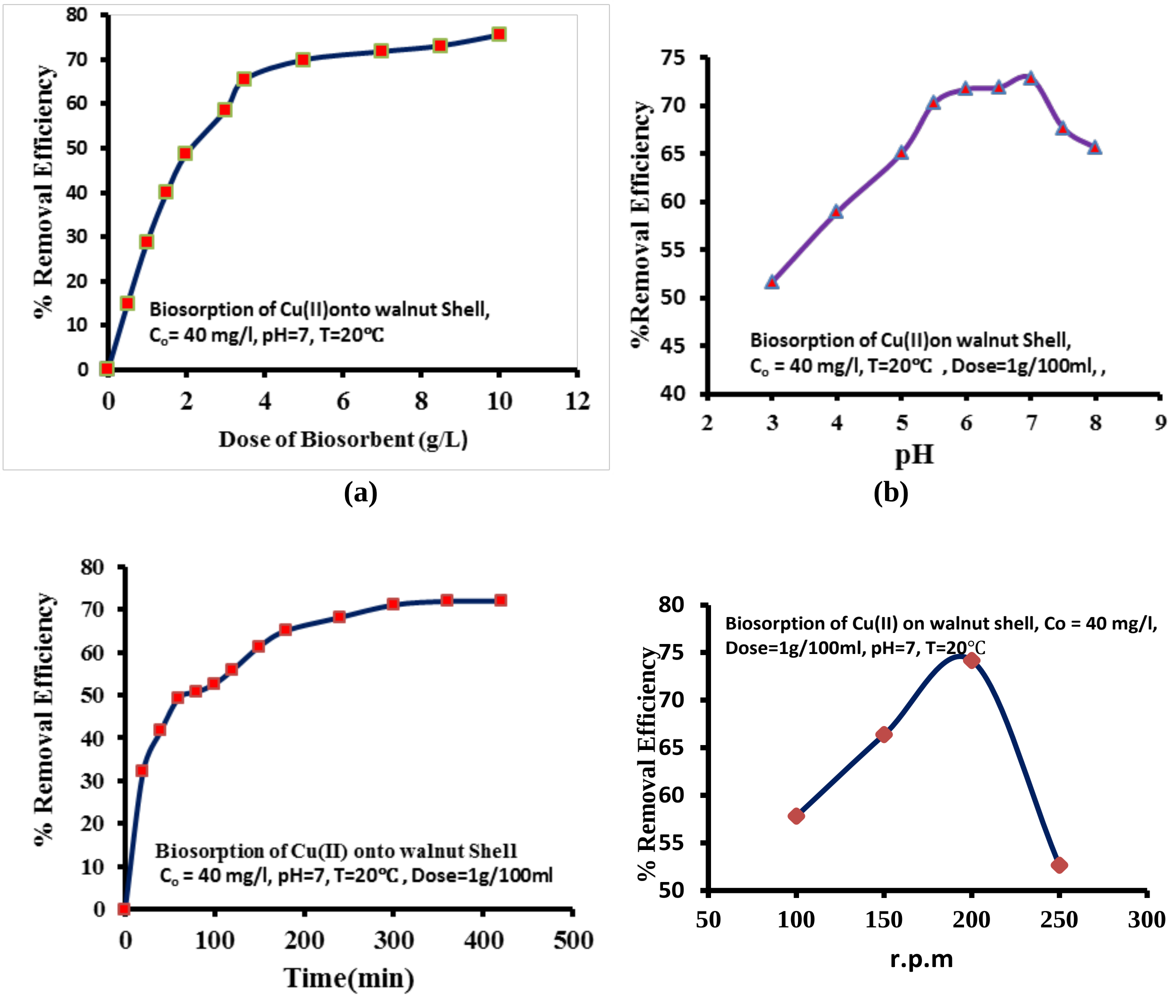
4.1 Optimum Operating Conditions

The biosorbent mass strongly influences the biosorption processes. Lower biosorbent mass yield higher uptakes and lower percentage removal efficiencies. This effect was explained in figure (2a). It was observed that the biosorption of Cu(II) increases rapidly with increasing mass of walnut shell from 0.05 to 1.0 g/100ml with removal efficiency from 14.93 to 75.55 %. This increase may be attributed to the fact that, with an increase in the adsorbent mass, more adsorbent surface available for the solute to be adsorbed. While a significant decrease in uptake was observed when the mass of walnut shell increased and the maximum uptake obtained was 11.94 mg of Cu(II) /g of walnut shell. The result agrees with that obtained by Murthy et al. (2011).

The value of pH used, ranged from 3 to 8. As shown in figure (2b) which represents the relation between the percentage of the removal efficiency of Cu(II) and different pH of the solution, the removal was appreciable when the pH medium of the solution approaches neutral. The Cu(II) removal was maximum at pH 7 and then there was a decreasing trend. This is due to the fact that at higher H^+ concentration, the biosorbent surface becomes more positively charged such that the attraction between biosorbent and Cu(II) is reduced. For this reason pH 7, in which maximum removal was observed, selected for subsequent experimental work. The result agrees with that obtained by Altun and Pehlivan, (2007) and Murthy et al., (2011).

The effect of contacting time is illustrated in figure (2c). This figure indicates that the copper ions in aqueous solution decreases rapidly at the beginning. This is probably due to a larger surface area of the walnut shell being available at the beginning. In addition to that, as the surface sites become exhausted, the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles. The increasing of contact time leads to increase biosorption of Cu(II) and it remains constant after reaching equilibrium. The maximum percentage of removal was attained after 6 h of contacting time. Therefore, 6 h was considered as the equilibrium time for subsequent experiments. This result agreed with that obtained by Sumanjit et al., (2008).

The effect of agitation speed is illustrated in figure (2d). It is showed that the percentage of removal efficiency of Cu(II) increased to extend as the agitation speed increased. This is due to the fact that, a higher agitation speed decreases the film thickness and eventually eliminates film resistance. Furthermore, agitation speed influences the degree of physicochemical interaction between walnut shell and Cu(II) in the solution. Therefore, 200 rpm was taken as the optimum agitation speed where maximum removal efficiency can be obtained. This results are analogous to that found by pehlivan and Altun, (2008).



(a) (b)

(c) (d)

Figure (2) a. Effect of different adsorbent mass on removal efficiency, b. Effect of different pH values c. Effect of different contact time, and d. Effect of different rpm

4.2 Adsorption Isotherm

The equilibrium isotherm for Cu (II) onto walnut shell is presented in figure (3). The adsorption data for the system was fitted by Langmuir, Freundlich, Toth, and Khan Isotherm Models (Lucas and Cocero, 2004).

The determination coefficients are shown in Table (2). It indicates that the highest determination coefficient belongs to Langmuir model depending on the experimental data.

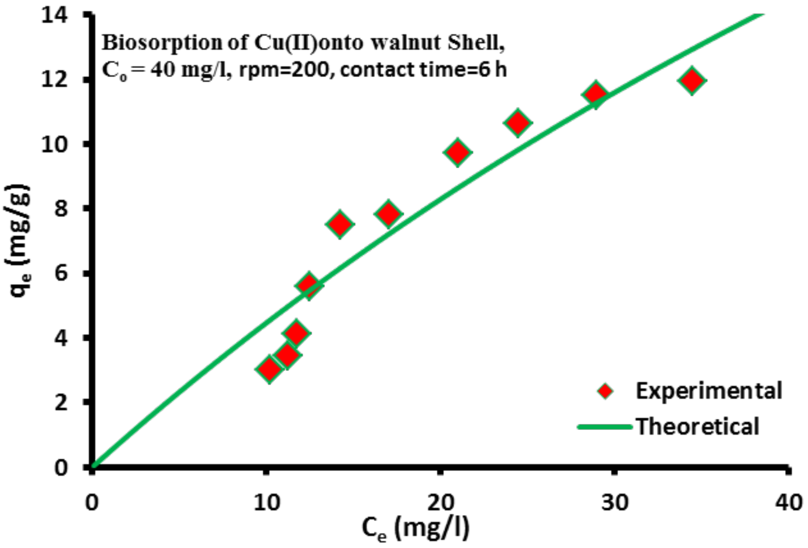


Figure (3): Biosorption isotherm for copper ions onto walnut shell at 20℃, and pH 7

Table (2): Parameters of isotherm for Cu(II) biosorption and determination coefficient for various models

Model	Parameters	Value
Freundlich Model Equation (2.3)	K (l/g)	0.561792
	n	1.119817
	R^2	0.922705
Langmuir Model Equations (2.1)	q_m (mg/g)	57.47867
	b (l/mg)	0.008426
	R^2	0.929066
	R_L	0.748
Toth Model Equation(2.7)	K_t(mg/g)	6.915541
	a_t	72.685
	t	1.607489
	R^2	0.92851
Khan Model Equation(2.9)	Q_m(mg/g)	21.92245
	b_k(l/mg)	0.021976
	a_k	0.434741
	R^2	0.92777

4.3 Mass transfer coefficient

The mass of walnut shell used for biosorption of Cu(II) was calculated for final equilibrium related concentration of C_e/C_o= 0.05. The initial concentration was 40mg/l with walnut shell mass of 39.89 g.

The typical concentration decay curves of Cu(II) in kinetic experiments were carried out at different agitation speeds as shown in figure (4 a).

The optimum agitation speed needed to achieve C_e/C_o= 0.05 was found to be 800 rpm. The adsorption data at optimum agitation speed was analyzed in terms of pseudo-first, second-order, intra-particle diffusion and Elovich models.

Figure (4 b) shows a good compliance with the pseudo second-order model with a high determination coefficient 0.9972. The results are summarized in Table (3).

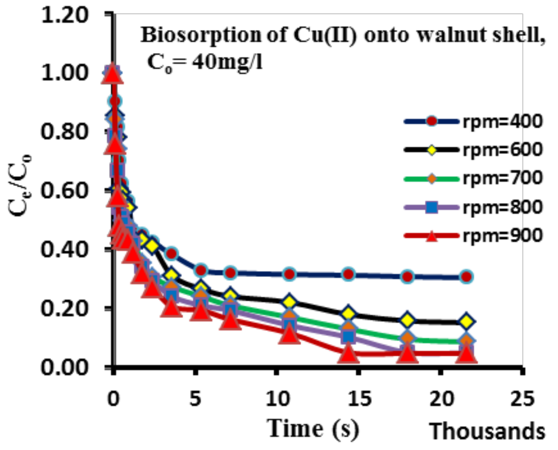


Figure (4a): Concentration-time decay curves for Cu(II) biosorption onto walnut shells at different agitation speed at 20℃, and pH 7

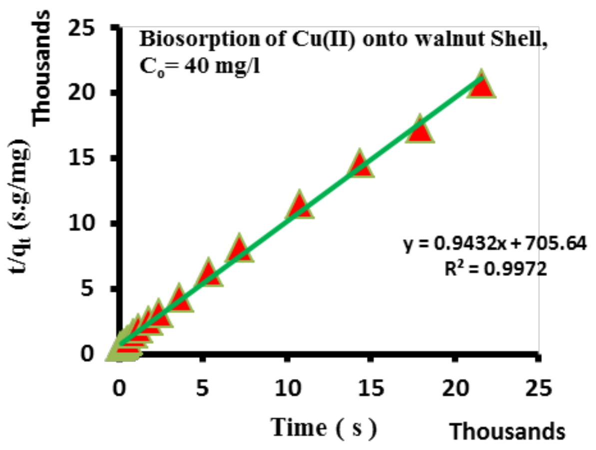


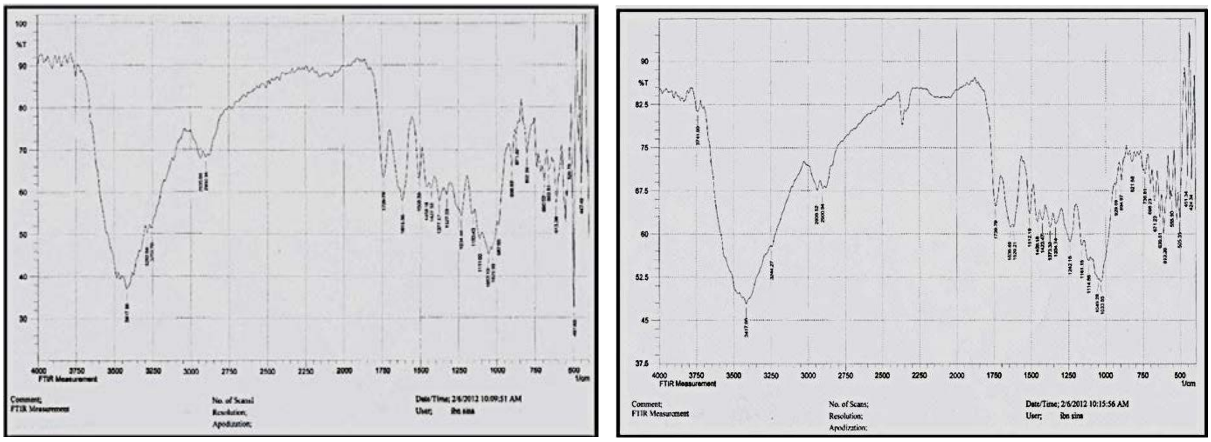
Figure (4b): Pseudo second order for biosorption of Cu(II) onto walnut shell 20℃, and pH 7

Table (3): The kinetic constants for the biosorption of Cu(II) onto walnut shell.

Model	Parameters	Value
Pseudo-First Order Model	q_e(mg/g)	0.616
	k_1(l/s)	2.303×10^{-4}
	R^2	0.9395
Pseudo-Second Order Model	q_e(mg/g)	1.06
	k_2 (g/mg.s)	1.261×10^{-3}
	R^2	0.9972
Intra-particle Diffusion Model	k_{id} (mg/g. $s^{0.5}$)	0.005
	C	0.4188
	R^2	0.8458
Elovich Model	a (mg/g.s)	9.36×10^{-3}
	$\bar{b}$ (g/mg)	6.752
	R^2	0.9845

4.4 FT-IR analysis of adsorbents

The FT-IR spectra of walnut shell before and after biosorption of Cu(II) was examined to determine the vibration frequency changes in the functional groups of the adsorbent walnut shell as show in figure (5). The spectra was measured within the range of 500–4000cm^{-1}. The results showed that Cu(II) was adsorbed or complexed by hydroxyl, carboxylic acids, alcohol, carboxylate and carbonyl groups (Garg et al., 2008). The results also indicated that hydroxyl functional group plays an important role in the biosorption process as the total displacement of this functional group was 15.43cm^{-1}.



(a) (b)

Figure (5) FTIR spectra for walnut shell biomass before and after loaded with 40 mg/l of Cu(II)

4.5 Breakthrough Curves for Fluidized

4.5.1 Minimum Fluidized Velocity

Minimum fluidized velocity in continuous experiments was determined by using the following equation (Ramaswamy et al., 2008):

$$U_m = \frac{\mu_l}{\rho_p \; d_p} \left[\sqrt{(33.7)^2 + 0.0408 \, \frac{d_p^3 \, \rho_l \left(\rho_p - \rho_l\right) g}{\mu_l^2}} - 33.7 \right] \qquad (8)$$

$U_m = 1.223 \times 10^{-3}$ m/s = 4.4028 m/h

($ID_{col.}$ = 0.05m, minimum flow rate = 8.64 l/h).

4.5.2 Effect of Flow rate

Effect of different flowrate (10, 15, 20 l/h) of Cu (II) solution at constant initial concentration (20mg/l), pH 7, and constant bed depth of walnut shells (10 cm) was investigated. Figure (6a) presents the breakthrough curves for fluidized beds in term of C_e/C_o versus time.

It is observed that the breakthrough curves generally occurred rapidly with high flowrate because the Cu(II) had less time to contact with the walnut shells that resulted in lower removal of Cu(II). The greater the hydraulic loading is, the smaller the biosorption is. The value of (C_e/C_o) increased quickly for higher flowrate.

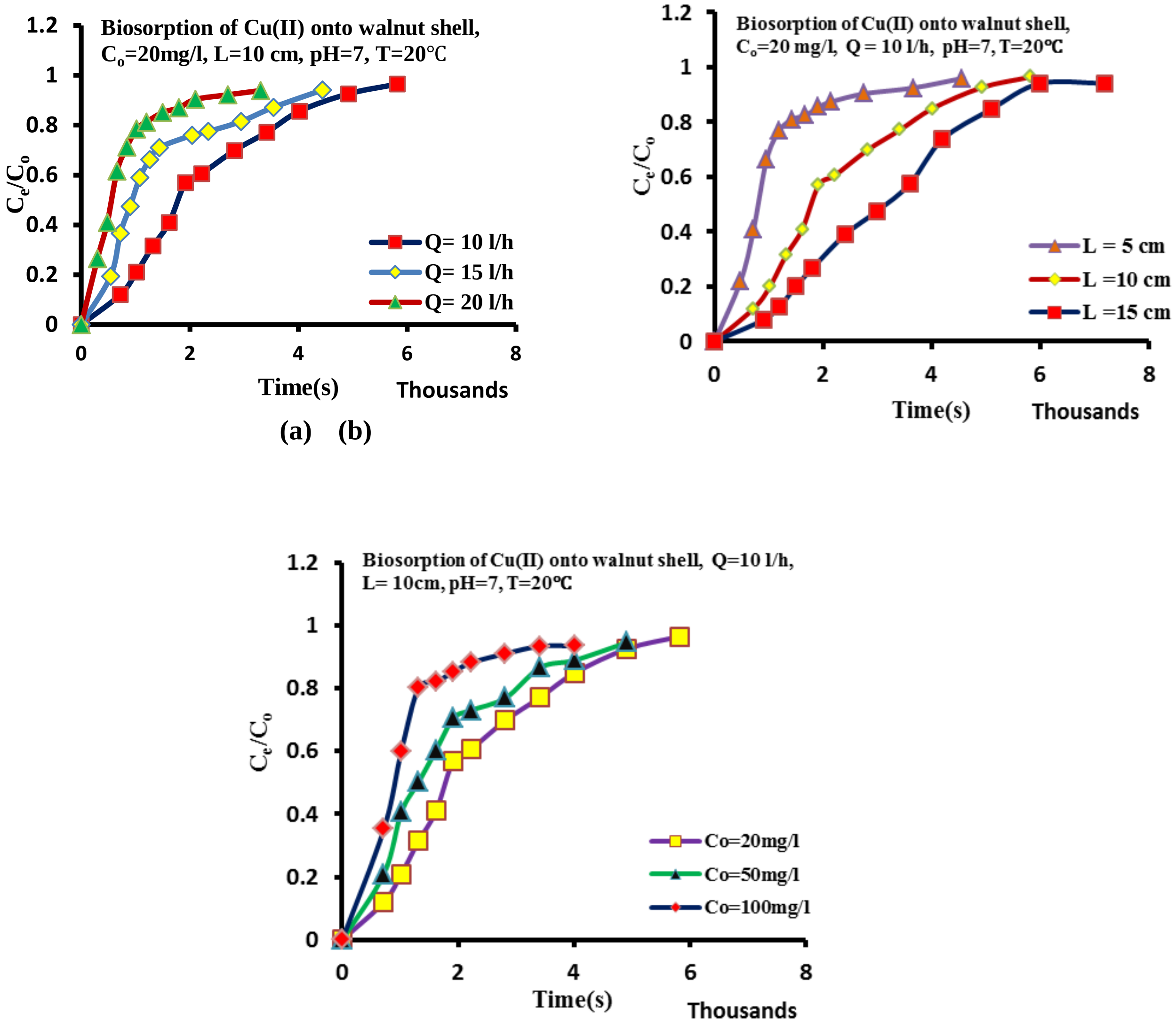
4.5.3 Effect of Bed Depth

Effect of different bed depths (5, 10, and 15cm) at constant flowrate (10 l/h) and initial concentration (20mg/l) was investigated as shown in figure (6b). It is observed that the slope of breakthrough curves in fluidized bed is decreased as the bed depth of particles increases. For a higher level of bed, a larger volume of the Cu(II) solution could be treated and a higher percentage of C(II) removal was obtained. The increases in bed depth results a greater biosorption capacity of the column. This shows that at low bed depth the effluent adsorbate concentration ratio increases more rapidly than for a higher bed depth. Furthermore, in low bed depth, the bed is saturated in less time.

4.5.4 Effect of Initial Concentration

The effect of different initial concentrations of the Cu(II) (20, 50 and 100 mg/l) was investigated at constant flow rate 10 l/h and bed depth10cm. The experimental breakthrough curves are presented in figure (6c).

It is observed that biosorption capacity increased as the influent Cu(II) concentration increased and it would spend less time reaching saturation. The rate of biosorption increases with increasing the initial concentration. This is due to the diffusion rate which is controlled by the concentration gradient. The breakpoint was inversely related to the initial concentration, i.e., the time required to reach saturation decreases with increasing the inlet concentration of copper ions. A high copper ions concentration may saturate the walnut shell more quickly, thereby decreasing the breakthrough time. Therefore, the larger the inlet concentration, the steeper is the slope of breakthrough curve. These results agree with that found by Dahman (1996).



(a) (b)

(c)

Figure (6) The experimental breakthrough curves in fluidized bed for biosorption of Cu(II) onto walnut shell at different , (a) Flow rates (b) Bed depths (c) Initial concentrations.

CONCLUSION

The biosorption of Cu(II) increases rapidly with increasing adsorbent mass from 0.05 to 1.0 g/100ml with removal efficiency range from 14.93 to 75.55 %, while maximum uptake 11.94mg/g was achieved. The percentage removal of Cu(II) decreased with the decrease in pH and the optimum pH value was 7 in which maximum removal efficiency was observed. The Cu(II) concentration in aqueous solution decreases rapidly at the beginning. This is probably due to presence a number of fresh adsorption sites on the walnut shell surface at the beginning. In addition to that higher driving forces exist in the beginning of the process between the Cu(II) and the walnut shell biosorbent surface. The increasing in contact time increased the Cu(II) biosorption and it remained constant after reaching equilibrium. The maximum percentage of Cu(II) removal was attained after 6 h of contacting time.

Hydroxyl (-OH), Carboxylic (C-O), aromatic compound, carboxylate (COO) and carbonyl (C=O) functional groups on the surface of walnut shell play the major role in the biosorption of Cu(II) ions by complex mechanism. The type of equilibrium isotherm for biosorption of Cu(II) onto walnut shells was favorable since separation factor $0 < R_L < 1$ ($R_L = 0.748$), being convex upward. Langmuir isotherm was the best fit model to describe the biosorption of Cu(II) onto walnut shell with high determination coefficient 0.929066. The optimum agitation speed needed to achieve $C/C_o = 0.05$ was 800 rpm.

The mass transfer coefficient (k_2) of the biosorption of Cu(II) onto walnut shell was 1.261×10^{-3} g/mg.s and Pseudo-second order kinetic model was the best model to explain the biosorption of Cu(II), it gave the higher determination coefficients as compared with other models. The breakthrough curves were related to the variation of flow rates, initial concentrations and bed depths.

The breakthrough time in fluidized beds increases as the bed depth increases. However, it decreases as the flowrate or initial concentration increases. The head loss through fluidized column increased when the velocity of flow increased. Furthermore the higher bed depth also affects head loss to be increased.

NOMENCLATURE

a	Parameter of the Elovich equation (mg/g.s)
a_t	Toth isothermal model constant
a_k	Khan model parameter.
b	Langmuir constant , l/mg
b_k	Khan model parameter related to affinity between adsorbate and adsorbent(l/mg).
$\bar{b}$	Parameter of the Elovich equation (g/mg)
C_o	Initial concentration, mg/l
C_e	Equilibrium concentration, mg/l
d_p	Particle diameter (m).
g	Gravitational acceleration (= 9.81 m/s^2)
k_{id}	Rate constant of intra-particle diffusion (mg/g s$^{1/2}$).
K_l	Equilibrium rate constant of pseudo-first sorption (l/s).
K_t	Toth isothermal model constant
k_2	Rate constant of second-order adsorption (g/mg.s)
L	Bed depth, cm
C	Value of intercept which gives an idea about the boundary layer Thickness.
W_o	Mass of adsorbent (g).
n	Freundlich constant.
q_e	Amount of adsorbate adsorbed per unit mass of adsorbent (mg/g).
q_m	Adsorption equilibrium constant defined by Langmuir equation (mg/g)
q_t	Amount of pollutant adsorbed at time t (mg/g)
R^2	Determination coefficient.
R_L	Separation factor.
Q	Flowrate, l/h
Q_m	Khan Model constant related to maximum biosorption capacity, mg/g
t	Time (s).
t	Toth isotherm model constant.
U_m	Minimum fluidized velocity (m/s).
V	Volume of solution (l).

GREEK SYMBOL

μ_l	liquid viscosity (for water =1×10^{-3}Pa.s)
ρ_l	Density of liquid (kg/m^3)
ρ_p	Density of solid (kg/m^3)

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