EUROPEAN ACADEMIC RESEARCH
Vol. II, Issue 10/ January 2015

Impact Factor: 3.1 (UIF)
DRJI Value: 5.9 (B+)

ISSN 2286-4822
www.euacademic.org

MATLAB Modeling for Adsorption Removal of Toxic Ions from Aquatic Media

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Abstract:

This search is concerned with study the potential of Iraqi Rice Husk (IRH) (which considered as a type of agricultural waste that difficult to discard it in a conventional methods in Iraq) using different design parameters of adsorption process on the removal of lead ions as a pollutant. The design parameters studied are initial concentration of lead ions Pb(II), absorbance material packing weight, pH and flow rate to remove lead, which considered one of the heavy metals pollutant by using IRH as an adsorbent material at room temperature 25°C . Results show that the removal efficiency of lead from aquatic solution decreased with increase of different initial concentrations (50, 75 and 100) mg/l and the removal efficiency increase with increase of different adsorbed material weight (5, 10 and 15) g while the removal efficiency decreases with increase of different flow rate (10, 20 and 30) ml/min. The results also show that the removal efficiency decreases with increase of different pH (4, 5 and 6). Freundlich and Langmuir adsorption isotherms were also applied and they showed good fits to the experimental data. A mathematical model using MATLAB is proposed for a packed bed isothermal adsorption column with porous adsorbent. The mathematical model takes account of both external and internal mass-transfer resistances as well as of nonideal plug flow along the column. Statistical model is also achieved to find an expression relates the overall operating parameters used in this investigation in a general equation.

Key words: MATLAB, Lead Removal, Rice Husk, and Freundlich and Langmuir isotherms.

1. Introduction

The greater environmental awareness in both and regulatory sphere in recent years has necessitated greater treatment of industrial effluent (1). The interest have been increased in recent years over the discharge of pollutants from industrial wastewater and how to treat this wastewater to reach the standard values of these pollutants before their discharge to the aquatic system (like river) or to the sewer network (2). According to the World Health Organization (WHO), the metals of most immediate concern are aluminum, chromium, manganese, iron, cobalt, nickel, copper, zinc, cadmium, mercury and lead (3). Heavy metal is a general collective term applying to the group of metals and metalloids with an atomic density greater than 6 g/cm^3. Although it is only a loosely defined term, it is widely recognized and usually applied to the elements such as Cd, Cr, Cu, Hg, Ni, Pb and Zn, which are commonly associated with pollution and toxicity problem. An alternative (and theoretically more acceptable) name for this group of elements is 'trace metal' but it is not as widely used (4). The presence of heavy metal ions in the environmental has been a matter of major concern due to their toxicity to human life. Unlike organic pollutants, the majority of which are susceptible to biological degradation, heavy metal ions will not degrade into harmless end products (5). It should be noted that certain heavy metals, including aluminum, copper, cadmium, iron, lead, manganese and nickel are essential, beneficial, or harmful in trace quantities (6). The toxicity of a given heavy metal depends on the total amount ingested, pH of treated water as well as a number of factors. Therefore, the so-called “heavy metals” which are five times denser than water or more, have been the cause of particular environmental concern (7). Heavy metal ions can come from many sources like industrial and municipal wastewater in the absence of the effective treatment, urban runoff, rainwater and agricultural fertilizer may be most important sources of heavy metals in aquatic environment. A large number of different industries produce effluents contaminated with heavy metal ions. Industries such as minerals and metallurgical processing, leather, textile, chemical manufacture, metal finishing and many other industries produce heavy metals in aqueous solution as waste (8).

2. Theory

2.1: Sorption isotherm

Different isotherm models have been utilized for describing sorption equilibrium for wastewater treatment. Langmuir and Freundlich equations are being used for present work.

Positive adsorption in a solid-liquid system results in the removal of solute from solution and its concentration at the surface of the solid, to such time as the concentration of the solute remaining in solution is in dynamic equilibrium with that at the surface. At this position of equilibrium, there is a defined distribution of solution between the liquid and solid phases.

The distribution ratio is a measure of the position of equilibrium in the adsorption process; it may be a function of the concentration of the solute, the concentration and nature of computing solutes, the nature of the solution, and so on.

The preferred form for depicting this distribution is to express the quantity (q_e) as a function of (C_{eq}) at a fixed temperature, where the quantity (q_e) *is the amount of solute adsorbed per unit weight of solid adsorbent*, and (C_{eq}) *is the concentration of solute remaining in solution at equilibrium*. An expression of this type is termed an adsorption isotherm.

The adsorption isotherm is a functional expression for the variation of adsorption concentration of adsorbate in bulk solution.

Commonly, the amount of adsorbed material per unit weight of adsorbent increases with the increase in concentration but not in direct proportion (9).

2.1.1: Langmuir Equation:

The Langmuir equation for adsorption model is valid for single layer adsorption. The Langmuir equation is limited by the assumption of uniform energies of adsorption on the surface (10). The Langmuir equation is based on the assumption that:

a- Adsorption takes place on localized (fixed) sites.
b- All sites are of equal energy, which means that the energy of adsorption on the surface is uniform (constant).
c- The maximum adsorption corresponds to the formation of saturated monolayer of solute molecules on the adsorbent surface.
d- There is no transmigration of adsorbate in the plane of the surface

In other words, the Langmuir sorption isotherm describes the surface as homogeneous assuming that all the sorption sites have equal sorbate affinity and that adsorption at one site does not affect sorption at an adjacent site (11). The Langmuir's equation is

$$q_e = \frac{Q^\circ b C_e}{1 + b C_e} \quad \ldots (1)$$

where:

q_e:- is the amount of solute adsorbed per unit mass of adsorbent at concentration (C).

C_e:- is the adsorbate concentration in the solution at equilibrium.

Q^o:-is the amount of solute adsorbed per unit mass of adsorbent in forming a complete monolayer on the adsorbent surface.

b:-is a constant related to the energy or net enthalpy of adsorption.

For very small amount of adsorption, when bC_e <<1 it yields a linear adsorption isotherm: $q_e = Q^o\, b\, C_e$

For large amount of adsorption, when bC_e >>1 (q) it will be equal to a, i.e.

$q_e = Q^o$, rearranging equation (1) gives the following modified Langmuir equation.

The linear form of the Langmuir isotherms may be represented as:

$$\frac{C_e}{q_e} = \frac{1}{bQ^\circ} + \frac{C_e}{Q^\circ} \qquad \dots (2)$$

A plot of C_e/q_e against C_e will give a straight line in which $(1/bQ^o)$ is the intercept and $(1/Q^o)$ is the slop of Equation (2) (11).

2.1.2: Freundlich Equation

The Freundlich equation [Freundlich, 1926] has been widely used for many years. The Freundlich Equation has the general form:

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

where n and K_F are the Freundlich isotherm constants.

The Freundlich sorption isotherm (an empirical equation) however, describes the equilibrium on heterogeneous surfaces and does not assume monolayer capacity. The linear form of Freundlich sorption isotherm can be represented as (10):

$$\log q_e = \log K_F + 1/n \log C_e$$

The values of n and K_F can be calculated from the slope and intercept of the plot log q_e verses log C_e.

The slop (1/n) is an indicator of adsorption intensity and the intercept of sorption capacity.

The Freundlich equation generally agrees quite well with the Langmuir equation and experimental data over a moderate range of concentration. Unlike the Langmuir equation, however, it does not reduce to a linear adsorption expression at very low concentration (12).

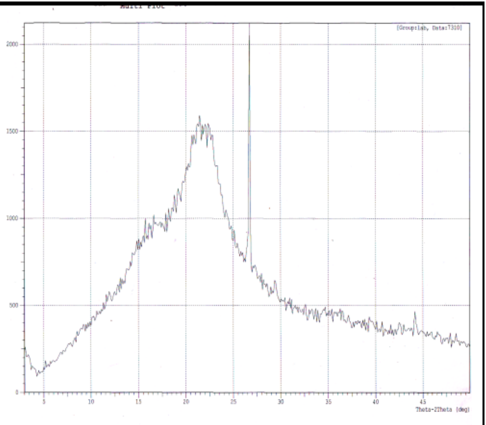
3. Experimental Work

3.1. *Materials*

3.1.1. Iraqi Rice Husk (*adsorbent material*)

Iraqi rice husk was collected from Al-Shanafia fields for rice in the Southern of Iraq. The rice husk was washed three times with doubled distilled water. Excess distilled water was used to remove the soluble materials present in the rice husk bringing from the field, boiled to remove colour and other fine impurities may be found in the rice husk, and then dried at 105°C for 24 hours and the adsorbent thus processed was used in its original piece size. The surface area of Iraqi Rice Husk was measured by BET (Brunauer – Emmett – Teller nitrogen adsorption technique). Charact-eristics of Iraqi Rice Husk were presented in Table 1. When the Iraqi Rice Husk was heated at 105°C in an oven, most of the water had been removed from the rice husk while the second major mass loss of about 45-65% was attributed to the breakdown of cellulose constituent char, which is a carbonaceous residue (13).

Table1: Characterization Properties of Rice Husk

<table>
<tr><td>Chemical Composition</td><td>XRD of Iraqi Rice Husk</td></tr>
<tr><td>
<table>
<tr><th>Compound</th><th>Composition wt %</th></tr>
<tr><td>SiO_2</td><td>90.70</td></tr>
<tr><td>Al_2O_3</td><td>0.13</td></tr>
<tr><td>Fe_2O_3</td><td>0.06</td></tr>
<tr><td>TiO_2</td><td>0.015</td></tr>
<tr><td>CaO</td><td>0.61</td></tr>
<tr><td>MgO</td><td>0.25</td></tr>
<tr><td>Na_2O</td><td>0.09</td></tr>
<tr><td>K_2O</td><td>2.64</td></tr>
<tr><td>P_2O_5</td><td>0.73</td></tr>
<tr><td>LOI</td><td>4.71</td></tr>
<tr><td>S.A (m^2/g)</td><td>57.5</td></tr>
</table>
</td><td>


</td></tr>
</table>

3.1.2. Stock Solution:

In order to avoid interference with other elements in wastewater, the experiments of this investigation were carried out using simulated synthesis aqueous solutions of lead Pb(II). Stock solution containing (1000 mg/l) of lead Pb(II) was prepared by dissolving (1.6064 gram) of lead nitrite $[Pb(NO_3)_2]$ in 1000 ml of double distilled water. All the working solutions using in the experiments were prepared by diluting the stock solution with double distilled water to the desired concentrations for the experimental work of this investigation. The lead ion Pb(II) concentrations were measured using Atomic Adsorption Spectrophotometer (AAS) (A-6200, Shimadzu) (14,15).

3.2. Sorption Unit:

Semi continuous mode experiments were conducted in this research by treated 250 ml of simulated synthesis aqueous solution of lead ion Pb(II) at desired concentrations with the various amounts of the adsorbent material (Iraqi Rice Husk) using different flow rates of simulated synthesis aqueous solution of lead ion Pb(II) at various pH. The pH value was adjusted using 0.1 N NaOH and 0.1 N HCl. The sorption unit using to achieve the experiments of this investigation is shown in Figure1. The sorption unit consists of packed bed sorption column, feeding burette and sample flask collector. The packed bed sorption column consisted of a clear glass tube of (5 cm ID, 5.3 cm OD and 55 cm height) and has a perforated disk in the bottom. The sorption column packed with Iraqi rice husk mass of 5, 10 and 15 gm supported from the top and the bottom by glass hollow cylinder layer, each cylinder have (0.5 cm diameter, 0.1 cm thickness and 1 cm long). Before starting the runs, the packed bed sorption column was rinsed by double deionized water down flow through the column. After the packed bed sorption column was accommodation and putting the required amount of adsorbent material (Iraqi Rice Husk), the adsorption process started by allowing the desired simulated synthesis aqueous solution of lead ion Pb(II) of required concentration and pH down flow through the sorption column from a 250 ml feeding burette at a precise flow rate in experiment. For the evaluation of the best operational condition, the experiments were carried out at constant environment temperature of 25°C corresponding to working temperature in the tannery, at various pH values which are (4, 5 and 6) at three initial feed concentrations of simulated synthesis aqueous solution of lead ion Pb(II) which are 50, 75 and 100 mg/l and at different flow rates which are 10, 20 and 30 ml/min for each initial feed concentration. Outlet samples after treatment in each experiment were collected from the bottom of packed bed sorption column at a regulated running treatment time each 5 minutes from entering the initial feed concentrations of simulated synthesis aqueous solution of lead ion Pb(II) through the packed bed sorption column.

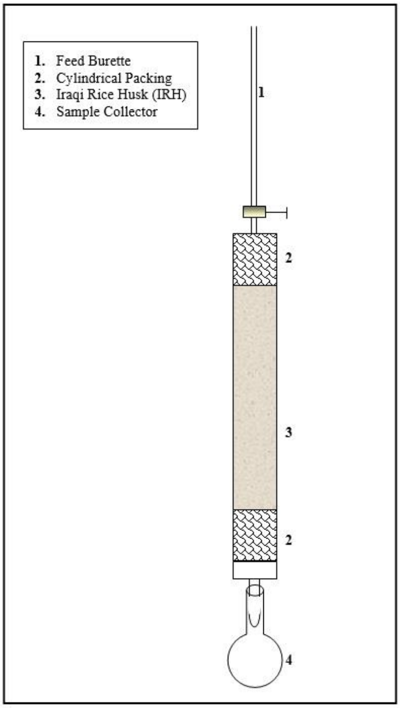


Figure 1: Sorption Unit

3.3. Determination of lead ion Pb(II) in the samples after treating:

A Shimadzu/Japan, AA-6200 Atomic adsorption flame emission spectrophotometer, connected to a computer unit is used to measure the concentration of lead in the sample after treatment. The instrument is calibrated by successive dilutions from a stock lead solution containing 1000 mg/l. Standard curve is plotted, as shown in Figure 2. Each measure for each sample represents the average of three readings (for more accuracy). Correct absorbance reading of sample by subtracting absorbance of a blank carried through the method. From the correct absorbance, determine lead ion Pb(II) present by reference to the calibration curve, prepared prematurely. Sorption percent of lead ion Pb(II) was calculated from the equation of

$\{([Pb^{+2}]_o - [Pb^{+2}])/[Pb^{+2}]_o\} \times 100$

where: $[Pb^{+2}]$ and $[Pb^{+2}]_o$ are the unadsorbed and initial concentration of unadsorbed lead ion Pb(II) respectively.

The percentage of desorption was calculated from the equation of $\{[Pb^{+2}] / [Pb^{+2}]_o\} \times 100$

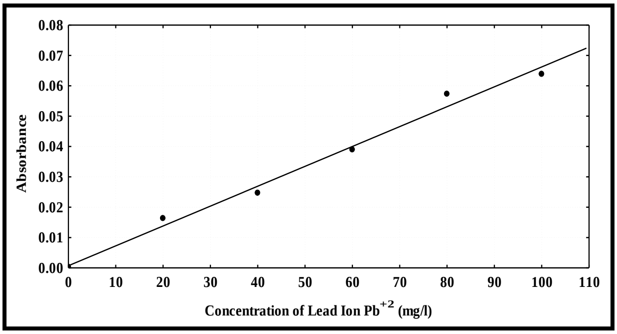


Figure 2: Calibration Curve of Lead Ion Pb(II)

4. Mathematical Model

Fixed bed dynamics are describing by a set of convection-diffusion equations, coupled with source terms due to adsorption and diffusion inside adsorbent particles. Inside the particle, molecules of adsorbate diffuse into the inner portions of particle via surface diffusion, pore diffusion, or both. The solution of these equations will give rise to the prediction of the needed concentration distribution. This investigation focuses on understanding the mechanism of both surface diffusion and pore diffusion. To formulate a generalized model corresponding to the dispersion flow, surface diffusion and pore diffusion mechanism, following assumptions are made:

1. The system operates under isothermal conditions.
2. The equilibrium of adsorption is described by Langmuir isotherm.

3. Intraparticle mass transport is due to Fickian diffusion, and it is characterized by the pore diffusion coefficient, D_p and the surface diffusion, D_s.
4. Mass transfer across the boundary layer surrounding the solid particles is characterized by the external-film mass transfer coefficient, k_f.
5. Film transfer resistance for mass transport from the mobile to the stationary phase.
6. Local adsorption equilibrium between the adsorbate adsorbed onto the adsorbent surface and the adsorbate in the intraparticle stagnation fluid.
7. Both surface and pore diffusion are included in the mass transport mechanism.
8. Axial dispersion.

The partial differential equations describing fixed bed dynamic are:

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2 D_s \rho_a \frac{\partial q}{\partial r} + r^2 D_p \varepsilon_p \frac{\partial C_p}{\partial r}\right] = \frac{\partial}{\partial t}\left[\rho_a q + \varepsilon_p C_p\right] \tag{3}$$

$$\frac{\partial C}{\partial t} = D_Z \frac{\partial^2 C}{\partial Z^2} - V_i \frac{\partial C_b}{\partial Z} - \frac{3k_f(1-\varepsilon)}{R\varepsilon}\left[C - C_p(r=R)\right] \tag{4}$$

Together equations (1) and (2) complete the system of non-linear partial differential equations that when solved yields the concentration distribution along the fixed bed. In addition, the initial condition for equation (1) is:

$$q(r,0) + \frac{\varepsilon_p}{\rho_a} C_p(r,0) = 0 \tag{5}$$

The first boundary condition for equation (13) is:

$$\frac{\partial}{\partial r}\left[q(0,t) + \frac{\varepsilon_p}{\rho_a} C_p(0,t)\right] = 0 \tag{6}$$

The second boundary condition for equation (13) is:

$$D_s\rho_a \frac{\partial q(R,t)}{\partial r} + D_p\varepsilon_p \frac{\partial C_p(R,t)}{\partial r} = k_f\left[C(t) - C_p(R,t)\right] \tag{7}$$

The initial condition for equation (14) is:

$$C_b(Z,0) = 0 \tag{8}$$

The boundary conditions for equation (14) are:

$$C_b(0,t) = C_\circ \tag{9}$$

and

$$\frac{\partial C_b(L,t)}{\partial Z} = 0 \tag{10}$$

The adsorption isotherm is nonlinear and favorable type, and is described by Freundlich isotherm equation (Eq.21):

$q_e = K_F\, C_e^{1/n}$ (11)

4.1: *Dimensionless form equations*

The equations describing the dispersion flow, surface diffusion and pore diffusion model (equations (3) to (11)) can be written in dimensionless form as follow:

$$\frac{\partial U}{\partial T} = \frac{1}{Pe}\frac{\partial^2 U}{\partial Z^2} - \frac{\partial U}{\partial Z} - 3St\ (U - U_p) \tag{12}$$

$$U(Z,0) = 0 \tag{13}$$

$$U(0,t) = 1 \tag{14}$$

$$\frac{\partial U(1,T)}{\partial Z} = 0 \tag{15}$$

$$\frac{1}{\bar{r}^2}\frac{\partial}{\partial \bar{r}}\left[\bar{r}^2 E_s \frac{\partial Q}{\partial \bar{r}} + \bar{r}^2 \varepsilon_p E_p \frac{\partial U_p}{\partial \bar{r}}\right] = \frac{\partial}{\partial \tau}\left[Q + \varepsilon_p U_p\right] \tag{16}$$

$$Q(\bar{r},0) + \frac{\varepsilon_p}{\rho_a} U_p(\bar{r},0) = 0 \tag{17}$$

$$\frac{\partial}{\partial r}\left[Q(0,T) + \frac{\varepsilon_p}{\rho_a} U_p(0,T) \right] = 0 \tag{18}$$

$$D_s \rho_a \frac{\partial q(1,T)}{\partial r} + D_p \varepsilon_p \frac{\partial U_p(1,T)}{\partial r} = k_f \left[U - U_p(1,T) \right] \tag{19}$$

$$Q(\bar{r},T) = KC_{\circ}^{1-{}^{n}\!/_{n}} \rho_a U_p^{{}^{1}\!/_{n}}(\bar{r},T) \tag{20}$$

The Dimensionless quantities used in defining the above set of equations can be defined in turn as follows:

U	Dimensionless adsorbate concentration in bulk	$= C_b\ C_o$
Q	Dimensionless adsorbate phase concentration	$= q\ C_o\ \rho_a$
U_p	Dimensionless adsorbate concentration in adsorbent pores	$= C_p\ C_o$
$\bar{r}$	Dimensionless particle radius	$= r\ R$
Z	Dimensionless column coordinate	$= Z\ L$
E_s	Surface diffusion modulus =Rate of transport by intra-particle surface diffusion to rate of transport by convection	$= \dfrac{D_s L}{R^2 V}$
E_p	Pore diffusion modulus = Rate of transport by intra-particle surface diffusion to rate of transport by convection	$= \dfrac{D_p L}{R^2 V_i}$
St	Stanton Number = Rate of transport by film transfer to rate of transport by convection	$= \dfrac{k_f L(1-\varepsilon)}{R V_i \varepsilon}$
Pe	Peclet Number; The ratio between the rate of transport by advection to the rate of transport by axial dispersion	$= \dfrac{V_i L}{D_z}$

4.2 Simulation technique

Equations (12) to (20) represent a set of simultaneous, nonlinear, partial differential equations (PDEs) that can be solved numerically. The discretatization was applied to space coordinates (Z and r) to convert the PODs to a set of ordinary differential equations(ODEs). The resulting ODEs can be solved using an existing ODE solver provided by MATLAB. (16).

5. Results and Discussion

The ability of Iraqi Rice Husk to remove lead ion Pb(II) from simulated synthesis aqueous solution in semi continuous packed bed column at various parameters which are pHs of simulated synthesis aqueous solution (*pH*), weight of adsorbent material (Iraqi Rice Husk) (*w*), flow rates of simulated synthesis aqueous solution (*F*), and time of treatment (*t*) was investigated. 81 experiments were achieved by varying all above parameters for three initial concentrations (C_o) of simulated synthesis aqueous solution of lead ion Pb(II). Thus, the results obtained are explained below.

5.1 Effect of Initial Concentration

The effects of three different initial concentrations (C_o) of simulated synthesis aqueous solution of lead ion Pb(II) which were (50, 75 and 100 mg/l) on the removal of lead ion Pb(II) using Iraqi Rice Husk at different pHs (4, 5 and 6), weight of adsorbent material (Iraqi Rice Husk) (5, 10 and 15 gram), flow rates of simulated synthesis aqueous solution (10, 20 and 30 ml/min.) and draw a sample each 5 minutes until reach to equilibrium were performed at constant temperature of 30ºC are shown in Figure 3. The results indicated that using Iraqi Rice Husk as an absorbent material, the percentage removal of lead ion Pb(II) was decreased from (99.99% to 94.96%), from (89.52 to 83.25%) and from (85.80 to 75.59%) at pH4, 5 and 6 respectively when the initial concentration (C_o) of simulated synthesis aqueous solution of lead ion Pb(II) was increased from 50 to 100 mg/l.

This can be explained by the fact that initial concentration of lead ion Pb(II) solution had a restricted effect on lead ion Pb(II) adsorption capacity, simultaneously the adsorbent material had a limited number of active sites, which would have become saturated at a certain concentration. This was lead to the increase in the number of metal ions (lead ion Pb(II)) competing for the available functions groups on the surface of adsorbent material (Iraqi Rice Husk). Since the solution of lower concentration has a small amount of metal ions (lead ion Pb(II)) than the solution of higher concentration of metal ions, so the percentage removal of metal ion (lead ion Pb(II)) was decreased with increasing initial concentration of metal ion (lead ion Pb(II)). For adsorbent material (Iraqi Rice Husk), higher percentage removal was 99.99% at initial concentration of lead ion Pb(II) 50 mg/l and higher percentage removal was 85.80% at initial concentration of lead ion Pb(II)100 mg/l, so Iraqi Rice Husk was found to be very efficient in lead ion Pb(II) removal.

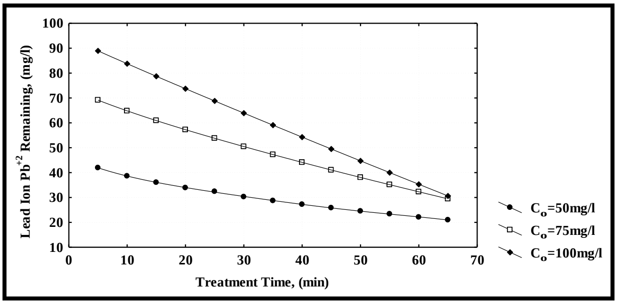


Figure 3: Effect of Initial Concentration on Lead Ion Pb(II) Removal Using IRH at *pH*=5, *w*=5g and *F*=10 ml/min

5.2. Effect of pH

The effects of three different pHs (4, 5 and 6) on the removal of lead ion Pb(II) by Iraqi Rice Husk at an lead ion Pb(II) initial concentration of (50, 75 and 100 mg/l), weight of adsorbent material (Iraqi Rice Husk) (5, 10 and 15 gram), flow rates of simulated synthesis aqueous solution (10, 20 and 30 ml/min.), and draw a sample each 5 minutes until reach to equilibrium at constant temperature of 25°C are shown in Figure 4.

These results show that the percentage removal of lead ion Pb(II) using Iraqi Rice Husk as an absorbent material was decreased from 98.90% to 30.65% for initial concentration 100 mg/l, decreased from 98.13% to 76.38% and decreased from 99.99% to 53.21% for initial concentration 50 mg/l when pH increased from 2 to 6 respectively for three initial concentrations above.

The variation in adsorption capacity in this pH range (4, 5 and 6) is largely due to the influence of pH on the adsorption material characteristics of the Iraqi Rice Husk, which indicates that the adsorption capacity of the adsorbent is clearly pH dependent (17).

The pH of the solution is an important factor that controls the uptake of lead ion Pb(II). pH dependence of metal adsorption can largely be related to type and ionic state of the functional group present in the adsorbent and also to the metal chemistry in the solution (18).

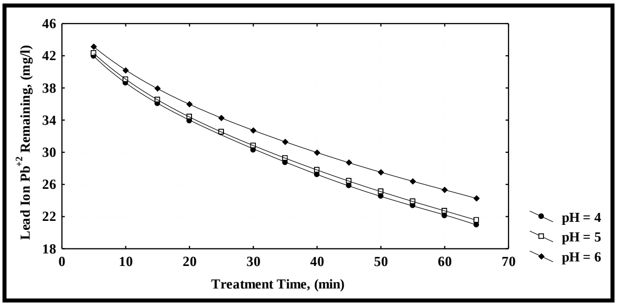


Figure 4: Effect of *pH* on Lead Ion Pb(II) Removal Using IRH at Initial Concentration =50 mg/l, *w*=5g and *F*=10 ml/min

5.3. Effect of adsorbent material weight

The effects of three different adsorbent material weight (*w*) (Iraqi Rice Husk) which were (5, 10 and 15 gm) on the removal of lead ion Pb(II) from simulated synthesis aqueous solution of at different pHs (4, 5 and 6), an initial concentration of lead ion Pb(II) (50, 75 and 100 mg/l), flow rates of simulated synthesis aqueous solution (10, 20 and 30 ml/min.) and draw a sample each 5 minutes until reach to equilibrium were carried out at constant temperature of 25°C is shown in Figure 5.

The results elucidated that when the adsorbent material weight (Iraqi Rice Husk) was increased from (5 to 15 gm) the percent removal of lead ion Pb(II) was increased from (45.73% to 99.90%), (55.51% to 93.56%) and (30.65% to 87.91%) when pH varied from (4-6) and the initial concentration varied from (50 -100) mg/l respectively.

The increased of adsorbent material weight (*w*) (Iraqi Rice Husk) meaning increased in the surface area of adsorbent material, as a result increased the number of active sites in the adsorbent material i.e. increased the availability of binding sites for adsorption and consequently increase the adsorption capacity of adsorbent material weight (Iraqi Rice Husk). This lead to increase the ability of adsorbent material to adsorb greater amount of lead ion Pb(II) from simulated synthesis aqueous solution at different initial concentrations and ultimately the percentage removal of lead ion Pb(II) increased.

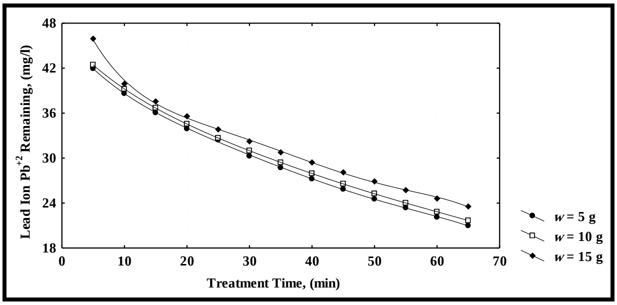


Figure 5: Effect of adsorbent material weight (*w*) on Lead Ion Pb(II) Removal Using IRH at Initial Concentration =50 mg/l, *pH* =4 and *F*=10 ml/min

5.4. Effect of flow rate

The effects of three different flow rates (*F*) of simulated synthesis aqueous solution which were (10, 20 and 30 ml/min.) on the removal of lead ion Pb(II) at different pHs (4, 5 and 6), weight of adsorbent material (Iraqi Rice Husk) (5, 10 and 15 gm), an initial concentration of lead ion Pb(II) (50, 75 and 100 mg/l), and draw a sample each 5 minutes until reach to equilibrium were studied at constant temperature of 25°C is shown in Figure 6 for initial concentration 50 mg/l.

The figure illustrated that when the flow rate of simulated synthesis aqueous solution of lead ion Pb(II) was increased from (10 to 30 ml/min.) the percentage removal of lead ion Pb(II) was decreased from (99.90 to 77.75), (83.65 to 63.57) when pH varied from (4-6) and the initial concentration varied from (50 -100) mg/l respectively.

This may be due to the fact that when the flow of simulated aqueous solution increasing, the velocity of solution in the column packed with the adsorbent material (Iraqi Rice Husk) was increasing too, so the solution spend shorter time than that spend it when the flow rate decreased, thus the adsorbent material (Iraqi Rice Husk) uptake low amount of lead ion Pb(II) from simulated aqueous solution, therefore the percentage removal of lead ion Pb(II) from simulated aqueous solution was decreased.

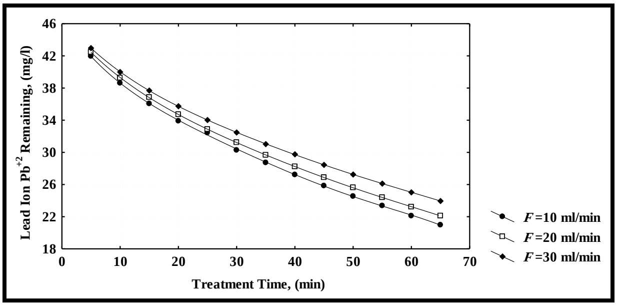


Figure 6: Effect of Flow Rate (*F*) on Lead Ion Pb(II) Removal Using IRH at Initial Concentration =50 mg/l, *pH* =4 and *w*=5g

5.5. Effect of treatment time

The effect of treatment times (*t*) of simulated synthesis aqueous solution loaded with lead ion Pb(II) at different pHs (4, 5 and 6), weight of adsorbent material (Iraqi Rice Husk) (5, 10 and 15 gm), an initial concentration of lead ion Pb(II) (50, 75 and 100 mg/l), and flow rates of simulated synthesis aqueous solution (10, 20 and 30 ml/min.) were studied at constant temperature of 25°C are shown in Figures (1-6) above.

These figures demonstrated that when the treatment time of simulated synthesis aqueous solution of metal ion of lead Pb(II) was increased the percentage removal of lead ion Pb(II) was increased when pH varied from (4-6) and the initial concentration varied from (50 -100) mg/l .

This may be due to that when the time of treatment of simulated aqueous solution increasing and the velocity of solution in the column packed with the adsorbent material (Iraqi Rice Husk) was remaining constant, the solution spend longer time than that spend it when the time of treatment decreased, so the adsorbent material (Iraqi Rice Husk) uptake more amount of lead ion Pb(II) from simulated aqueous solution, therefore the percentage removal of lead ion Pb(II) from simulated aqueous solution was increased.

5.6. Sorption isotherms

The isotherm constants were calculated from the slopes and intercepts of Figure 7 (Langmuir isotherm) and Figure 8 (Freundlich isotherm) and presented in Table 2. The value of R^2 was higher for Freundlich isotherm than the Langmuir isotherm; that means Freundlich equation represented the adsorption process very well. Value of Q^o, which is defined as the maximum capacity of sorbent, was calculated from the Langmuir plots.

The maximum capacity of Iraqi Rice Husk for lead ion Pb(II) was calculated in the range of 3.347 mg/g for initial concentration of 50 mg/l – 2.349 mg/g for initial concentration of

100 mg/l at constant temperature that indicated the best sorbing capacity of Iraqi Rice Husk for lead ion Pb(II).

The equilibrium parameter R_L, which is defined as $R_L = 1/(1 + bC_{Ao})$ in the range $0 < R_L < 1$ reflects the favorable adsorption process⁽¹⁹⁾.

Table 2: Values of Langmuir and Freundlich Sorption Constants and R_L Values for Sorption of lead ion Pb(II) on Iraqi Rice Husk at Different pH's

Langmuir Isotherm			Freundlich Isotherm			R_L
Constants		R^2	Constants		R^2	
Q^o (mg/g)	b (l/mg)		K_F	$1/n$		
6.25	0.291	0.914	9.59	4.799	0.959	0.5959

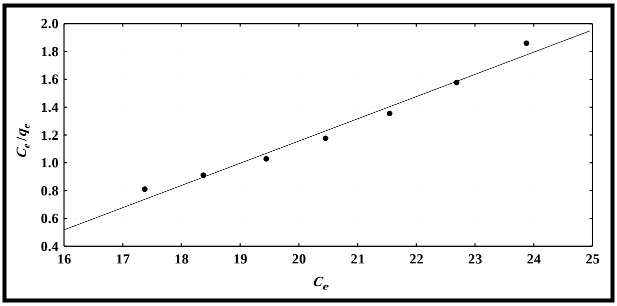


Figure (7) Langmuir isotherm plot for lead ion Pb(II) removal using Iraqi Rice Husk. Conditions: pH: 4.0; temperature: 25°C; Initial concentration (50 mg/l); weight (5 g) and flow rate (10 ml/min)

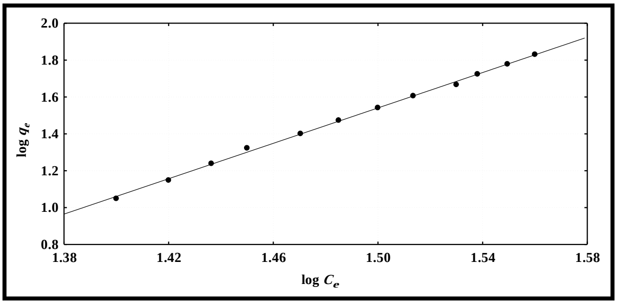


Figure (8) Freundlich isotherm plot for lead ion Pb(II) removal using Iraqi Rice Husk. Conditions: pH: 4.0; temperature: 25°C; Initial concentration (50 mg/l); weight (5 g); flow rate (10 ml/min).

5.8 Comparison between the theoretical and experimental results

The model used, as described above, determines the removal concentration of lead ion Pb(II) at different times based on different operating conditions. The results simulated using the model is compared with the experimental data obtained from sorption unit. The comparison between the experimental results and the results obtained from theoretical model is carried out in order to obtain the most acceptable values for the model parameters (Table 3), and to find the effect of each parameter on the prediction of the results. The results predicted by our proposed model show a good agreement with the experimental data (Figures 9, 10 and 11) with a standard deviation of 5.4% or 94.6% accuracy. Based on the good agreement of the model results, an exhaustive parametric study is carried out to understand the influence of various important parameters such as flow rate, weight of adsorbent and initial concentration.

Table 3: Model and Required Parameters

Model Designation	Solution Method	Required Parameters
Dispersed flow, pore and surface model	Numerical solution	Pe, D_s, D_p, k_f, K, n

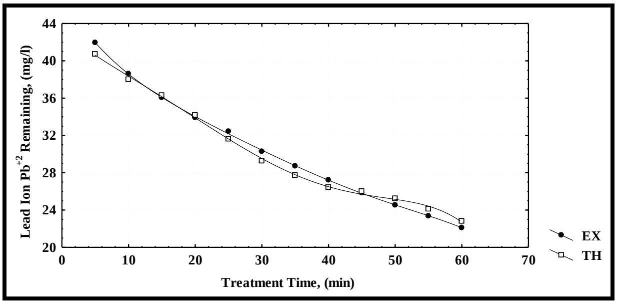


Figure 9: Comparison of experimental and modeling results for data obtained from sorption unit for (Initial concentration =50 mg/lit., Flowrate = 10 ml/min., pH = 4 and weight of adsorbent = 5g)
(EX: Experimental Results, TH: Theoretical Results)

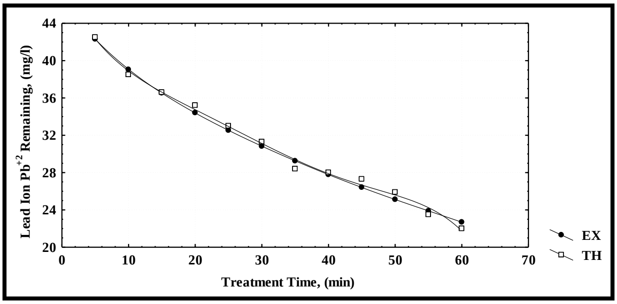


Figure 10: Comparison of experimental and modeling results for data obtained from sorption unit for (Initial concentration =50 mg/lit., Flowrate = 10 ml/min., pH = 5 and weight of adsorbent = 5 g)
(EX: Experimental Results, TH: Theoretical Results)

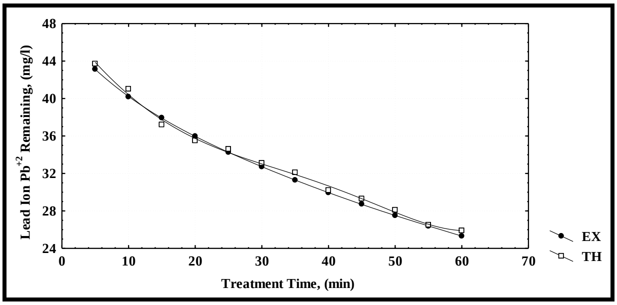


Figure 11: Comparison of experimental and modeling results for data obtained from sorption unit for (Initial concentration =50 mg/lit., Flowrate = 10 ml/min., pH = 6 and weight of adsorbent = 5 g)
(EX: Experimental Results, TH: Theoretical Results)

5.9: Statistical Model

A statistical model was carried out on the results obtained from this study. Regression Analysis and **π** Theorem was adopted to maintain a relation between the percentage removal of lead ion Pb(II) after treatment and the flow rate, time of treatment, initial concentration of lead ion Pb(II) and weight of adsorbent material. This relation is shown in equation (21), which has a correlation coefficient (r) equal to 86.3%.

$$\%R = 263.03\frac{w^{0.12}}{pH^{0.14}\,F^{0.12}\,t^{0.12}\,C_{\circ}^{0.12}} \qquad \text{... (21)}$$

where:
%*R*: Percent Removal Of lead ion Pb(II)
F: Flow rate of Samples, (ml/min)
t: Time of Treatment , (min)
C_o: Initial Concentration of lead ion Pb(II), (mg/l)
w: Weight of Adsorbent Material, (g)

6. Conclusions

The following conclusions can be drawn:

1. Iraqi Rice Husk showed a good ability to remove lead ion Pb(II) from aqueous solution using semi continuous adsorption unit. So, it could be recommended for removal of lead ion Pb(II) from different industrial wastewater in Iraq in stead of other material like activated carbon because it is valid, cheaper, economical, ease and simplicity for using, has a high ability to adsorb metal ions, can be use several times by costly regeneration method and can be used finally in another benefit uses.
2. Maximum removal of lead ion Pb(II) was 99.99% performed at initial Pb(II) concentration =50 mg/l, flow rate = 10 ml/min treatment time = 225 min and pH =4.
3. The percentage removal of lead ion Pb(II) was increased with decreeing pH, flow rate of simulated synthesis aqueous solution and initial concentration of lead ion Pb(II) while the percentage removal was increasing with increasing the weight of adsorbent material (Iraqi Rice Husk)

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