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Experimental and Theoretical Investigations of Biosorption of Lead Mercury Chromium and Arsenic onto Dry Activated Sludge from Wastewater

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Abstract – *The biosorption of lead, mercury, chromium and arsenic ions from simulated of wastewater onto dry activated sludge in single component systems has been studied using batch adsorber. A film-pore diffusion model has been used to predict concentration-time decay curves successfully for metals ions using COMSOL multiphysics software. The external mass transfer coefficient and diffusion coefficient were determined from the model at optimum agitation speed, 600 rpm and optimum weight of sewage sludge biomass. Eleven isotherm models were used. Among these, Langmuir model gave the best fit to an experimental data.* **Copyright © 2013 Praise Worthy Prize S.r.l. - All rights reserved.**

***Keywords**: Pore Diffusion, Batch Adsorber, COMSOL Software, Lead, Mercury, Chromium, Arsenic Cations*

Nomenclature

a_K	Khan model parameter
a_t	Toth model parameter
A_R	Reddlich-Peterson model parameter, (l/mg)
B	BET model parameter, (l/mg)
b	Temkin isotherm constant, (kj/mole)
B_D	Dubinin-Radsukevch model parameter, (mole/J)
b_K	Khan model parameter, (l/mg)
B_R	Reddlich-Peterson model parameter, $(l/mg)^m$
b	Langmuir constant, (l/mg)
C_b	Solute concentration in the fluid-bulk phase, (kg/m^3)
C_e	Equilibrium concentration, (mg/l)
C_o	Initial solute concentration. (mg/l)
C_p	Solute concentration in the particle phase, (kg/m^3)
D_p	Pore diffusion coefficient, (m^2/s)
F_{RP}	Radke-Praunsitz model parameter, $(l^n mg^{1-N}/g)$
k_f	External mass transfer coefficient, (m/s)
k_{id}	Intraparticle diffusion rate constant, $(s^{-1/2})$
K	Freundlich equilibrium parameter, $(mg/g)(l/mg)^{1/n}$
K_h	Harkins-Henderson model parameter, $(mg/g)(l/mg)^{1/n}$
K_{RP}	Radke- Praunsitz model parameter, (l/mg)
K_T	Equilibrium binding constant in Temkin model, (l/mg)
m_R	Reddlich-Peterson model parameter
n	Freundlich and combination of Langmuir and Freundlich equilibrium parameter model parameter
n_h	Harkins-Henderson model parameter
N_{RP}	Radke-Praunsitz model parameter
Q	BET model parameter, (mg/g)
$Qmax$	Khan model parameter, (mg/g)
q_D	Dubinin-Radsukevch model parameter, (mg/g)
q_e	Internal concentration of solute in particle at equilibrium, (mg/g)
q_m	Adsorption equilibrium constant defined by Langmuir equation, (mg/g)
R	Universal gas constant (=8.314) , (kj/mol.K)
R_p	Radius of particle, (m)
R_s	Separation factor
T	Absolute temperature , (K)
t	Toth model parameter
V_f	Final Volume of solution, (m^3)
V_L	Initial Volume of solution, (m^3)
W_A	Mass of activated sludge, (g)
Greek	
ε_p	Particles porosity
ρ_p	Particle density, (kg/m^3)

I. Introduction

The presence of heavy metals in the environment is a major concern because of their toxicity and threat to human life and to the environment. Lead, mercury, chromium, and arsenic are examples of heavy metals that have been classified as priority pollutants.

Compared the conventional methods for removing toxic metals from industrial effluents, biosorption offers the advantages of low operating cost, minimization the volume of chemical or biological sludge to be disposed , high efficiency in detoxifying very dilute effluents and no nutrients are required, regeneration of the biosorbent,

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and the possibility of metal recovery. These advantages have served as the primary incentives for developing full-scale biosorption process to clean up heavy-metal pollution [1].

Adsorbate removal in adsorption depends on several factors such as, operating parameters (pH, adsorbent dose, contact time, agitation speed etc), adsorbent characteristics (particle density, particle diameter, porosity, surface area etc.), and process parameters (rate constant, isotherm constants, mass transfer coefficients etc.) [2]. The key parameters for design of the adsorption system are the process parameters that are used for modeling the system for predicting the quality of effluent under a wide range of operating conditions.

The key process parameters in adsorption such as, isotherm constants and mass transfer coefficients are established by conducting batch studies of adsorption. Suitability of a relevant isotherm is essential to predict the adsorbate removal profiles either in batch studies or column studies. The adsorbate removal is basically a mass transfer operation and is primarily dependent upon the release of the adsorbate molecule from liquid phase and its accumulation and diffusion on solid adsorbent.

Reference [3] used different batch models for dye adsorption by activated carbon. They suggested that the inclusion of pore diffusion is essential to obtain accurate values of mass transfer coefficients. The method of lines was used as numerical tool and orthogonal collocation was chosen for spatial discretisation.

The objective of this work is to conduct batch biosorbtion experiments to adsorb Pb^{2+}, Hg^{2+}, Cr^{3+} and As^{5+} from simulated waste water by an abundant and low cost biosorbent, namely, dry activated sludge (DAS). Mathematical model for batch adsorber will be proposed which takes account of both external and internal mass-transfer resistances to find out key parameters for design of the adsorption system, such as an external mass transfer coefficient and diffusion coefficient by using COMSOL multiphysics software as a numerical tool.

II. Mathematical Model

The overall rate of adsorption in a porous adsorbent can be described by a mechanism of three consecutive steps:

1) external mass transport;
2) intraparticular diffusion;
3) adsorption at an interior site.

Moreover, intraparticular diffusion may be governed by pore volume diffusion or surface diffusion or a combination of both.

Models play a key role in transferring technologies from the laboratory to a full scale application. Good models can help not only in analyzing and interpreting experimental data, but also in predicting the response of the systems to changing conditions. For batch adsorber, the mathematical model with pore diffusion model is [4]-[5]:

- Mass balance in fluid-bulk phase:

$$V_L \frac{dC_b}{dt} + \frac{3W_A}{\rho_p R_p} k_f \left(C_b - C_{p,r=Rp} \right) = 0 \qquad (1)$$

- Mass balance inside particle phase:

$$\varepsilon_p \frac{\partial C_p}{\partial t} + \rho_p \frac{\partial q}{\partial t} = \varepsilon_p D_p \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C_p}{\partial r} \right) \qquad (2)$$

- Initial and boundary conditions:

$$t=0;\ C_b = C_o,\ C_p = 0,\ q = 0$$

$$r=0;\ \left(\frac{\partial C_p}{\partial r} \right) = 0 \qquad \left(\frac{dq}{dr} \right)_{r=o} = 0$$

$$r=R_p;\ \varepsilon_p D_p \left(\frac{\partial C_p}{\partial r} \right)_{r=Rp} = k_f \left[C_b - C_{p,r=Rp} \right]$$

In case of applying Langmuir isotherm model:

$$q = \frac{q_m b C_p}{1 + b C_p} \qquad (3)$$

For scaled bulk concentration, $C'_b = C_b / C_o$, Eq. (1) becomes:

$$V_L \frac{dC'_p}{dt} + \frac{3W_A k_f}{\rho_p R_p} \left(C'_b - C'_{p_{r=R_p}} \right) = 0 \qquad (4)$$

For scaled particle phase concentration, $C'_p = C_p / C_o$, and taking into account that,

$$\frac{\partial q}{\partial t} = \frac{\partial q}{\partial C'_p} \cdot \frac{\partial C'_p}{\partial t}$$

where:

$$\frac{\partial q}{\partial C'_p} = \frac{q_m b}{\left(1 + b C_o C'_p \right)^2}$$

equation (2) becomes:

$$\left[\varepsilon_p + \frac{\rho_p q_m b}{\left(1 + b C'_p C_0 \right)^2} \right] \frac{\partial C'_p}{\partial t} = = \varepsilon_p D_p \frac{\partial^2 C'_p}{\partial t^2} + \frac{2 \varepsilon_p D_p}{r} \frac{\partial C'_p}{\partial r} \qquad (5)$$

with the scaled initial and boundary conditions:

$$t=0;\ C'_b = 1,\ C'_p = 0,\ q = 0$$

$$r = 0; \quad \left(\frac{\partial C'_p}{\partial r} \right) = 0 \qquad \left(\frac{dq}{dr} \right)_{r=o} = 0$$

$$r = R_p; \quad \varepsilon_p D_p \left(\frac{\partial C'_p}{\partial r} \right)_{r=Rp} = k_f \left[C'_b - C'_{p,r=Rp} \right]$$

An external mass transfer coefficient for the solute adsorbed at certain particle size and optimum agitation speed, can be obtained by the analytical solution of equation (1) [6], where at $t = 0$, $C_{P,r=Rp} = 0$ and $C_b = 0$, hence:

$$k_f = -\frac{R_p \rho_p V_L}{3 W_o t} ln \left(\frac{C_b}{C_o} \right) \qquad (6)$$

where, t is the sampling time period.

III. Materials and Experimental Methods

III.1. Dry Activated Sludge

Activated sludge was used as an biosorbent in the present work. It was obtained from aerobic secondary unit in Hamdan waste water treatment station in Basrah city, Iraq. The sludge was washed several times with distilled water to remove undesired solid materials and dissolved heavy metals, dried under sun light, and then dried in oven at 60°C until having constant weight (24 hr). The dry sludge was crushed by jaw crusher (Retsch, type-BB1A, Germany) and sieved by successive sieves (Retsch, ASTM-E11, Germany) after which the biosorbent was kept in a desiccators for use. The physical and chemical properties of DAS biomass were listed in Table I.

TABLE I
PHYSICAL AND CHEMICAL PROPERTIES OF DRY ACTIVATED SLUDGE

Particle size, mm	0.38
Particle density, kg/m^3	1968
Bulk density, kg/m^3	784.34
Specific surface area, m^2/g	6.999
Particle porosity	0.6014
pH	7.3
Ash content%	12
Cation exchange capacity (CEC), meq/100 g	51.153

Specific surface area, CEC and SEM image were conducted at laboratories of Iraqi technological and science ministry, while other properties were measured at chemical engineering department, Basrah university.

The particles mean diameter was calculated from the geometric mean of the two consecutive sieve openings [7].

To measure particle density, empty pychnometer flask with stopper was weighted, and 10 g (Denver balance, Tp-214, Germany) of oven-dried activated sludge was added into the flask. Boiled and cooled distilled water was added to the half of the flask.

The solution was then shaken to dismiss the air from biosorbent pores, and water volume was completed. The stopper was put in its place and the outside of the flask was cleaned, dried and re-weighed.

The flask was then emptied, cleaned, dried, filled with pre-boiled distilled water and reweighed [8]. Particle density was calculated according to Eq. (7):

$$\rho_p = \frac{DAS\ mass\ \ x\ water\ density}{\left(DAS\ mass + \atop - \left(bottle\ \ mass\ with\ DAS\ and\ water + \atop -bottle\ \ mass\ \ with\ \ water \right) \right)} \qquad (7)$$

To quantify bulk density, a glass beaker was emptied, dried, then filled to overflowing with oven-dried activated sludge. The sides of the beaker were tapped lightly ten times with a glass rod, then leveled by rolling the rod across the top edge of the beaker six times. The beaker was then reweighed, and density of the medium was calculated by dividing DAS mass over beaker volume [8].

A porosity was determined using Eq. (8):

$$\varepsilon_p = 1 - \frac{\rho_b}{\rho_p} \qquad (8)$$

The specific surface area of activated sludge was measured using the multi-point-N_2-BET method, on the (Quantachrome NovaWin2 system, USA).

The pH was measured by suspending one gram of DAS in 100 ml distilled water and heating at 363K for 20 min. The solution was then cooled and pH measured using pH meter (Hanna pH-211, USA) with electrode type HI-1131. The pH was calibrated prior to analysis using standard buffer with in the range of the pH to be measured.

Ash content was measured by weighing a 2g of DAS in a porcelain crucible and heating the sample to 388 K for 16 h. The sample was then heated in a furnace at (1223 K for 1.5 h). The crucible was then removed and placed in a desiccators and weighed after cooling. The ash content was calculated as:

$$Ash(\%) = \frac{Finalweight(g)}{Initialweight(g)} \times 100 \qquad (9)$$

Ammonium saturation method was used to determine CEC [9]. 20 ml of 1M potassium acetate (CH_3COOK) was added to 1 g of the DAS in a centrifuge tube. The sample was shaken in a shaker (Memmert, type WNB-22, Germany) for 30 minutes at a speed of 75 rpm.

The samples was centrifuged in a centrifugal (Baird and Tatlock, UK) for 10 minutes. The clear supernatant was discarded.

This process was done twice to ensure effective washing of the DAS. 20 ml of distilled water was added to the DAS and the sample was shaken for 30 minutes at a speed of 75 rpm. The samples was centrifuged for 10 minutes. The clear supernatant was discarded. This process was done twice. 25 ml of 1 M ammonium acetate was added to the DAS. The sample was shaken for 30 minutes at a speed of 75 rpm and then centrifuge for 10 minutes. The clear supernatant was collected in a clean 50 ml centrifuge tube. This process was repeated twice pouring the clear supernatant into the same centrifuge tube. The concentration of K^{1+} was measured by Flame Photometer (Jenway, PFP7 Flame, UK).

III.2. Adsorbate

1000 mg/l of stock solution of each metal ions of Pb^{2+}, Hg^{2+}, Cr^{3+} and As^{5+} where prepared by dissolving $Pb(NO_3)_2$, $Hg(NO_3)_2.1/2H_2O$, $Cr(NO_3)_3.9H_2O$ and $3As_2O_5.5H_2O$ salts respectively in distilled water, then stored in acid washed polyethylene and glass containers and kept in refrigerator at 4 °C.

A solution of ions concentration of 50 mg/l was prepared by dilution of stock solution. The chemicals used are annular grade produced by Fluka, Switzerland and BDH, UK.

III.3. Methods

The effect of pH on biosorption of Pb^{2+}, Hg^{2+}, Hg^{2+} and As^{5+} onto DAS was investigated. A sample of (100 ml) of each single metal ion solution was placed in a beaker of (200 ml). The solution was agitated (constant temperature 298 K) at 800 rpm. Activated sludge of weight 0.25 g and size 0.38 mm was added gradually.

The solution pH was maintained at different values ranging from 2 to 7 by adding (0.5 N) HCl or NaOH to each solution and measuring the pH value continuously till reaching the desired value. After 4-7 hrs of agitation which is enough to reach equilibrium [1], the solution was filtrated using filter paper type (Wattmann no. 4) and a sample of (2 ml) was taken for analysis. An ion concentration in the supernatant was measured using atomic absorption spectrophotometer (model VGP-210 Buck scientific, USA) at 283.3, 253.7, 357.9 and 193.7 nm wavelength for lead. mercury, chromium and arsenic metals, respectively, and computed from the calibration curves. For the determination of equilibrium biosorption isotherm, the same above procedure was performed. pH was kept at optimum value in each run. Different weights of activated sludge (0.0625, 0.125, 0.25, 0.375, 0.5, 1, 1.5, 2, 2.5, 3, 4 and 5 g) were used for each metal ions isotherm. The adsorbed amount was calculated using the following mass balance equation:

$$q_e = \frac{\left(V_L C_o - V_f C_e\right)}{W_A} \qquad (10)$$

To determine optimum agitation speed, a wide range of speeds were performed 200, 400, 600, and 800 rpm.

A (250 ml) beaker was used and an adjustable speed mixer was connected to this beaker, the beaker was filled with (100 ml) at the same initial concentration of (50 mg/l) for each solution. A mass of (2 g) of activated sludge was used in lead and mercury solutions in each experiment. While for chromium, the mass is 3 g and 4 g for arsenic solution of activated sludge used in each experiment. A sample was then taken at (15, 30, 60, 120, 180, and 240 min) and a decay curve was plotted for (C_b/C_o) against time and as soon as (C_b/C_o) reaches (0.05) this speed of agitation considered as an optimum speed. The optimum activated sludge weight for each pollutant was determined according to the optimum agitation speed. The optimum activated sludge weight to reach equilibrium concentration of C_e/C_o=0.05 was calculated from isotherm equation for each solute.

The external mass transfer coefficient (k_f) and the pore diffusion coefficient (D_p) were determined from the concentration decay curves data at optimum sludge dosage and optimum agitation speed by using a well stirred batch contactor. In this method, a known amount of adsorbent (optimum dosage for each pollutant) is added to a constant volume of solution. The rate of adsorption of solute was found by measuring the solute concentration with time, using atomic absorption.

A 2000 ml Pyrex beaker was used which is fitted with electrical mixer with glass impeller manufactured at chemistry department workshop, Basrah university. The beaker was filled with 1000 ml of (50 mg/l) pollutant initial concentration and the agitation speed is adjusted on (600 rpm) as an optimum speed. At time zero, samples of (2 ml) were taken after (2, 4, 6, 8 and 10 min) during the experiment for analysis.

The functional groups of activated sludge were detected by FT-IR analysis before and after biosorption.

The proportion of activated sludge biomass/KBr is 1/100. The background was obtained from the scan of pure KBr. (Shimadsu- S1394, spectrum system, Japan) was used for FT-IR analysis of DAS.

IV. Use of COMSOL Multiphysics

When setting up the model in COMSOL Multiphysics it is important to follow four basic steps, namely: creation of the geometry, definition of physical laws and equations of the model, mesh generation and running the solution of the model.

IV.1. Creation of the Geometry

The process will take place in the bulk, in the film around the biosorbent particle, and in the pores, so the particle was considered as the system represented by a line with length equivalent to particle radius (1D).

IV.2. Definition of Physical Laws and Equations

The Chemical Engineering module (COMSOL Multiphysics, 3.5) [10] was chosen for this modeling exercise. In the mass transport mode, COMSOL Multiphysics allows the user to work with the transient mass transport equation by diffusion which is shown below (Eq. (11)). The user must provide the numerical values or expressions for the constants in the model such as dispersion coefficients:

$$\delta_{ts}\, \partial C / \partial t + \Delta\left(-D\Delta C\right) = R \tag{11}$$

In Eq. (11) the first term of the LHS refers to the accumulation in the system and the second termaccounts for the diffusion that may take place in any direction. On the RHS of Eq. (11) the term is a chemical reaction. Table II relates the COMSOL coefficients in equation (10) with the equivalent terms in our model defined by Eqs (4) and (5). Having in mind that there are two different heavy metal phases (or "species") we will need a set of expressions for each one.

TABLE II
COEFFICIENT IN EQUATION 8 AND EQUIVALENT IN EQUATIONS 4 AND 5

Coefficient	Expression C'_b	Expression C'_p
δ_{ts}	V_L	$\varepsilon_p + \dfrac{\rho_p q_m b}{\left(1+bC'_p C_0\right)^2}$
D	0	$\varepsilon_p D_p$
R	$\dfrac{3W_o k_f}{\rho_p R_p}\left(C'_b - C'_{p_{r=R_p}}\right)$	$\dfrac{2\varepsilon_p D_p}{r}\dfrac{\partial C'_p}{\partial r}$

IV.3. Mesh Generation

The generation of an appropriate mesh is very important in order to achieve accurate results without unnecessary computational demand. For one-dimensional problems, the mesh will consist of small triangles that can have up to seven nodes each.

The solution will use degree 5 polynomials maximum so the central node will not be necessary. COMSOL may generate the mesh automatically.

IV.4. Running the Solution

The solution is based on a finite element solution algorithm. Once the elements are defined on the previous step, the concentration values for each node will be estimated using a polynomial expression. Note that in order to obtain more precise results, the number of elements in the mesh must be increased by refining the mesh. The polynomial degree was fixed at value 2.

It is crucial to specify from the beginning that the model is time-dependant in order to be able to see how the bulk concentration varies as the process takes place. When using this method, time limits and time steps have to be defined.However, note that these steps are only used for post-processing purposes.

The time step for solving the equations is defined independently. Specific and absolute tolerances will also have to be defined in this step.

V. Results and Discussion

V.1. Optimum pH

It is well known that pH is one of the major parameters controlling the sorption of metals with biosorbents.

Fig. 1 shows the effect of pH on the adsorption capacity of dried activated sludge. As can be seen from the figure, there was an increase in biosorption capacity of biomass with increasing pH from 2.0 to 4.0.

As the pH increased, the overall surface charge of the dried activated sludge became negative and adsorption increased. At pH values higher than 4.0, biosorption studies could not be performed due to the precipitation of metal hydroxide from the solution.

The isoelectric point of activated sludge was usually between pH 1 and 3 [11] which means that the overall surface charge on the sludge was predominantly positive at a pH less than 3, and became negatively charged when the pH was higher than 3.

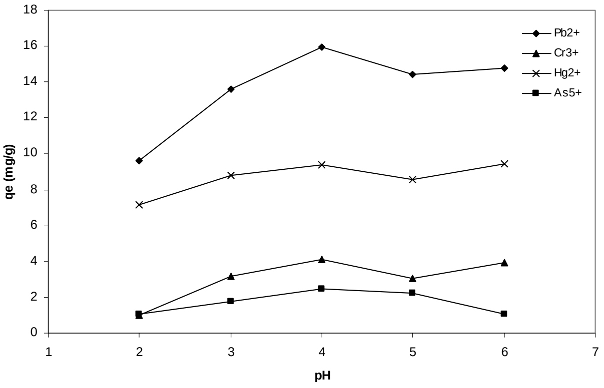


Fig. 1. Effect of pH on the uptake of Pb^{2+}, Hg^{2+}, Cr^{3+} and As^{5+} onto DAS at 298 K. C_o=50 mg/l for each component

V.2. Equilibrium Isotherms

The biosorption isotherms were obtained by plotting the weight of the solute adsorbed per unit weight of activated sludge (q_e) against the equilibrium concentration of the solute in the solution (C_e) at constant temperature [12]. The equilibrium isotherms of Pb^{2+}, Hg^{2+}, Cr^{3+} and As^{5+}, were conducted at (298 K) with initial concentration of each component, C_o=50 mg/l.

These isotherms are shown in Fig. 2. Eleven isotherm models were used to fit the experimental data. Isotherm models are given in Table III. The values of model parameters are evaluated by non-linear curve fitting method using DataFit version 9.0.59, Oakdale Engineering software. Table III represents the values of the parameters of each model, the correlation coefficients (R^2). It is clear from Fig. 1 and Table III that the equilibrium isotherm for each single component is of favorable type, since $0 < Rs < 1$ (Rs = 0.4228 , 0.0623, 0.0771 and 0.0862 for Pb^{2+}, Hg^{2+}, Cr^{3+} and As^{5+} respectively).

For lead; Langmuir, Radke-Praunsitz, Khan, Reddlich-Peterson and Toth gave the best fit of experimental data with high correlation coefficients (R^2=0.9979). while, the experimental data for mercury, chromium and arsenic where described successfully with Langmuir model with correlation coefficient 0.9923, 0.9897 and 0.9868 respectively. Thus, Langmuir model was used in the modeling of batch adsorber for all of heavy metals in this study.

Using Langmuir model, it was found that the maximum metal uptake (q_m) for Pb^{+2} is greater than that for Cr^{3+}, Hg^{2+}, and As^{5+} ($q_{m,Pb}{}^{2+}$ = 77.4857, $q_{m,Hg}{}^{2+}$ = 10.7876, $q_{m,Cr}{}^{3+}$ = 4.6404 and $q_{m,As}{}^{5+}$ = 2.8289 mg/g respectively). These are in agreement with other studies ($q_{m,Pb}{}^{2+}$ = 87.7, $q_{m,Cr}{}^{3+}$ = 3 mg/g) [24]-[25]. Higher q_m value for Pb^{2+} confirms the stronger bonding affinity of DAS to Pb^{2+} than to that of Cr^{3+}, Hg^{2+}, and As^{5+}.

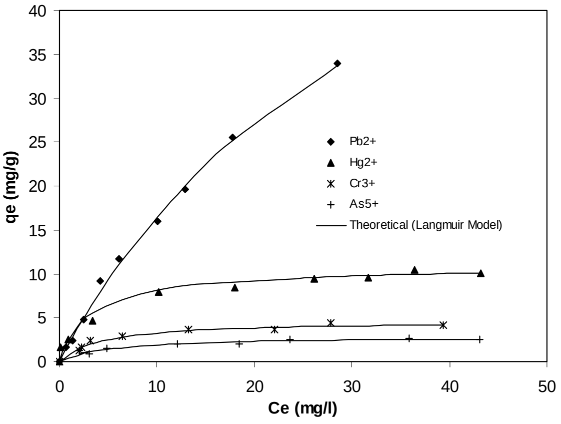


Fig. 2. Biosorption isotherm for single component system of Pb^{2+}, Hg^{2+}, Cr^{3+} and As^{5+} onto DAS at 298 K. C_o=50 mg/l for each component

V.3. Characterization of DAS Biomass

In order to find out which functional groups were responsible for the Pb^{2+}, Hg^{2+}, Cr^{3+}, and As^{5+} biosorption, FT-IR analysis of raw and loaded dried activated sludge was experienced before and after cations binding as listed in Table IV.

The difference between the two spectra was in the absorbance wave number and intensity. Different functional groups were detected on the DAS surface. Spectra analysis of FT-TR spectrum after cations adsorption showed that there was a substantial decrease in the wave number and adsorption intensity of carboxylic acid group with O-H stretch, amide group with N-H stretch and amine group with $N-H_2$ stretch at 3411.84, 2929.81, 1652.88, 1570, and 1450 cm^{-1}.

These groups were mainly from polysaccharidic and protein materials which constitute most of the cell wall.

The results show that cations may be complexed by H and O atoms of hydroxyl bonds, which shifted the bands to lower frequencies. These results agreed with reference [26]. According to table IV, lead cations exhibited more decrease in wave number and adsorption intensity compared to the other cations which explained its high affinity to the biosorbent. Table I showed that the sewage sludge used in this work contained a much higher cation exchange capacity (51.153 meq/100 g),. This indicates that CEC was an important mechanism in biosorption of of Pb^{2+}, Hg^{2+}, Cr^{3+} and As^{5+} onto DAS.

Electron scanning microscopy (1450VP, Leo Co., Ltd., Hong-Kong) evidenced that the sewage sludge possessed a very rough surface that could provide a large chemical binding area, Fig. 3.

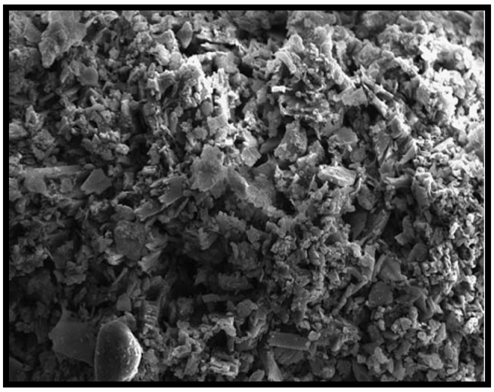


Fig. 3. SEM image of dry activated sludge shows the amorphous structures

V.4. Determination of Optimum Agitation Speed

The concentration decay curves of solute in the batch experiments were shown in Fig. 4 for each pollutants at different agitation speeds (200, 400, 600, and 800 rpm).

Due to the pulverization and crushing of the DAS at relatively high agitation speeds and the adsorbent is begin to turn to a powder, the optimum agitation speed needed to achieve C_e/C_o=0.05 will consider as (600 rpm) although the speed above (600 rpm), the equilibrium concentration ratio is reaches less than 0.05.

V.5. Determination of the Optimum Weight

This will refer to the optimum amount of the adsorbent to be used to get the maximum removal for each pollutant. Determination this amount will depend on some environmental aspects regarding the presence of such heavy metals in the environment, aqua and eco-system. The adopted criterion will depend on the fact that the optimum weight will depend on (C_e/C_o) to be at least equal to 0.05 or less in addition to the environmental considerations. The approach of (C_e/C_o=0.05) refers to the optimum operational, durability and sustainability of the adsorption process by using biosorbent.

This process will be more practical, economic wise and operational when imposing such conditions [27]. Conducting this approach the optimum weight of adsorbent can be calculated as follows:

$$W_A = \frac{\left(V_L C_o - V_f C_e\right)}{q_e} \tag{12}$$

Replacing (C_e/C_o=0.05) into Eq. (12) and using Langmuir model for q_e, the following equation can be obtained:

$$W_A = \frac{V_L C_o \left(1 - 0.05\frac{V_f}{V_L}\right)}{\left(\frac{q_m b C_e}{1 + bC_e}\right)} \tag{13}$$

V_L is constant (1×10^{-3} m^3) and applying the value of (q_e) related to the (C_e/C_o=0.05) one can calculate the optimum weight for each pollutant for all systems and these values are listed in Table V.

Table V indicates clearly that for a single system the highly amount of removal achieved for Pb^{2+} with less mass of biosorbent compared with Hg^{2+}, Cr^{3+} and As^{5+}.

This related to the nature of the chemical properties and the highly affinity of Pb^{2+} to be lied and set an unoccupied sites of activated sludge.

V.6. Determination of the External Mass Transfer Coefficient

The external mass transfer coefficients in batch adsorber were determined from the concentration decay curves data at optimum speed and optimum dosage of activated sludge, using Eq. (6). The average calculated values of the external mass transfer coefficient of each pollutant are tabulated in Table VI. From Table VI, Pb^{2+} has the largest value of external mass transfer coefficient in comparison with Hg^{2+}, Cr^{3+} and As^{5+}. This enhances the results regarding Pb^{2+} for its fastest biosorption by activated sludge.

V.7. Determination of Pore Diffusion Coefficient

Pore diffusion coefficients for each solute were obtained from the numerical solution via COMSOL multiphysics of Eqs. (4) and (5) with the appropriate initial and boundary conditions that describe the film and inter-particle transport mechanisms in batch-wise experiments.

TABLE III

PARAMETERS OF SINGLE SOLUTE ISOTHERM FOR PB^{2+}, HG^{2+}, CR^{3+} AND AS^{5+}

Model	Parameters	Pb^{2+}	Hg^{2+}	Cr^{3+}	As^{5+}
Langmuir [13] $q_e = \frac{q_m b C_e}{1 + bC_e}$	q_m	77.486	10.788	4.6404	2.8289
	b	0.0273	0.3011	0.2395	0.2119
	R^2	0.9979	0.9923	0.9897	0.9868
	R_s	0.4228	0.0623	0.0771	0.0862
Freundlich [14] $q_e = K\, C_e^{1/n}$	K	2.9086	3.2796	1.4419	0.8997
	n	1.3487	3.1683	3.2110	3.4287
	R^2	0.9952	0.9716	0.9383	0.9594
Combination of Langmuir-Freundlich [15] $q_e = \frac{b q_m C_e^{1/n}}{1 + bC_e^{1/n}}$	q_m	92.918	14.789	4.2787	3.7637
	b	0.0249	0.2430	0.1954	0.2404
	n	1.0645	1.6653	0.7518	1.6711
	R^2	0.9978	0.9903	0.9853	0.9748
Radke-Praunsitz [16] $q_e = \frac{K_{RP}\, C_e}{1 + \left(\frac{K_{RP}}{F_{RP}}\right) C_e^{1-N_{RP}}}$	K_{RP}	31.412	5.5240	6.2218	1.4705
	F_{RP}	2.3963	5.7108	0.9846	1.2384
	N_{RP}	0.2315	0.1798	0.0804	0.1677
	R^2	0.9979	0.9858	0.9839	0.9638
Khan [17] $q_e = \frac{Q_{max} b_k C_e}{\left(1 + b_k C_e\right)^{a_k}}$	Qmax	25.102	5.7536	5.919	1.4092
	b_K	0.0920	0.7247	0.1747	0.7238
	a_K	0.5099	0.8215	1.1072	0.8112
	R^2	0.9979	0.9848	0.9837	0.9633
Reddlich-Peterson [18] $q_e = \frac{A_R C_e}{1 + B_R C_e^{m_R}}$	A_R	2.3963	5.7107	0.9846	1.2384
	B_R	0.0763	1.0338	0.1582	0.8422
	m_R	0.7685	0.8202	1.0801	0.8323
	R^2	0.9979	0.9858	0.9839	0.9746
Toth [19] $q_e = \frac{K_t C_e}{\left(a_t + C_e\right)^{1/t}}$	K_t	7.7968	5.4323	7.1359	1.3258
	a_t	10.866	1.3799	5.7225	1.3816
	t	1.9612	1.2172	0.9032	1.2327
	R^2	0.9979	0.9848	0.9837	0.9633
Temkin [20] $q_e = \frac{RT}{b} ln\left(K_T C_e\right)$	b	8.5310	1.6750	0.9610	0.5310
	K_T	0.9345	9.1780	2.5650	3.2380
	R^2	0.9855	0.9472	0.9364	0.9214
Dubinin-Radsukevch [21] $q_e = q_D\ exp\left[-B_D \left(RT\, ln\left(1 + 1/C_e\right)\right)^2\right]$	q_D	29.5382	9.5898	3.9281	2.3131
	B_D	$6.76\text{x}10^{-6}$	$1.88\text{x}10^{-6}$	$1.29\text{x}10^{-6}$	$1.21\text{x}10^{-6}$
	R^2	0.8777	0.8778	0.9417	0.7348
Harkins-Henderson [22] $q_e = \frac{K_h^{1/n_h}}{C_e^{1/n_h}}$	K_h	0.2369	0.0232	0.3088	1.4370
	n_h	-1.3487	-3.1683	-3.2110	-3.4288
	R^2	0.9943	0.9716	0.8871	0.9131
BET [23] $q_e = \frac{BQC_e}{\left(C_s - C_e\right)\left[1 + \left(B-1\right)\left(C_e/C_s\right)\right]}$	Q	16.865	2.0937	1.1189	0.4761
	B	-10.762	-8.7000	-11.796	-7.0504
	R^2	0.9774	0.7203	0.8159	0.7557

TABLE IV
FT-IR ANALYSIS FOR RAW AND LOADED DRY ACTIVATED SLUDGE

Functional group	Type of bond	Raw DAS		Loaded DAS							
				Pb^{2+}		Hg^{2+}		Cr^{3+}		As^{5+}	
		wave No. cm^{-1}	Tr (%)*	wave No. cm^{-1}	Tr (%)	wave No. cm^{-1}	Tr (%)	wave No. cm^{-1}	Tr (%)	wave No. cm^{-1}	Tr (%)
Carboxylic acid, Amine, Amide	O-H stretch, N-H_2 stretch, N-H stretch	3411.84	0.21	3404.13	0.66	3411.84	0.54	3411.84	0.32	3406.05	0.38
Alkanes, Carboxylic acid	C-H stretch, O-H stretch	2925.81	0.31	2923.88	0.88	2923.88	0.8	2923.88	0.74	2923.88	0.625
Alkanes, Carboxylic acid	C-H stretch, O-H stretch	2854.45	0.55	2854.45	1.22	2854.45	1.08	2854.45	1.03	2854.45	1
Carboxylic acid, Alkenes, Amides, Imines	C=O stretch, C=C stretch, N-H stretch, R_2C=N-R stretch	1652.88	0.155	1647.1	0.6	1652.88	0.58	1650.95	0.6	1652.88	0.38
Amides, Nitro groups, Amines	N-H bend, NO_2 (aliphatic), N-H_2 bend	1570	0.225	1560	0.64	1550	0.65	1550	0.78	1570	0.6
Amines, Amides, Nitro groups,	N-H_2 bend, N-H bend, NO_2 (aromatic)	1520	0.15	1520	0.6	------	------	------	-----	1520	0.51
Carboxylic acids	O-H bend	1450	0.058	1440.73	0.52	1442.66	0.535	1445	0.65	1434.94	0.4
Alkenes, Carboxylic acid,	C-H in-plane bend, C=O stretch, O-H bend	1417.5	0.058	-----	-----	------	-----	1417.5	0.6	1417.5	0.4
Alcohols, Ethers, Carboxylic acid, Alkyl halides, phosphines	-OH stretch, C-O-C stretch, C=O stretch, C-F stretch, P-H bend	1016.42	0.05	1016.42	0.21	1016.42	0.26	1016.42	0.2	1016.42	0.06
Sulfonates, phosphines	S-O stretch, P-H bend	873.69	0.20	873.69	0.9	873.69	0.875	873.69	1.1	873.69	0.68

Note: * Transmittance %, ------: No peak

TABLE V
OPTIMUM WEIGHT OF DAS FOR REACHING VALUES OF C_E/C_O EQUAL TO 0.05

Pollutants	Optimum weight (g)
Pb^{2+}	9.6939
Hg^{2+}	10.2719
Cr^{3+}	27.3703
As^{5+}	48.4872

TABLE VI
AVERAGE CALCULATED VALUES OF MASS TRANSFER COEFFICIENT OF EACH POLLUTANT

Pollutant	k_f (m/s)
Pb^{2+}	16.1629 x 10^{-6}
Hg^{2+}	9.8385 x 10^{-6}
Cr^{3+}	5.0256 x 10^{-6}
As^{5+}	0.8357 x 10^{-6}

The pore diffusion coefficient was found from typical concentration decay curve for each solute at optimum agitation speed and dosage of activated sludge by trial and error technique predicted on the minimization of the square difference between experimental and predicted data from pore diffusion model. These results are shown in Fig. 3.

It is clear from Figs. 5, there was approximately a good matching between experimental and predicted data by using pore diffusion model.

From the previous figure and calculated values of (D_p), the highest value of pore diffusion coefficient was for Pb^{2+} then Hg^{2+}, Cr^{3+} and As^{5+}.

This reveals the adsorption process is very dominant for removing of Pb^{2+} more efficiently then Hg^{2+}, Cr^{3+} and As^{3+}.

The pore diffusion coefficient for each pollutant with the correlation coefficient was found in Table VII.

V.8. Rate Limiting Mass Transfer Mechanisms

The controlling mass transfer rate was determined by verification of experimental data to Weber and Morris model [28], Eq. (14):

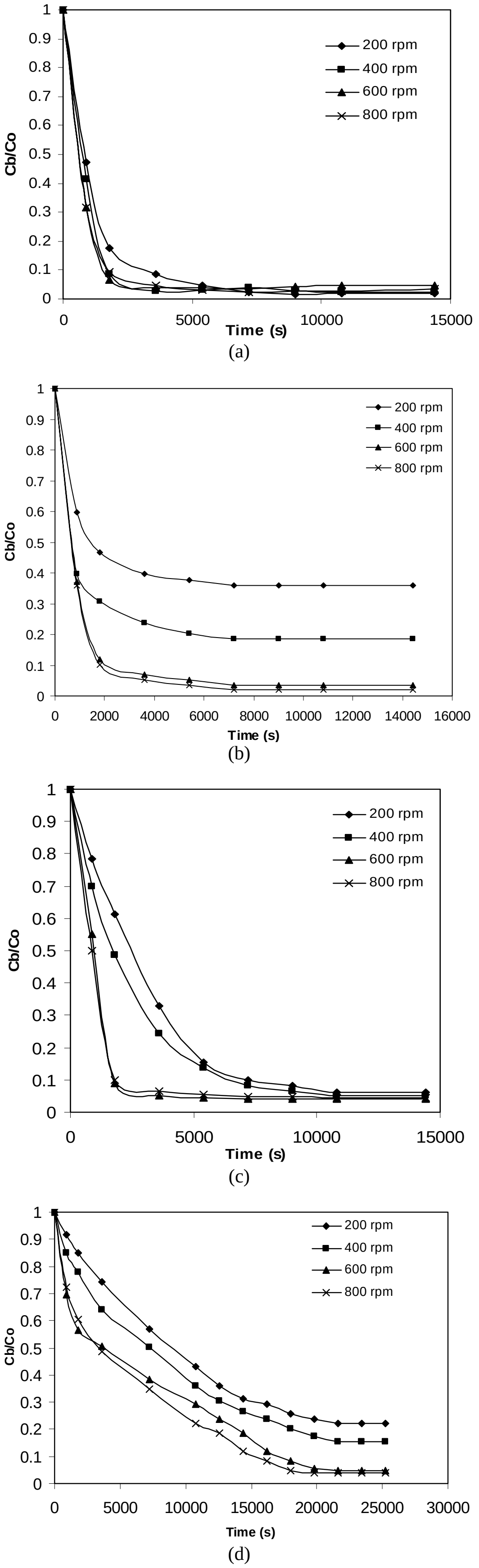
$$q = k_{id}\, t^{1/2} \tag{14}$$

Figs. 4 relate biosorption capacity to sequare root of time.

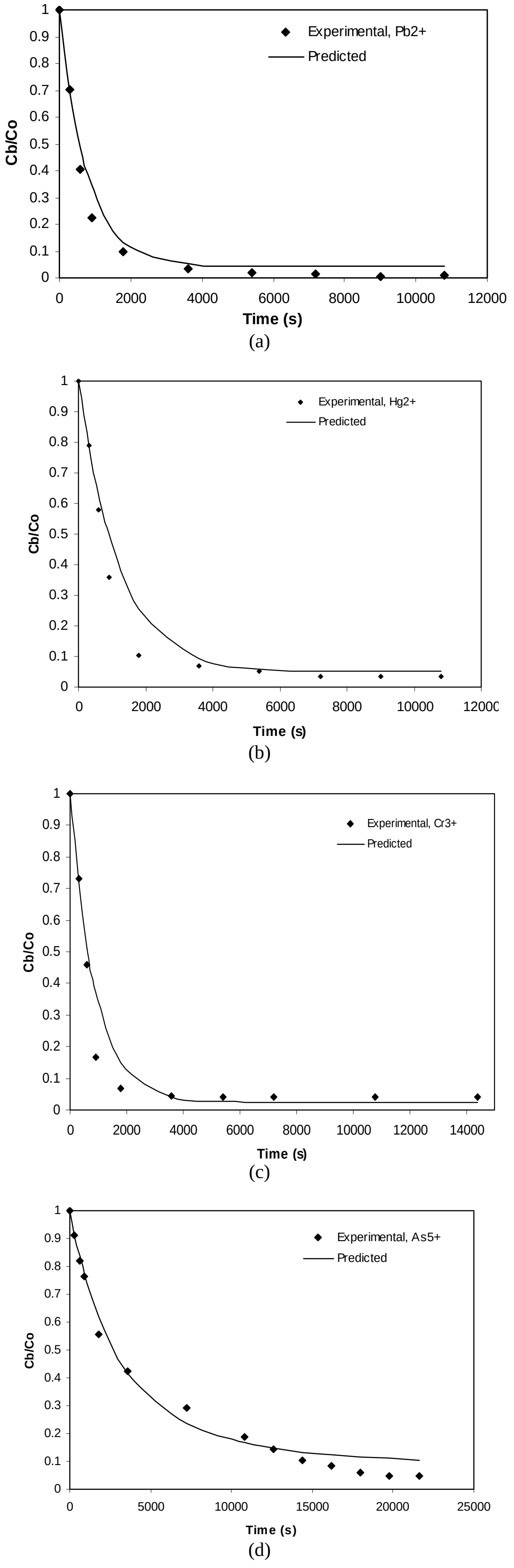
It is obvious that regressed data gave straight lines of intercepts different from zero for all metal species: in this case two mechanisms were assumed to be limiting, external mass transfer and intraparticle diffusion [29].

TABLE VII
PORE DIFFUSION COEFFICIENT OF THE POLLUTANTS AND RELATED CORRELATION COEFFICIENT (R^2)

Pollutants	D_p m^2/s	R^2
Pb^{2+}	5.9030 x10^{-9}	0.9889
Hg^{2+}	3.0551 x10^{-9}	0.9748
Cr^{3+}	1.990 x10^{-9}	0.9579
As^{5+}	1.3335 x10^{-10}	0.9905



Figs. 4. Concentration-time decay curves at variable agitation speeds. (a) Pb^{2+}, (b) Hg^{2+}, (c) Cr^{3+}, (d) As^{5+}



Figs. 5. Experimental and predicted concentration-time decay curves. (a) Pb^{2+}, (b) Hg^{2+}, (c) Cr^{3+}, (d) As^{5+}.

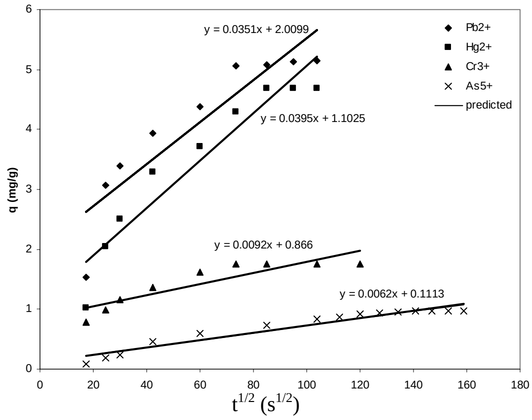


Fig. 6. Biosorption capacity versur sequare root of time for of Pb^{2+}, Hg^{2+}, Cr^{3+} and As^{5+} onto DAS

VI. Conclusion

A wide range of batch experiments were carried out covering four metals ions. Results adopted that dried activated sludge was suitable for the removal of lead, mercury, chromium and arsenic ions from aqueous solution.

The Langmuir isotherm model was well described the sorption process of single component systems onto dried activated sludge. The maximum biosorption uptake of the studied metal ions showed the following affinity order $Pb^{2+} > Hg^{2+} > Cr^{3+} > As^{5+}$. FT-IR analysis adopted that carboxylic acid, amide, and amine groups played the most important role in binding lead, chromium, mercury and arsenic cations onto DAS. An optimum agitation speed was found 600 rpm and optimum biosorbent dosage was determined for each metal ions. Kinetic data proved that both of the external mass transfer and intraparticle resistances were the controlling mass transfer rate. COMSOL multiphvsics software was used to predict biosorption dynamics in batch system and showed a good agreement with experimental data.

The results of this study in batch system provide the process parameters, i.e., pore diffusion coefficient, and isotherm equilibrium constants required for design purpose of continuous fixed bed adsorber.

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