Multicomponent Biosorption of Heavy Metals Using Fluidized Bed of Algal Biomass

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ABSTRACT:

This paper aims to study the biosorption for removal of lead, cadmium, copper and arsenic ions using algae as a biosorbent. A series of experiments were carried out to obtain the breakthrough data in a fluidized bed reactor. The minimum fluidization velocities of beds were found to be 2.27 and 3.64 mm/s for mish sizes of 0.4-0.6 and 0.6-1 mm diameters, respectively. An ideal plug flow model has been adopted to characterize the fluidized bed reactor. This model has been solved numerically using MATLAB version 6.5. The results showed a well fitting with the experimental data. Different operating conditions were varied: static bed height, superficial velocity and particle diameter. The breakthrough curves were plotted for each metal. Pb^{2+} showed the largest breakthrough time compared with others, while Cd^{2+} had the lowest value.

Keywords: Algae; Heavy metals; Fluidized bed; Breakthrough curve.

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الخلاصة:

يهدف البحث الى دراسة الامتزاز الحيوي للرصاص، الكادميوم، النحاس والزرنيخ باستخدام الطحالب كمادة ممتزة. اجريت العديد من التجارب باستخدام مفاعل الحشوة المتميعة لغرض الحصول على مخططات الامتزاز الحيوي لكل عنصر. وجد ان سرعة التميع تساوي 2.27 و 3.64 ملم/ثا لحشوة ذات اقطار 0.4-0.6 و 0.6-1 ملم على التوالي. تم اعتماد موديل ثبوت الجريان لغرض تمثيل عملية التميع رياضياً حيث تم حل المعادلات التفاضلية عددياً وباستخدام برنامج MATLAB. اوضحت النتائج تطابق جيد بين النتائج العملية ونتائج الموديل الرياضي. تم دراسة تغيير بعض العوامل مثل ارتفاع الحشوة، سرعة المائع وقطر الحبيبات. واوضحت نتائج مخططات الانفصال ان للرصاص اعلى قيمة وقت للوصول الى التشبع بينما كان للكادميوم اقل قيمة.

كلمات رئيسية: طحالب، عناصر ثقيلة، الحشوة المتميعة، مخطط الانفصال.

1. INTRODUCTION

One of the most challenging environmental problems is the removal of heavy metals and other toxic contaminants from industrial wastewater. Many aquatic environments face metal concentrations that exceed water quality criteria designed to protect humans, environment, animals and (**Gin et al., 2002**). Metals can be distinguished from other toxic pollutants, since are non-biodegradable and can accumulate in the living tissues, thus becoming concentrated throughout the food chain (**Williams et al., 1998**). The metals hazardous to humans include lead, cadmium, mercury, arsenic, copper, zinc, and chromium. Arsenic and cadmium can cause cancer. Mercury can cause mutations and genetic damage, while copper, lead, chromium can cause brain and bone damage (**Wang and Chen, 2009**). Biosorption is an innovative technology that employs inactive and dead biomass for the removal and recovery of metals from aqueous solutions (**Romera et al., 2007; Cui and Grace, 2007**). Various biomasses such as bacteria (**Ridha, 2011**), sludge (**Ali, 2011**), yeast (**Sulaymon et al., 2010**), algae (**Kratochvil, 1997**), fungi (**Brady et al., 1999**) and plants (**Melcakova and Ruzovic, 2010**) have been used to adsorb metal ions from the environment. Among the most promising types of biosorbents studied are algal biomass (**Romera et al., 2006; Figueria et al., 2000**), algal biomass have been reported to have high metal binding capacities due to their containing of functional groups on the cell wall. These functional groups are carboxyl, hydroxyl and sulphate, which can act as binding sites for metals (**Crist et al., 1994**). The term algae refers to a large and diverse assemblage of organisms that contain chlorophyll and carry out oxygenic photosynthesis. Although most algae are microscopic in size and are thus considered to be microorganisms, several forms are macroscopic in morphology (**Davis et al., 2003**). The algae are included in the plant kingdom and are distinguished from other Chlorophyllous plants on the basis of sexual reproduction. There are seven divisions of algae, divisions which include the larger visible algae are: Cyanophyta (blue-green algae), Chlorophyta (green algae), Rhodphyta (red algae) and Phaeophyta (brown algae). These divisions are subdivided into orders, which are subsequently divided into families and then into genus and species. Differences between these types of algae are mainly in the cell wall, where sorption takes place (**Romera et al., 2007**). The annual production of algae in the world lately reached to 5.9 million ton (**Sunduqgee, 2006**). Green and blue green algae in Iraq are available in huge quantities, approximately in all surface water resources and marshes (**Al-Hassany, 2003; Kassim, 2007**). Fixed and fluidized beds have been used widely by chemical industry, pharmaceutical industry, food industry, wastewater treatment and recovery of different substance (**Park et al., 1999**). Fluidized beds are common and important reactors in process engineering because of the good mass and heat transfer rate between the fluid and the particles, and between the particles and the side wall of the column (**Fu and Liu, 2007**). The term fluidization is used to describe the condition of fully suspended particles. Liquids or gases are passed at certain velocity up through a bed of solid particles, at this velocity the pressure drop across the bed counter balances the force of gravity on the particles and further increase in velocity achieve fluidization at a minimum fluidization velocity. Fluidization quality is closely related to the intrinsic properties of particles, e.g. particle density, particle size and size distribution, and also their surface characteristics **(Richardson, et al., 2002). Diniz et al., (2008**) studied the fixed bed biosorption of lanthanum (La^{3+}) and europium (Eu^{3+}) using protonated Sargassum polycystum biomass (brown algae). The sorption mechanism was based on the ion exchange mechanism. The experimental results were fitted with an ion exchange model, good matching and high regression coefficient were obtained. The calculated affinity constants were 2.7 and 4.7 for La^{3+} and Eu^{3+} respectively, demonstrating a higher affinity of biomass towards Eu^{3+}. Column experiments were carried out in fixed bed system to estimate the mass transfer coefficient for each metal. A series of consecutive sorption/desorption runs demonstrated that the two metals could be recovered. **Rathinam et al., (2010)** studied the batch **biosorption** of cadmium onto Hypnea valentiae biomass (red algae). The results showed that the biosorption capacity was low at pH 3.0, but increased considerably from 4.30 to 14.54 mg/g as the pH solution increased to 5.0. On further increase in pH to 6.0 and 7.0 the biosorption capacity remained almost stable at 16.89 and 17.02 mg/g, respectively. **Wang et al., (2011)** studied the removal of emulsified oil from water by inverse fluidization of hydrophobic silica aerogels (Nanogel). The hydrodynamics characteristics of the Nanogel granules of different size ranges are studied by measuring the pressure drop and bed expansion as a function of superficial water velocity. The minimum fluidization velocity was measured experimentally by plotting the pressure drop against the superficial fluid velocity. The results showed that the major factors which affect the oil removal efficiency and capacity are the size of Nanogel granules, bed height, and fluid superficial velocity.. Also the experimental data showed that the Nanogel particles can absorb as much as 2.8 times their weight of oil by the inverse fluidization process.

From the previous literature related to the biosorption of heavy metal using algae, it can be concluded the following points:

- In recent years, there have been a significant increase in the studies concerning algae as biosorbents for removal of heavy metal due to their binding ability, availability and low cost.
- It was found that there is lack in literature of using algal biomass as a biosorbent in Iraq
- Several studies concluded that the biosorption mechanisms involving algae are an ion exchange reaction type between light metals already bound to the algae and other metals present in the aqueous solution. Also, the optimum pH for removal was around 3 to 5.

This work aims to study some parameters that influenced the behavior of liquid fluidized bed for removal of Pb^{2+}, Cd^{2+}, Cu^{2+} and As^{3+} from wastewater using algal biomass.

2. FLUIDIZED BED MODELS

Breakthrough curves serve two purposes (a) to decide whether the adsorbate is efficient for the required separation and (b) to establish break point (process interpretation), based on some criterion, either technical, economic or legal (**Knaebel, 1999**).

In the fluidized bed, the aqueous solution with influent concentration flows from the bottom to the top. The variation of the pollutant concentration in the liquid phase with time at different bed lengths can be measured. In the present work, a fluidized bed reactor was adopted for the continuous removal of metal. **Fig.1** shows a model of fluidized bed reactor.

The first assumption considers that the concentration is uniform in the radial direction. Secondly, there is no material product in the reactor (no chemical reaction between the fluid and bed). Finally, the fluid stream is plug flow and mixed solid flow. Based on the above assumptions, the governing equation can be obtained from differential mass balance of the bulk-fluid phase. The following equations can also be derived from equations of continuity (**Park et al., 1999**):

$$\begin{pmatrix}\text{Rate of input conc. by}\\ \text{convective flow}\end{pmatrix} + \begin{pmatrix}\text{Rate of input conc. by}\\ \text{dispersion}\end{pmatrix} - \begin{pmatrix}\text{Rate of output conc. by}\\ \text{convective flow}\end{pmatrix} - \begin{pmatrix}\text{Rate of output conc. by}\\ \text{dispersion}\end{pmatrix} - \begin{pmatrix}\text{Solute lost by}\\ \text{sorption}\end{pmatrix} = \frac{\partial c}{\partial t}.\varepsilon.dz \qquad (1)$$

Then:

$$\frac{U}{\varepsilon}.C + E_z.\frac{\partial C}{\partial z} - \frac{U}{\varepsilon}\left[C + \frac{\partial C}{\partial z}dz\right] - E_z.\left[\frac{\partial C}{\partial z} - \frac{\partial}{\partial z}\left(\frac{\partial C}{\partial z}\right)dz\right] - \frac{(1-\varepsilon)}{\varepsilon}\rho_p\frac{\partial q}{\partial t}dz = \frac{\partial C}{\partial t}.dz \qquad (2)$$

Then, equation (2) can be written as follows:

$$\frac{U}{\varepsilon}.C + E_z.\frac{\partial C}{\partial z} - \frac{U}{\varepsilon}.C - \frac{U}{\varepsilon}.\frac{\partial C}{\partial z}dz - E_z.\frac{\partial C}{\partial z} + E_z.\frac{\partial^2 C}{\partial z^2}dz - \frac{(1-\varepsilon)}{\varepsilon}\rho_p\frac{\partial q}{\partial t}dz = \frac{\partial C}{\partial t}.dz \qquad (3)$$

Simplified equation (3) to the following:

$$\frac{\partial C}{\partial t} = E_z\frac{\partial^2 C}{\partial z^2} - \frac{U}{\varepsilon}\frac{\partial C}{\partial z} - \frac{1-\varepsilon}{\varepsilon}\rho_P\frac{\partial q}{\partial t} \qquad (4)$$

The mass balance for the solid phase is expressed as:

$$(1-\varepsilon)\rho_p\frac{\partial q}{\partial t} = K_L.a.(C - C^*) \qquad (5)$$

Substituting Eq.(5) into Eq.(4), the following equation can be obtained:

$$\frac{\partial C}{\partial t} = E_z\frac{\partial^2 C}{\partial z^2} - \frac{U}{\varepsilon}\frac{\partial C}{\partial z} - \frac{K_L.a}{\varepsilon}(C - C^*) \qquad (6)$$

The initial and boundary conditions are:

$0<z<L, t=0; C = C^* = 0$ (7)

$z=0, t\geq 0; C = C_i$ (8)

$z=L, t>0; \frac{\partial c}{\partial z} = 0$ (9)

The partial differential equation (eq. 6) was solved numerically using Matlab software Version 6.5.

3. EXPERIMENTS AND MATERIALS

3.1 Biomass and Solutions Preparation

Mixture of green (Chlorophyta) and blue-green (Cyanophyta) algae were used in this study as the biosorbent of heavy metal. Large quantities of algae have been observed their spreading along the artificial irrigation canal in Baghdad University. This canal feed by water from the Tigris River. For this study, algae were collected from the selected location of this canal in April and September 2011. Approximately greater than 5 kg of fresh algae was collected at each month. Sample of 0.5 kg of collected algae at each month were analyses for their genus and species and percentage weight by using microscope. These analyses were achieved according to the standard methods (**APHA, 2005**) in laboratories of Iraqi Ministry of Sciences and Technology/ Water Treatment Directory. The results showed that there are five species were dominated in these two samples, Oscillatoria princeps alga was the highest percentage, these results were listed in **Table 1.**

The collected algae were washed several times with tap water and deionized water to remove impurities and salts. The algal biomass was sun-dried and then dried in oven at 50 °C for 48 h. The dried algal biomass was shredded, ground in a mortar and sieved. Average size of 0.4-0.6 and 0.6-1 mm particle diameters was used for biosorption experiments in system. he biomass particle size distribution was determined using a set of standard sieves. Since the algal biomass could swell in water, therefore the biomass was initially soaked in water and then wet sieved. Particles density, surface area and voidage were measured and listed in **Table 2.**

Pb^{2+},Cd^{2+},Cu^{2+} and As^{3+} ions solutions were prepared by dissolving $Pb(NO_3)_2.2H_2O$, $Cd(NO_3)_2$, $Cu(NO_3)_2.3H_2O$ and As_2O_3 in distilled water. These solutions were kept at 25 °C. The pH was adjusted at 4 for all heavy metals solution using 0.1M HNO_3 and 0.1M NaOH solutions. A pH meter type WTW/ inoLab series was used for pH value reading. All chemicals used in this work were analytical reagent grade and were used without further purification. The solubility of $Pb(NO_3)_2.2H_2O$, $Cd(NO_3)_2$, $Cu(NO_3)_2.3H_2O$ and As_2O_3 in water are 54.3, 136, 125 and 1.8 g/100g H_2O, respectively.

3.2 Column Experiments

Fig.2 shows a schematic diagram of fluidized bed reactor used in the experiments. Experiments were carried out in a 7.5 cm inner diameter and 1 m high glass column, 0.5 mm stainless steel distributer was installed at the bottom of the reactor to distribute an influent flow smoothly. A U-tube manometer was connected to the reactor to read the pressure of water at each flow meter reading, the manometer has an inside diameter of 5 mm and length is 50 cm. The manometer liquid is Carbon Tetrachloride (CCl_4) with ρ_l=1590 kg/m^3. The feed containing 50 ppm for each element was pumped upward through the column at selected velocities (1.1U_{mf} and 1.5 U_{mf}) for each particle size. The samples were taken from an effluent of the reactor at time intervals 1, 2, 5, 10, 20, 30, 40, 50, 60, 70, 80, 90 min. During the experiment, the pressure drop, and fluidized bed height were measured at the corresponding time intervals.

4. RESULTS AND DISCUSSION

4.1 Mechanisms of Heavy Metal Binding in Algae

Several studies concluded that the major biosorption mechanism involving algae is an ion exchange reaction type between cations (light metals: Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}) already bound to the algae and other metals present in the aqueous solution (**Naja and Volesky, 2006**). **Fig.3** describes the progression of a molecule of adsorbate from the bulk towards the site of ion exchange on algae (**Hamm et al., 2002)**. There are two major determining factors for exchange biosorption: the first one is the strength of the charge on the ions (electronegativity), the other is the size of the adsorbate (atomic radius of metal ion). **Table 3** shows the atomic properties of Pb^{2+}, Cd^{2+}, Cu^{2+} and As^{3+} ions (**Wikipedia, 2012**). Algal biomass generally contains alkali and alkaline earth metals such as K^{+}, Na^{+}, Ca^{2+} and Mg^{2+} which are originally presented from fresh water. So that, when algal biomass reacts with the heavy metals bearing solution, the light metals released causing an increase in the pH of solution due to form of light metal alkalis. In addition, the release of these light metals caused the increase of electrical conductivity value (EC).

To find the pH and electrical conductivity variation along the biosorption process, four flasks of 250 ml were filled with 100 ml at pH value=4 of four metal solution (50 ppm) and 1 g of dried algae. The flasks were then placed on a shaker and agitated continuously for 4 h at 200 rpm. The pH and EC were measured at different time intervals during the agitation process. **Fig. 4 and 5** show the increase in the pH and electrical conductivity values with time. In this case, the cations of light metals were being eluted from the algal biomass during the experiments, while the heavy metals were being sorbed onto the biomass. **Fig.6** shows the amount of light metals released due to biosorption of these heavy metals onto algal biomass.

4.2 Minimum Fluidization Velocity

The minimum fluidization velocity (U_{mf}) was determined experimentally by measuring the pressure drop through the bed of algal particles. Two particle sizes were used in this study ranging from 0.4-0.6 mm and 0.6-1 mm diameter. The column was partially filled with particles of known mass and then vigorously agitated with water in order to arrange particles and break down any internal structure. After that the bed left to settle down, and then the flow rate increased incrementally from 0 to 100 l/h using a rotameter. At each flow rate increment, the pressure drop was recorded using manometer. **Fig.7** shows the pressure drops across the bed against the superficial fluid velocity in logarithmic scale. The graph is used to read the minimum fluidization velocity (U_{mf}), as well as to show the pressure drop rises linearly below minimum fluidization in the packed bed region and then plateaus above minimum fluidization. The U_{mf} can be read from the sharp change in the pressure drop over the fixed bed region. **Table 4** shows the minimum fluidization velocity, plateau pressure drop (ΔP) and fluidized bed height (h_{mf}) of two different size particles that used in biosorption process.

4.3 Bed Expansion

It is important to be able to establish the relationship between the superficial liquid velocity (U) and the bed voidage (ε) (**Ngian and Martin, 1980**).

The bed voidage can be found experimentally by subtracting the volume of the particles (V_p) from the total volume of the fluidized bed (V_b). Hence, the voidage of the fluidized bed is:

$$\varepsilon = \frac{V_\varepsilon}{V_b} = \frac{V_b - V_p}{V_b} = 1 - \frac{V_p}{V_b} = 1 - \frac{m_p}{\rho_p . V_b} = 1 - \frac{m_p}{\rho_p . A.H} \qquad (10)$$

where $V_{\square}$ is void volume, m_p is the mass of particles (kg), A is the cross sectional area of the bed (m^2), H is the bed height (m).

4.4 Mass Transfer Coefficient

Several authors proposed generalized correlation to predict the mass transfer coefficient. **Park et al., (1999)** concluded the following correlation obtained from experimental data of fluidized bed reactor:

$$\frac{Sh.\varepsilon^{0.5}}{Sc^{1/3}} = 0.62\ Re_p + 0.6 \qquad (11)$$

The diffusivity of each metal can be calculated from the following equation:

$$D_m = 2.74 * 10^{-9}(M_w)^{-1/3} \quad \ldots\ldots (12)$$

where M_w is the molecular weight of metal.

The calculated mass transfer coefficient values at fluid velocity $1.1U_{mf}$ were $2.975*10^{-5}$, $4.53*10^{-5}$, $4.02*10^{-5}$, and $4.887*10^{-5}$ m/s for Pb^{2+}, Cd^{2+}, Cu^{2+} and As^{3+} respectively. In case of fluid velocity equal to $1.5U_{mf}$, values of mass transfer coefficient were $4.86*10^{-5}$, $5.506*10^{-5}$, $5.31*10^{-5}$ and $5.887*10^{-5}$ mm/s respectively.

4.5 Breakthrough Curves

The breakthrough curves for each metal are obtained by plotting C/C_o versus time for Pb^{2+}, Cd^{2+}, Cu^{2+} and As^{3+} respectively. The experimental and predicted breakthrough curves are presented in **Figures (8 to 11)** at different operating conditions. The shape and sharpness of the breakthrough curve for a given adsorbent mainly depend on such factors: equilibrium adsorption isotherm, mass transfer rate, and hydrodynamic factors (such as bed height and contact time) (**Wang et al., 2011**). Different operating conditions were carried out, i.e., changing static bed height, fluid superficial velocity and particle diameter. The biosorption experiments were operated for each metal at static bed heights corresponded to the 50, 100 and 150 g for each particle (sizes 0.4-0.6 and 0.6-1 mm). The fluidizing velocities used in adsorption tests were equal to $1.1U_{mf}$ and $1.5U_{mf}$ mm/s.

The effect of varying the bed height of algal biomass on the biosorption process was investigated in **Fig. 8** for $U=1.1U_{mf}$, C_o=50 ppm, d_p=0.4-0.6 mm and bed weight 50, 100 and 150 g (corresponding to static bed heights 2.5, 5 and 7.5 cm). It can be seen in these Figures with increasing the weight of particles biomass the time at which an effluent concentration reached equilibrium increased, this is due to large contact time occurred between metal solution and particles at high bed height, smaller bed heights will be saturated in less time. Also, an increase in the bed depth will increase the surface area or adsorption site which improves the adsorption process.

The fluid velocity is a major parameter in the design of adsorption column due to its effect on the contact time between the particles and metal solution. **Fig. 9** shows the breakthrough curves that obtained for different fluid velocity ($U=1.1U_{mf}$, $U=1.5U_{mf}$) at bed height=7.5 cm and C_o=50 ppm are presented in. It can be seen that steeper curves occurred for all metals i.e increasing fluid velocity the breakthrough point appeared earlier, this is due to high fluid velocity of the metal in the solution leaves the bed before equilibrium occurs due to the reduction in the contact time. As well as, at low flow rate the metal molecules will have a sufficient contact time to occupy the spaces within the particles.The effect of particle diameter was investigated for four metal solutions at constant flow rate and bed height. **Fig. 10** shows the breakthrough curves at different particle sizes of 0.5 and 0.8 mm. It can be seen that an increase in particle size causes a decrease of the breakthrough time and makes the breakthrough curves much steeper, which would be anticipated with the decreasing the surface locations of ion exchange between the metals and particles.

In addition, the biosorption of each metal was investigated in quaternary system to find the effect of one metal ion on the other. **Fig. 11** shows the experimental and predicted breakthrough curves for the quaternary system. Comparison among the four metals shows that the time for reaching breakpoint (C/C_o=0.1) was 12, 10, 6 and 3 min. for Pb^{2+}, As^{3+}, Cu^{2+}, and Cd^{2+} respectively. This is due to higher affinity of algal biomass toward this metal for Pb than others. Also, due to competition effect occurs the weakest pollutant had a much steeper trend in its breakthrough curves. Additionally, It can be concluded that the adsorption capacity order for the quaternary system onto algal biomass are: Pb>As>Cu>Cd. Pb^{2+} demonstrated higher biosorption compared with others, this can be attributed to high electronagativty of this metal ion.

5. CONCLUSION

The present study evaluated the removal of Pb^{2+}, Cd^{2+}, Cu^{2+} and As^{3+} from wastewater using algal biomass as adsorbent material in fluidized bed reactor. The breakthrough curves were plotted for each metal, Pb^{2+} showed the largest breakthrough time compared with others, while the Cd^{2+} had the lowest value. This can be attributed to the largest electronegativity value compared with others.

In fluidized bed system, an increase in the bed depth of algal biomass will increase the breakthrough time. An increase in the bed depth will increase surface area of adsorption. Increasing the solution flow rate decreased the breakthrough time due to the decrease in the contact time between the adsorbate and the adsorbent, as well as, at low flow rate the metal ions will have a sufficient contact time to occupy the spaces within the particles. Also, it was found that an increase in particle size caused a decrease of the breakpoint time due to surface area of large particles is lower than small particles.

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NOMENCLATURE

a	Specific surface area (m^2/m^3)	m_p	Mass of particles (g)
A	Cross sectional area of the bed (m^2)	Mw	Molecular weight (g/mole)
C_i	Initial heavy metal conc. (mg/l)	ΔP	Pressure drop in fluidized bed (pa)
C*	Equilibrium heavy metal conc. (mg/l)	q_M	Adsorption amount of metal ions (mg/kg)
C	Conc. of heavy metal at any time (mg/l)	Sc	Schmidt number , $\mu/\rho.D$
d_p	Particle diameter (mm)	Sh	Sherwood number, $K_L.d/D$
D_m	Diffusivity coefficient (mm^2/s)	t	Time (min)
H	Bed height (cm)	U	Superficial velocity (mm/s)
h_{mf}	Fluidized bed height (cm)	U_{mf}	Minimum fluidization velocity (mm/s)
L	Total bed height (cm)	V	Volume of solution (l)
		z	Bed height (cm)

GREEK SYMBOLS

ρ_ℓ	Density of liquid (kg/m^3)	μ_ℓ	Viscosity of liquid (kg/m.s)
ρ_p	Real density of particles (kg/m^3)	ε	Bed voidage

Table 1. Division, genus, species and weighting percentage of collected algae

Division	Genus and Species	Percentage	
		June 2011	September 2011
Cyanophyta	Oscillatoria princeps	88 %	91 %
Chlorophyta	Spirogyra aequinoctialis	5 %	3 %
Cyanophyta	Oscillatoria subbrevis	2 %	2 %
Cyanophyta	Oscillatoria formosa	3 %	1 %
Chlorophyta	Mougeta sp	1 %	2 %
others	---	1 %	1 %

Table 2. Particles properties of algal biomass

Particle diameter (mm)	0.4-0.6	0.6-1
Bulk density (kg/m^3)	474	400
Real density (kg/m^3)	1120	1120
Surface area (m^2/g)	1.88	1.65
Particle porosity (--)	0.713	0.77
Bed Voidage ε(--)	0.577	0.642

Table 3. The atomic properties of Pb^{2+}, Cd^{2+}, Cu^{2+} and As^{3+} ions (Wikipedia, 2012)

Metal	Atomic Radius (pm)*	Electronegativity (Pauling scale)**
Pb^{2+}	175	2.33
Cd^{2+}	151	1.69
Cu^{2+}	128	1.9
As^{3+}	119	2.18
Sequence	Pb>Cd>Cu>As	Pb>As>Cu>Cd

* pico meter =10^{-12} m.

** Pauling Scale: A dimensionless quantity, on a relative scale running from around 0.7 to 3.98 (Hydrogen was chosen as the reference, its electronegativity was fixed first at 2.1, later revised to 2.20).

Table 4. U_{mf}, ΔP and h_{mf} of two different size particles

Particle size (mm)	Mass (g)	Static height (cm)	U_{mf} (mm/s)	ΔP (pa)	h_{mf} (cm)
0.4-0.6	50	2.5	2.27	56.3	5
	100	5	2.27	80.1	10
	150	7.5	2.27	112	15
0.6-1	50	3	3.64	66.1	6
	100	6	3.64	103.3	12
	150	9	3.64	124.8	18

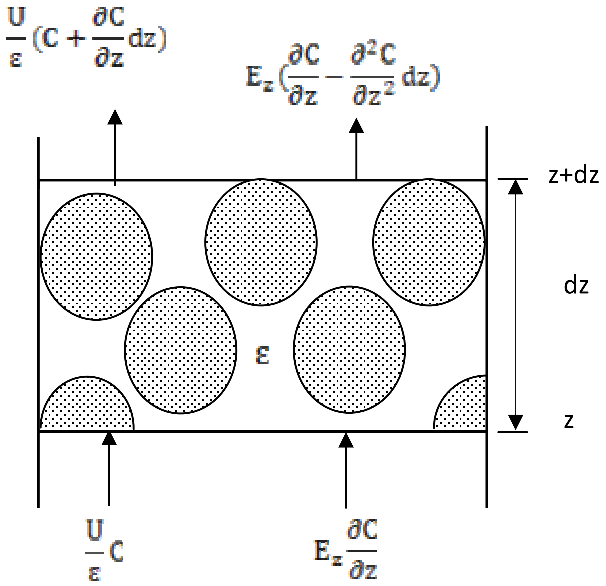

Fig.1 A model of a fluidized bed reactor (Park et al., 1999)

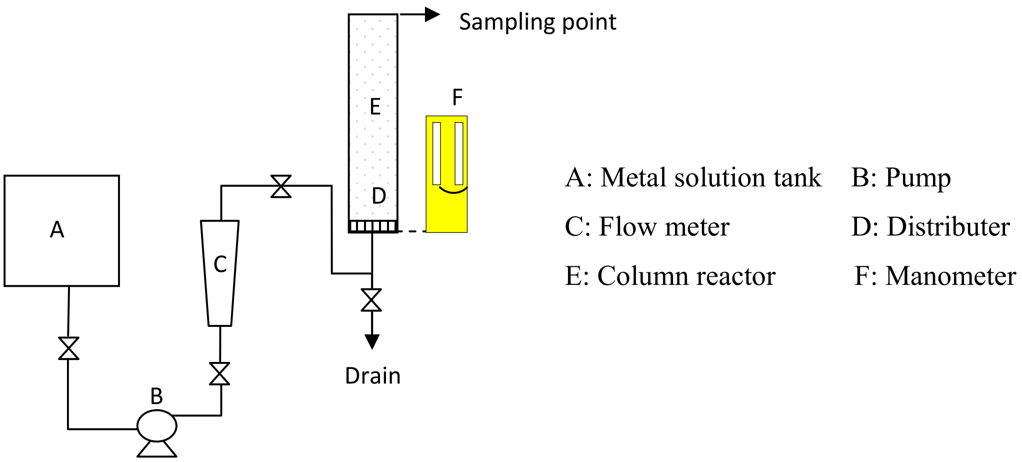

Fig.2 Schematic diagram of fluidization experimental setup

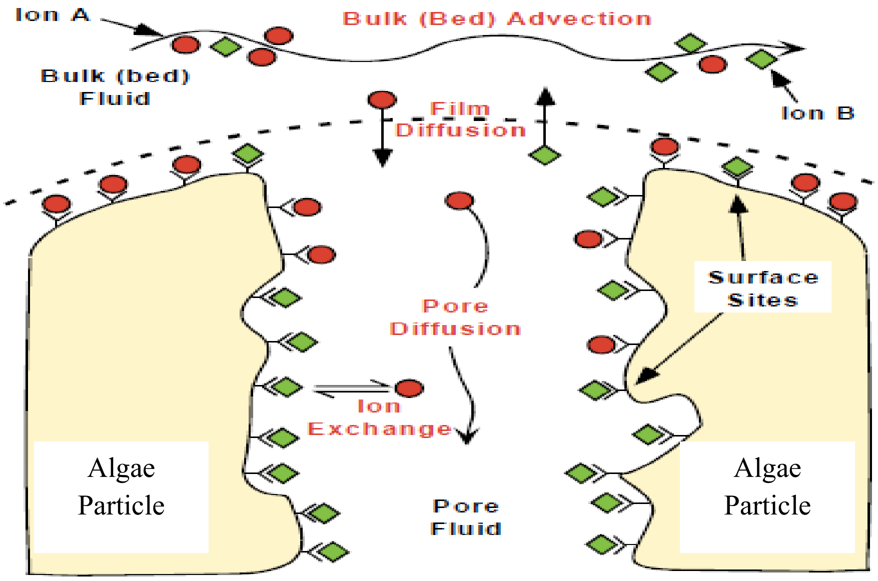

Fig. 3 Graphical representation of various mass transport mechanisms due to ion exchange between A and B ions in algae (Hamm et al., 2002)

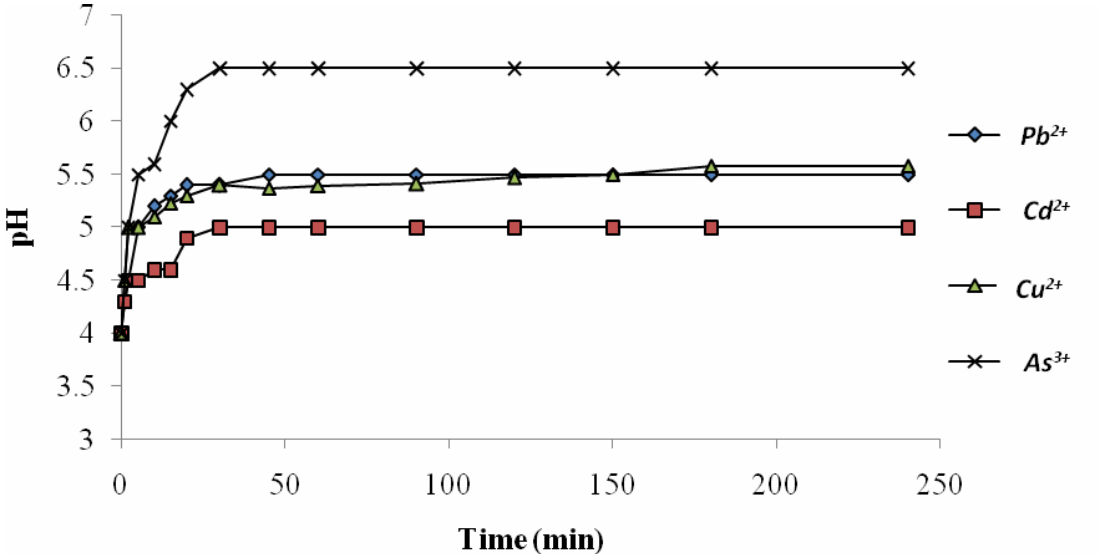

Fig.4 pH evolution as a function of time of Pb^{+2}, Cd^{+2}, Cu^{+2} and As^{+3} ions biosorption, C_o=50 ppm, contact time 4 h and 200 rpm

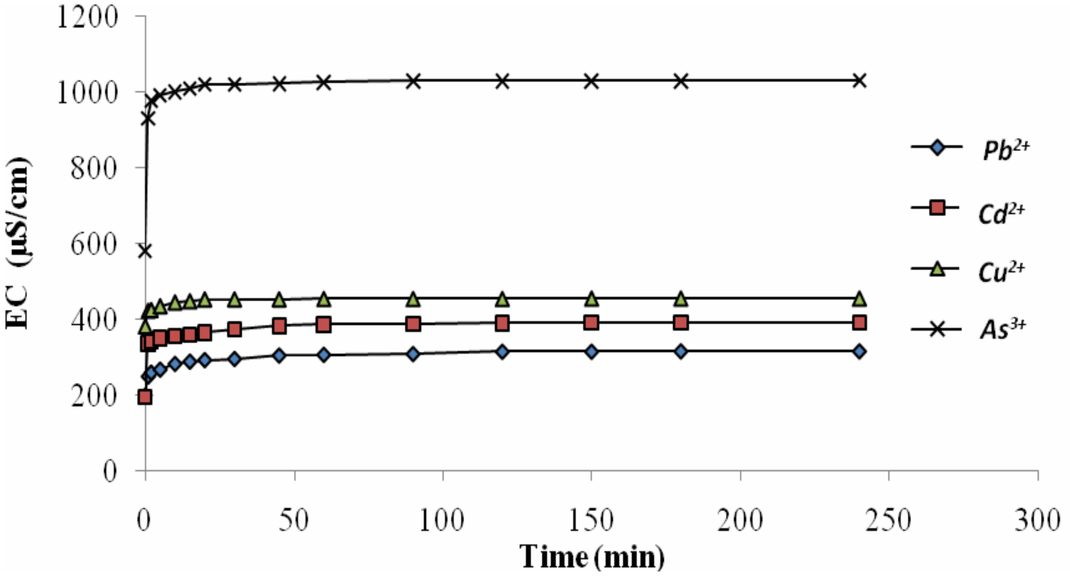

Fig. 5 EC evolution as a function of time of Pb^{+2}, Cd^{+2}, Cu^{+2} and As^{+3} ions biosorption, C_o=50 ppm, contact time 4 h and 200rpm

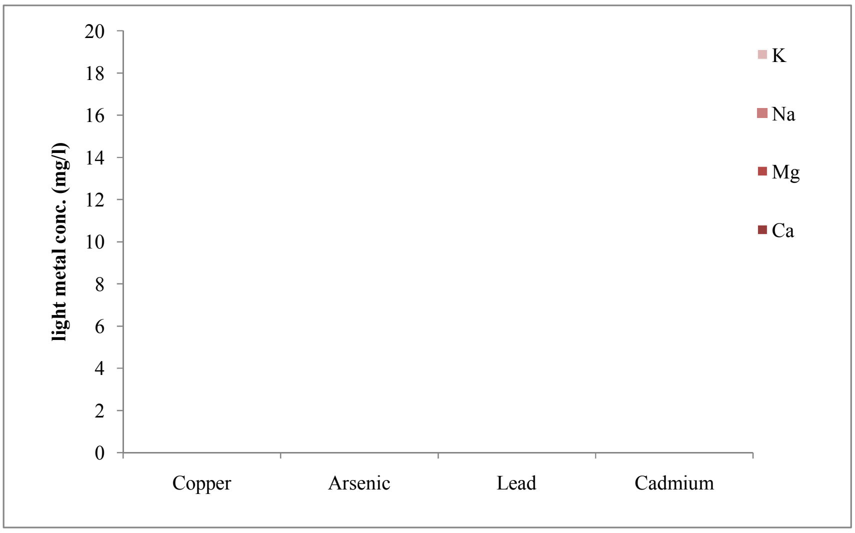

Fig.6 Amounts of light metals released due to heavy metal biosorption, C_o=50 ppm, contact time 4 h. and 200rpm

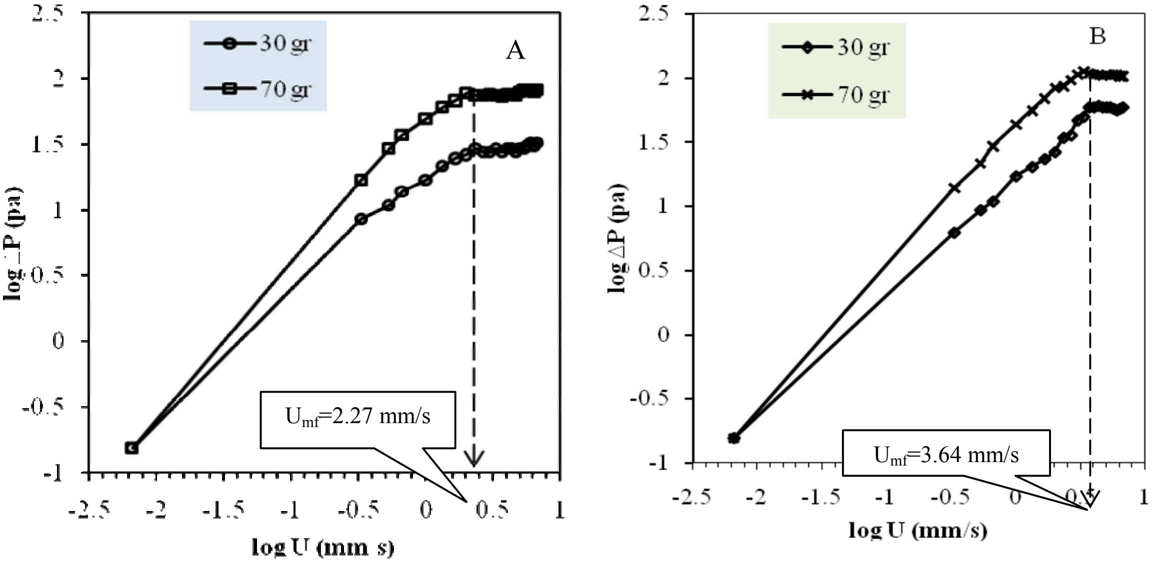

Fig.7 Pressure drop vs. superficial fluid velocity in algal bed, A: 0.4-0.6 mm and B: 0.6-1 mm diameter

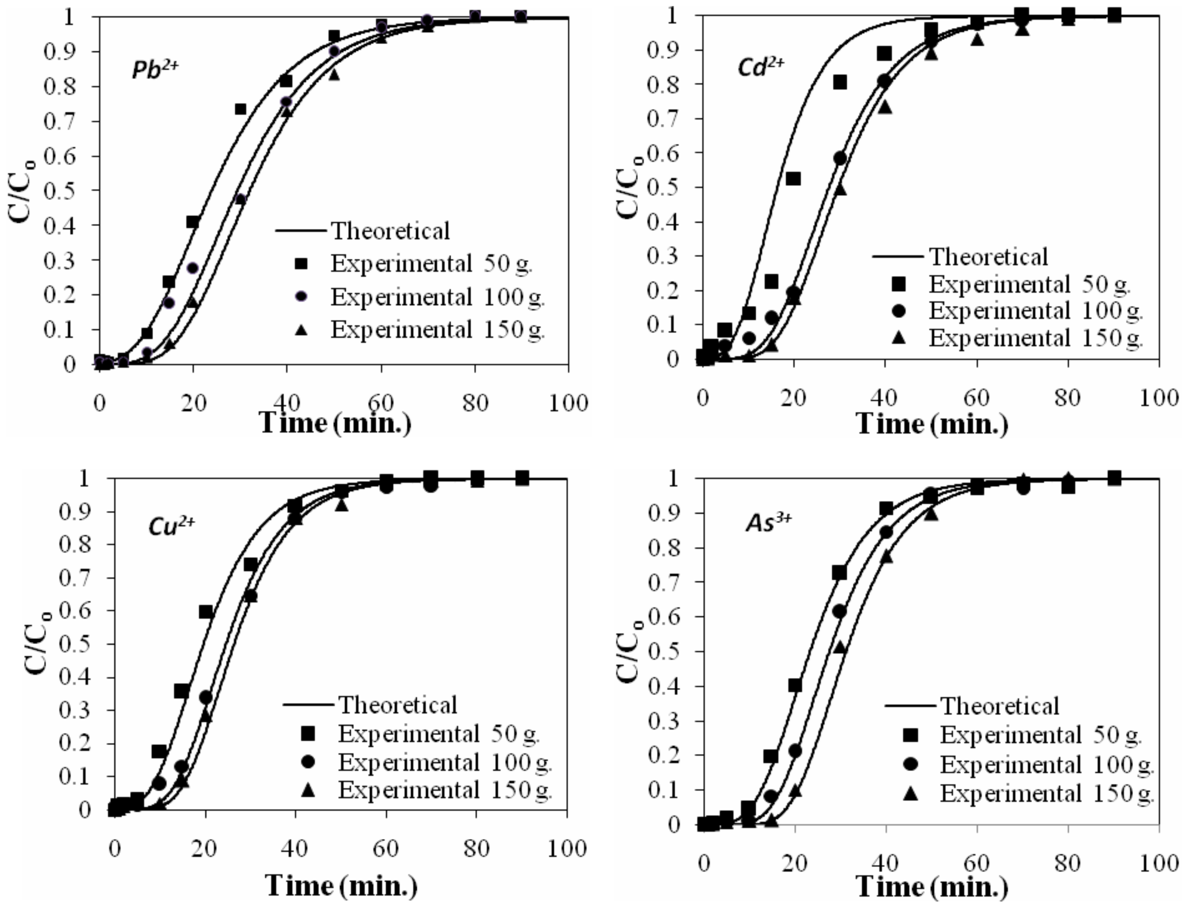

Fig.8. Experimental and theoretical breakthrough curves at different bed weight, Co=50 ppm, pH=3, 25°C, d_p=0.5 mm and U=1.1U_{mf}.

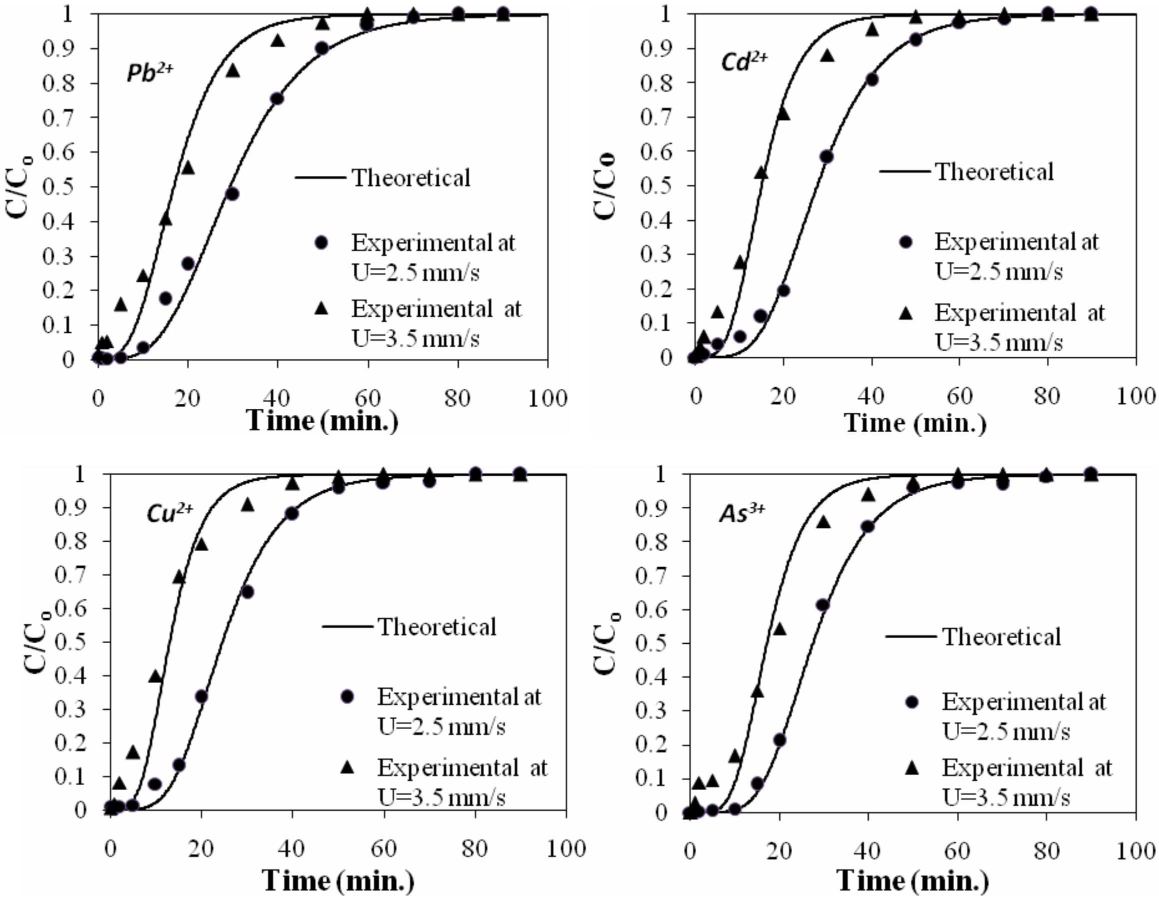

Fig.9. Experimental and theoretical breakthrough curves at 100 g algal biomass, Co=50 ppm, pH=4, 25°C, d_p=0.5 mm, U=2.5 and 3.5 mm/s

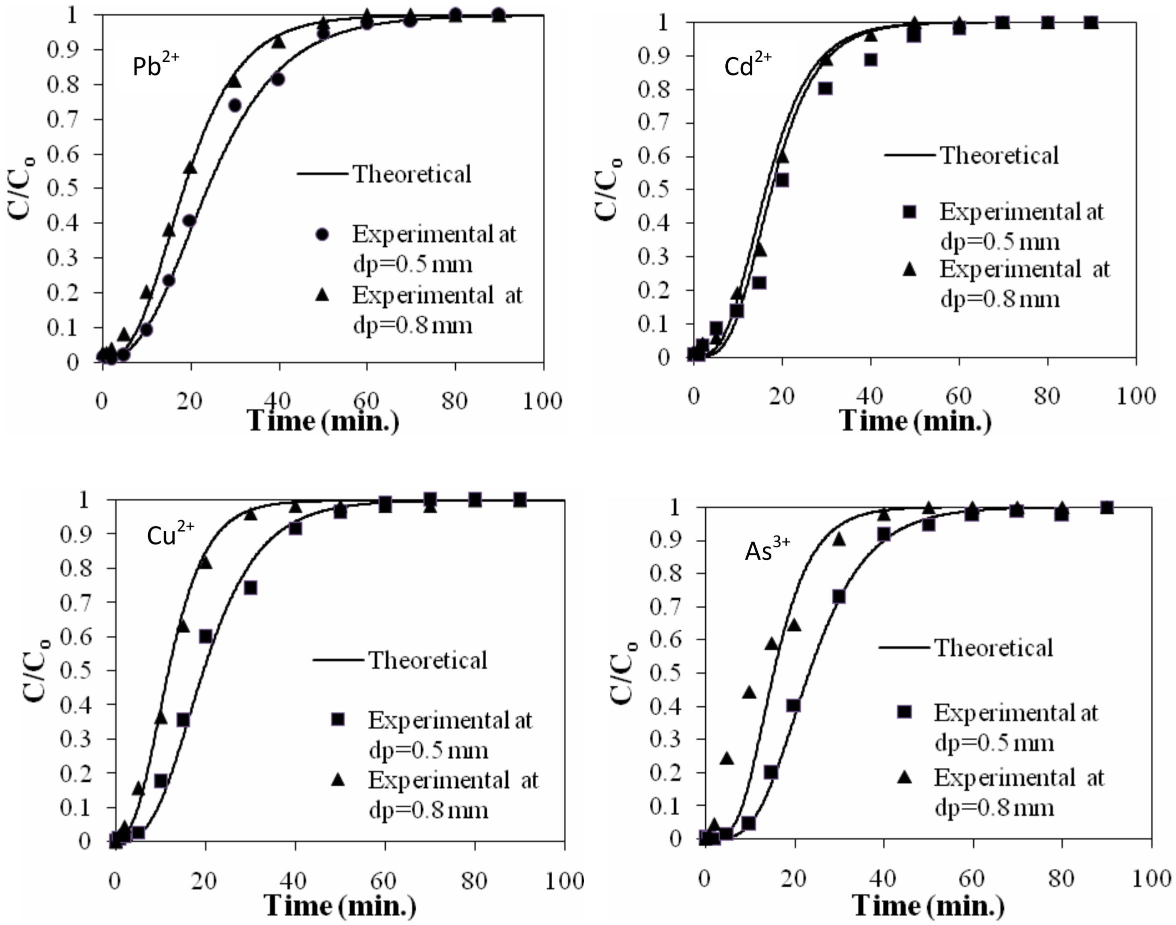

Fig.10. Experimental and theoretical breakthrough curves of 50 g, C_o=50 ppm, pH=4, 25°C, U=2.5 mm/s, d_p=0.5 and 0.8 mm

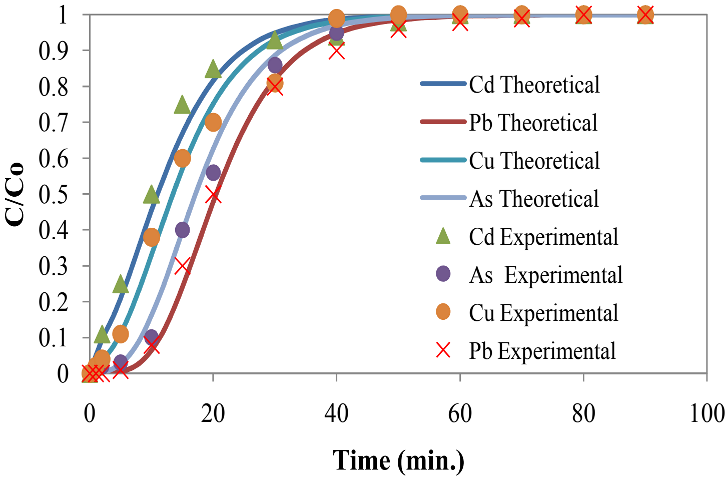

Fig.11. The experimental and predicted breakthrough curves for biosorption of quaternary system , pH=4, C_o=50 ppm, w=150 g