

# Competitive Biosorption of Lead Mercury Chromium and Arsenic Ions onto Activated Sludge in Batch Adsorber

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## Abstract

A wide range of batch experiments were carried out for estimation of the key process parameters in competitive biosorption of  $Pb^{2+}$ ,  $Hg^{2+}$ ,  $Cr^{3+}$  and  $As^{5+}$  from simulated of wastewater onto dry activated sludge in batch adsorber. Eleven isotherm models were used for single component and five models for multi-component systems. The Langmuir model gave the best fit for the data of single component, while the binary, ternary and quaternary systems were fitted successfully with extended Langmuir model. The biosorption capacity for single metal decreased by 11-51 %, 53-88 % and 79-94 % in the binary, ternary and quaternary systems respectively at the optimum agitation speed 600-800 rpm. An order of metal biosorption capacity onto dried activated sludge was the same in the case of

competitive multi-metal sorption conditions as it was for single-element sorption, namely  $Pb^{2+} > Cr^{3+} > Hg^{2+} > As^{5+}$ . FT-IR analysis was carried out before and after biosorption to determine which functional groups were responsible for binding the heavy metals. Kinetic study showed that pseudo- second order model was well fitted for all metals ions.  $R^2$  used to enhance the justification analysis for each used model.

**Keyword:** Activated sludge, Batch adsorber, Multi-component systems, Langmuir model,  $Pb^{2+}$ ,  $Hg^{2+}$ ,  $Cr^{3+}$ ,  $As^{5+}$

## 1. Introduction

The presence of heavy metal ions in the environment has been a matter of major concern due to their toxicity to human life. Heavy metals are major pollutants in marine, ground water, industrial and even treated wastewater (Bayrak, 2006). Industrial wastewater resulting from the petroleum industries and industrial activities represent the main source of environmental pollution with heavy metals. Their effects may increase nowadays because of the progressive in the industrial technologies and increasing the demand to petroleum and oil globally, thus, result in continuous increase of pollution. Among the toxic heavy metals, lead, mercury, chromium and arsenic are in the limelight due to their major impact on the environment. . Lead forms complexes with oxo-groups in enzymes to affect virtually all steps in the process of hemoglobin synthesis and prophyrin metabolism. Toxic levels of Pb (II) in man have been associated with encephalopathy seizures and mental retardation (Ademorati, 1996).

Mercury known from long ago as one of the most toxic and hazardous metals, and it was a cause of a number of disease like “mina-mata” syndrome, in addition to that its presence in the water in an exceeding limits cause a kidney failure and brain damage (Atknsn, 1999).

Arsenic causes skin keratosis, decreases the production of blood cells, and impaired nerve function (Thornton, 2001).

Chromium causes damage of nose and lungs, increases risks of non-cancer lung diseases, ulcers, kidney, and liver damage (Thornton, 2001).

A number of physico-chemical methods have been developed over the years to remove toxic metal ions from aqueous solution which includes chelation extraction, chemical coagulation, evaporation, adsorption, extraction, chemical precipitation, ion exchange, electrochemical processes, flotation, flocculation and membrane processes. However, the applications of such processes are sometimes restricted because of technical or economic constraints (Dobson & Burgess, 2007).

Conventional adsorption processes typically use activated carbon as the main adsorption medium, but it is expensive. Thus, attention to new natural low-cost materials as biosorbents with high metal-binding capacity , as alternatives to activated carbon, have been considered in a number of investigations (Rae & Gibb, 2003; Ulmanu et al., 2003; Bishnoi & Garirna, 2005; Cochrane et al., 2006; Sulaymon et al., 2010). These biomass include: chitin and chitosan, macroalgae, activated waste sludge, yeast, and fungi.

Sewage sludge is a biomass waste containing mainly bacteria and protozoa is generated from the regular biological activities of municipal wastewater treatment plants. The volume being produced is likely increased with increasing municipal wastewater to be treated. Sludge treatment/disposal represents 50% of the capital and operational costs of a wastewater treatment plant. Rather than simply disposing of the sludge, considered use of this waste material seems to be a promising way of turning it into a resource. One application that has received increasing attention is the utilization of sewage sludge as abundant low cost alternative adsorbent for the removal of pollutants from wastewater (Aksu, 2005). To

improve the biosorption capacity, (Hu et al., 2012) proposed a new biosorbent preparation method by alkali modification of sewage sludge. They found that the cadmium adsorption capacity of biosorbent increased by  $0.713 \text{ mmol}\cdot\text{g}^{-1}$  with NaOH solution concentration (range from  $0.25$  to  $7.5 \text{ mol}\cdot\text{L}^{-1}$ ) for sewage sludge modification.

Compared to 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, 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 (AjayKumar et al., 2009).

The complex structure of microorganisms implies that there are many mechanisms for the metal to be taken up by the microbial cell. These mechanisms are either metabolism dependent in which metal removal happens by transport across membrane cell and precipitation, or non-metabolism dependent with the mechanism of physical adsorption, ion exchange or complexation (Trangini, 2009).

Actual wastewater treatment systems often have to deal with a mixture of heavy metals, most research work still only focuses on a single and binary metal sorption. Only a few works on the biosorption of three or more of heavy metals were found in literature. For instance, (Kusvuran, et al., 2012) investigated the multi-metal biosorption of  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Pb}^{2+}$  from real industrial water and contaminated water using waste activated sludge biomass and reported that the adsorption capacity of activated sludge biomass was observed in the order of  $\text{Cu}^{2+} > \text{Cd}^{2+} > \text{Pb}^{2+}$ . In the presence of  $100 \text{ mmol}\cdot\text{L}^{-1} \text{ H}^{+}$  ion, the order of ion-exchange affinity with  $\text{H}^{+}$  was found as  $\text{Cu}^{2+} > \text{Cd}^{2+} > \text{Pb}^{2+}$ .

The aim of this study was to investigate the sorption capacity, kinetics and removal efficiency of toxic metals ions of lead, mercury, chromium and arsenic from simulated waste water as single, binary, ternary, and quaternary systems onto dry activated sludge (DAS).

## 2. Materials and Methods

### 2.1 Dry Activated Sludge

Activated sludge was used as a 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, then dried in oven at  $60^{\circ}\text{C}$  until having constant weight (24 hr). The dry sludge was crushed by jaw crusher and sieved by successive sieves, after which the biosorbent was kept in a desiccators for use. The physical properties were listed in table 1.

Table 1. Physical properties of dry activated sludge

| Physical properties                 |        |
|-------------------------------------|--------|
| Particle size, mm                   | 0.38   |
| Apparent density, kg/m <sup>3</sup> | 1968   |
| Bulk density, kg/m <sup>3</sup>     | 784.34 |
| Surface area, m <sup>2</sup> /g     | 6.999  |
| Particle porosity                   | 0.6014 |

## 2.2 Adsorbate

1000 mg/l of stock solution of each metal ions of Pb(II), Hg(II), Cr(III) and As(V) were prepared by dissolving Pb(NO<sub>3</sub>)<sub>2</sub>, Hg(NO<sub>3</sub>)<sub>2</sub>·1/2H<sub>2</sub>O, Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and 3As<sub>2</sub>O<sub>5</sub>·5H<sub>2</sub>O 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 and BDH.

## 2.3 Methods

For the determination of equilibrium biosorption isotherm, a sample of (100 ml) of each solution was placed in a beaker of (200 ml). The solution was agitated (constant temperature 298 K) at 800 rpm. Activated sludge of size 0.38 mm with different weights (0.0625, 0.125, 0.25, 0.375, 0.5, 1, 1.5, 2, 2.5, 3, 4 and 5 g) was added gradually. pH was adjusted throughout the runs around 4 which is an optimum value (Farah, et al., 2007; Tunali et al., 2006) since at low pH values the biosorption of metals decreases because of competition for binding sites between ions and protons, while at pH higher than 6, solubility of metal complexes decreases sufficiently allowing precipitation, which may complicate the sorption process and do not bind to the adsorption sites on the surface of the biomass. After 4-7 hrs of agitation which is enough to reach equilibrium (AjayKumar et al., 2009), 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) 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.

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. Shimadzu- S1394 spectrum system was used for FT-IR analysis of DAS.

Kinetic experiments were carried out for understanding of the biosorption dynamics of Pb<sup>2+</sup>, Hg<sup>2+</sup>, Cr<sup>3+</sup> and As<sup>5+</sup> onto DAS. A 2000 ml Pyrex beaker was filled with 1000 ml of 50 mg/l solution of heavy metal ions and the agitation started before adding the biosorbent. At zero time, an accurate weight of biosorbent was added. The suspensions were agitated at 600 rpm

for sufficient time and 2ml samples are collected at a pre-determined time intervals and filtered through a filter paper type (Wattmann no. 4), then a sample of (2 ml) was taken for analysis. The adsorbed amount was calculated using the following mass balance equation:

$$q_e = (V_i C_0 - V_f C_e) / W \quad (1)$$

The performance of DAS adsorption was evaluated in terms of its removal efficiency as RE(%), estimated by the following equation:

$$RE \% = (C_0 - C_e) / C_0 \times 100 \quad (2)$$

### 3. Results and Discussion

#### 3.1 Single Component Systems

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 (Crittenden, 1987). For a single component systems of  $Pb^{2+}$ ,  $Hg^{2+}$ ,  $Cr^{3+}$  and  $As^{5+}$ , the equilibrium isotherms were conducted at (298 K) with initial concentration of each component,  $C_0=50$  mg/l. These isotherms are shown in figure 1. Eleven isotherm models were used to fit the experimental data. Isotherm models are given in table 2. The values of model parameters are evaluated by non-linear curve fitting method using DataFit version 9.0.59, Oakdale Engineering software. Table 2 represents the values of the parameters of each model, the correlation coefficients ( $R^2$ ) and the percentage reduction of biosorption. It is clear from figure 1 and table 2 that the equilibrium isotherm for each single component is of favorable type, since  $0 < R_s < 1$  ( $R_s = 0.4228$ ,  $0.0623$ ,  $0.0771$  and  $0.0862$  for  $Pb^{2+}$ ,  $Hg^{2+}$ ,  $Cr^{3+}$  and  $As^{5+}$  respectively). For lead; Langmuir, Radke-Praunzitz, Khan, Redlich-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 were described successfully with Langmuir model with correlation coefficient 0.9923, 0.9897 and 0.9868 respectively. 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  $As^{5+}$  ( $q_{m,Pb^{2+}} = 0.3740$ ,  $q_{m,Cr^{3+}} = 0.0892$ ,  $q_{m,Hg^{2+}} = 0.0538$ , and  $q_{m,As^{5+}} = 0.0378$  mmol/g respectively). 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  $As^{5+}$ .

#### 3.2 Fourier-Transform Infrared Analysis (FT-IR)

In order to find out which functional groups were responsible for the  $Pb^{2+}$ ,  $Hg^{2+}$ ,  $Cr^{3+}$ , and  $As^{5+}$  adsorption, FT-IR analysis of raw and loaded dried activated sludge was carried out. Infrared spectra of DAS biomass samples before and after lead, mercury, chromium, and arsenic binding are shown in figure 2 and listed in table 3. The difference between the two spectra was in the absorbance wave number and intensities. Different functional groups listed in table 3 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, amide, and amine groups at 3411.84, 2929.81,

1652.88, 1570, and 1450  $\text{cm}^{-1}$  and this indicated that these groups played the most important role in binding lead, chromium, mercury and arsenic cations onto DAS. According to figure 2 and table 3, lead cations exhibited more decrease in wave number and adsorption intensities compared to the other cations which explained its high affinity to the biosorbent.

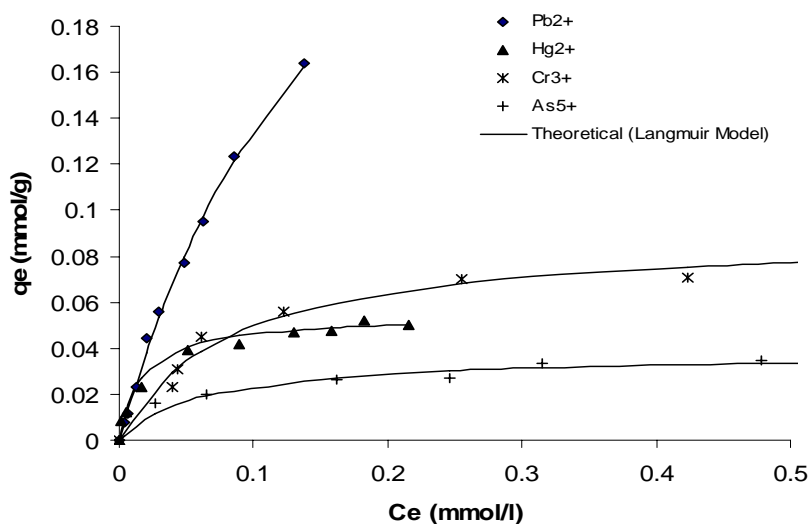


Figure 1. Biosorption isotherm for single component system of  $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Cr}^{3+}$  and  $\text{As}^{5+}$  onto DAS at 298 K

Note:  $C_0=50$  mg/l for each component.

Table 2. Parameters of single solute isotherm for  $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Cr}^{3+}$  and  $\text{As}^{5+}$

| Model  | Parameters | $\text{Pb}^{2+}$ | $\text{Hg}^{2+}$ | $\text{Cr}^{3+}$ | $\text{As}^{5+}$ |
|--|------------|------------------|------------------|------------------|------------------|
| Langmuir (Belfort, 1980)<br>$q_e = \frac{q_m b C_e}{1 + b C_e}$                                    | $q_m$      | 0.3740           | 0.0538           | 0.0892           | 0.0378           |
|  | $b$        | 5.6566           | 60.401           | 12.454           | 15.876           |
|  | $R^2$      | 0.9979           | 0.9923           | 0.9897           | 0.9868           |
|  | $R_s$      | 0.4228           | 0.0623           | 0.0771           | 0.0862           |
| Freundlich (Freundlich, 1907)<br>$q_e = K C_e^{1/n}$   | $K$        | 0.7325           | 0.0871           | 0.0949           | 0.0423           |
|  | $n$        | 1.3487           | 3.1683           | 3.2110           | 3.4287           |
|  | $R^2$      | 0.9952           | 0.9716           | 0.9383           | 0.9594           |
| Combination of Langmuir-Freundlich (Sips, 1984)<br>$q_e = \frac{b q_m C_e^{1/n}}{1 + b C_e^{1/n}}$ | $q_m$      | 0.4484           | 0.0737           | 0.0823           | 0.0582           |
|  | $b$        | 72.777           | 1658.4           | 3.8108           | 326.27           |
|  | $n$        | 1.0645           | 1.6653           | 0.7518           | 1.6711           |
|  | $R^2$      | 0.9978           | 0.9903           | 0.9853           | 0.9748           |

|  |           |                       |                       |                       |                       |
|--|-----------|-----------------------|-----------------------|-----------------------|-----------------------|
| Radke-Praunsitz (Radke & Praunsitz, 1972)  | $K_{RP}$  | 31.412                | 5.5240                | 6.2218                | 1.4705                |
|  | $F_{RP}$  | 0.0398                | 0.0738                | 0.0260                | 0.0341                |
|  | $N_{RP}$  | 0.2315                | 0.1798                | 0.0804                | 0.1677                |
|  | $R^2$     | 0.9979                | 0.9858                | 0.9839                | 0.9638                |
| $q_e = \frac{K_{RP} C_e}{1 + \left(\frac{K_{RP}}{F_{RP}}\right) C_e^{1-N_{RP}}}$ |           |                       |                       |                       |                       |
| Khan (Khan et al., 1997)   | $Q_{max}$ | 0.1211                | 0.0287                | 0.1138                | 0.0188                |
|  | $b_K$     | 19.062                | 145.37                | 9.0844                | 54.227                |
|  | $a_K$     | 0.5099                | 0.8215                | 1.1072                | 0.8112                |
|  | $R^2$     | 0.9979                | 0.9848                | 0.9837                | 0.9633                |
| $q_e = \frac{Q_{max} b_k C_e}{(1 + b_k C_e)^{a_k}}$                              |           |                       |                       |                       |                       |
| Reddlich-Peterson (Redlich & Peterson, 1959)                                     | $A_R$     | 2.3963                | 5.7107                | 0.9846                | 1.2384                |
|  | $B_R$     | 4.5991                | 79.948                | 11.289                | 30.594                |
|  | $m_R$     | 0.7685                | 0.8202                | 1.0801                | 0.8323                |
|  | $R^2$     | 0.9979                | 0.9858                | 0.9839                | 0.9746                |
| $q_e = \frac{A_R C_e}{1 + B_R C_e^{m_R}}$  |           |                       |                       |                       |                       |
| Toth (Toth, 1971)  | $K_t$     | 7.7968                | 5.4323                | 7.1359                | 1.3258                |
|  | $a_t$     | 0.0524                | 0.0069                | 0.1100                | 0.0184                |
|  | $t$       | 1.9612                | 1.2172                | 0.9032                | 1.2327                |
|  | $R^2$     | 0.9979                | 0.9848                | 0.9837                | 0.9633                |
| $q_e = \frac{K_t C_e}{(a_t + C_e)^{1/t}}$  |           |                       |                       |                       |                       |
| Temkin (Temkin, 1934)  | $b$       | 8.5310                | 1.6750                | 0.9610                | 0.5310                |
|  | $K_T$     | 193.63                | 1841.1                | 133.38                | 242.59                |
|  | $R^2$     | 0.9855                | 0.9472                | 0.9364                | 0.9214                |
| $q_e = \frac{RT}{b} \ln(K_T C_e)$  |           |                       |                       |                       |                       |
| Dubinin-Radsukevch (Dubinin & Radushkevich, 1947)                                | $q_D$     | 0.1426                | 0.0478                | 0.0755                | 0.0309                |
|  | $B_D$     | $6.76 \times 10^{-6}$ | $1.88 \times 10^{-6}$ | $1.29 \times 10^{-6}$ | $1.21 \times 10^{-6}$ |
|  | $R^2$     | 0.8777                | 0.8778                | 0.9417                | 0.7348                |
| $q_e = q_D \exp[-B_D \{RT \ln(1+1/C_e)\}^2]$                                     |           |                       |                       |                       |                       |
| Harkins-Henderson (Harkins & Henderson, 1952)                                    | $K_h$     | 1.5216                | 2278.4                | 1922.03               | 51343                 |
|  | $n_h$     | -1.3487               | -3.1683               | -3.2110               | -3.4288               |
|  | $R^2$     | 0.9943                | 0.9716                | 0.8871                | 0.9131                |
| $q_e = K_h^{1/n_h} / C_e^{1/n_h}$  |           |                       |                       |                       |                       |
| BET (Brunauer et al., 1938)  | $Q$       | 0.0814                | 0.0104                | 0.0215                | 0.0064                |
|  | $B$       | -2229.9               | -1745.2               | -613.39               | -528.22               |
|  | $R^2$     | 0.9774                | 0.7203                | 0.8159                | 0.7557                |
| $q_e = \frac{BQC_e}{(C_s - C_e)[1 + (B-1)(C_e/C_s)]}$                            |           |                       |                       |                       |                       |



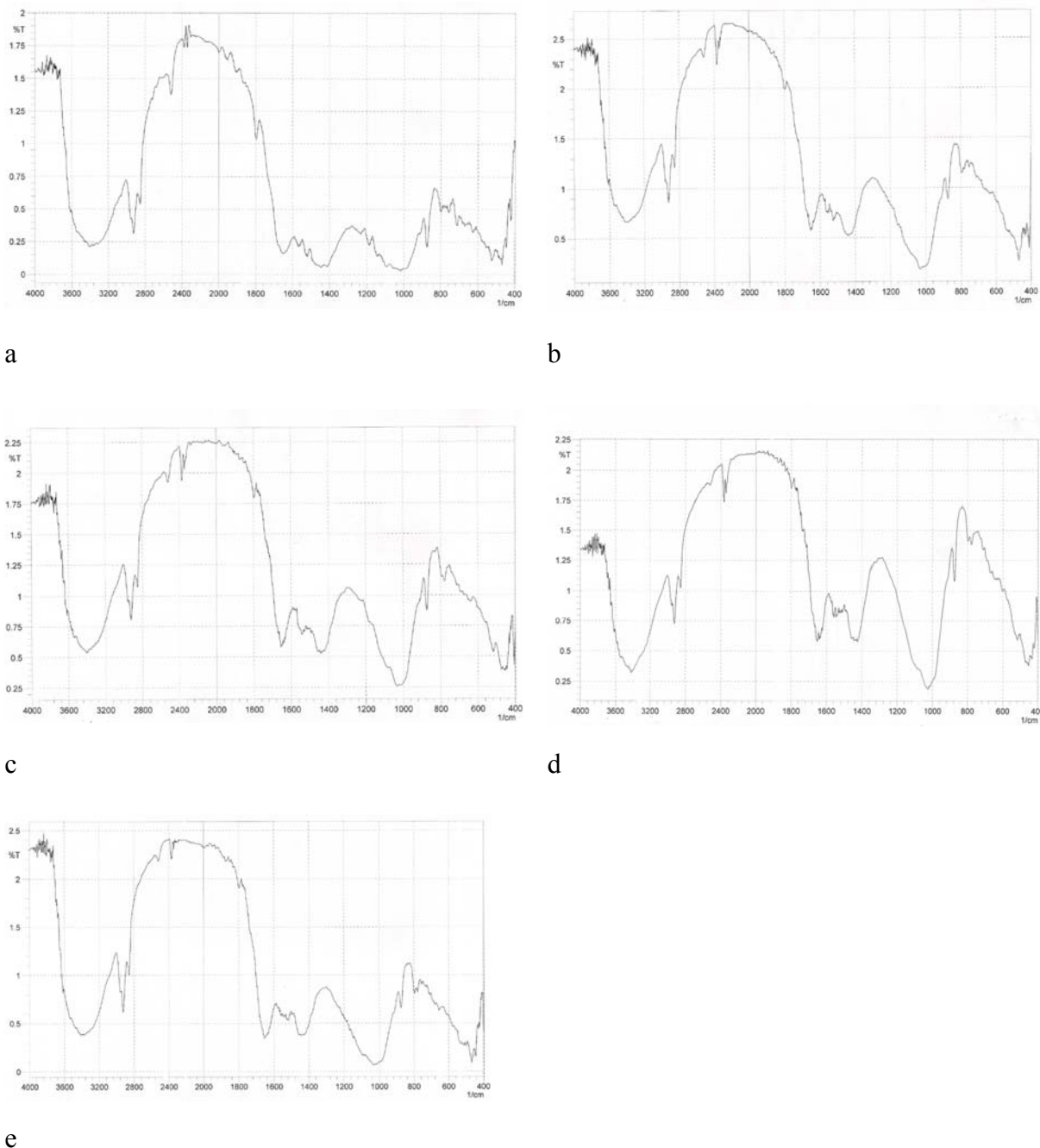


Figure 2. FT-IR analysis for dry activated sludge (a) raw DAS, (b) Pb-loaded DAS, (c) Hg-loaded DAS, (d) Cr-loaded DAS, (e) As-loaded DAS

### 3.3 Comparison of Present Biosorbent with Commercial Activated Carbon

Table 4 explained the adsorption capacity of a DAS, in the present study and a commercial activated carbon to adsorb lead, mercury chromium and arsenic cations. It is clear that DAS was efficient to adsorb  $Pb^{2+}$  and  $Cr^{3+}$  while it was poor to adsorb other two metals. This

variety in adsorption capacities is due to the difference in adsorption nature for the both adsorbents, i.e. pore surface area, functional groups and selectivity. Although DAS was poor to adsorb  $\text{Hg}^{2+}$  and  $\text{As}^{5+}$ , but its availability and low cost make it promising alternative.

Table 3. FT-IR analysis for raw and loaded dry activated sludge

| Functional group   | Type of bond  | Raw DAS                   |                     | Loaded DAS                |        |                           |        |                           |        |                           |        |
|--|---|---------------------------|---------------------|---------------------------|--------|---------------------------|--------|---------------------------|--------|---------------------------|--------|
|  |   |                           |                     | $\text{Pb}^{2+}$          |        | $\text{Hg}^{2+}$          |        | $\text{Cr}^{3+}$          |        | $\text{As}^{5+}$          |        |
|  |   | wave No. $\text{cm}^{-1}$ | Tr (%) <sup>*</sup> | wave No. $\text{cm}^{-1}$ | Tr (%) | wave No. $\text{cm}^{-1}$ | Tr (%) | wave No. $\text{cm}^{-1}$ | Tr (%) | wave No. $\text{cm}^{-1}$ | Tr (%) |
| Carboxylic acid, Amine, Amide                                | O-H stretch, N-H <sub>2</sub> 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 <sub>2</sub> C=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 <sub>2</sub> (aliphatic), N-H <sub>2</sub> bend        | 1570                      | 0.225               | 1560                      | 0.64   | 1550                      | 0.65   | 1550                      | 0.78   | 1570                      | 0.6    |
| Amines, Amides, Nitro groups,                                | N-H <sub>2</sub> bend, N-H bend, NO <sub>2</sub> (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 %.

Table 4. Comparison of DAS with commercial activated carbon

| Cations          | $q_m$ , mmol/g      |                  | References                  |
|------------------|---------------------|------------------|-----------------------------|
|                  | DAS (present study) | Activated carbon |                             |
| Pb <sup>2+</sup> | 0.3740              | 0.064            | Sulaymon, et al, 2009       |
| Hg <sup>2+</sup> | 0.0538              | 0.356            | Oubagaranadin, et al., 2007 |
| Cr <sup>3+</sup> | 0.0892              | 0.053            | Sulaymon, et al, 2009       |
| As <sup>5+</sup> | 0.0378              | 0.27             | Rajaković, 1992             |

### 3.4 Multi-Component Systems

For a binary, ternary, and quaternary component systems of Pb<sup>2+</sup>, Hg<sup>2+</sup>, Cr<sup>3+</sup> and As<sup>5+</sup>, the equilibrium isotherms were conducted at (298 K) with initial concentration of each component, C<sub>0</sub>=50 mg/l. These isotherms are shown in figures 3, 4 and 5. Five isotherm models were used to fit the experimental data. The isotherm models are given in table 5. Tables 5, 6 and 7 represent the values of the parameters of each used model, the correlation coefficients (R<sup>2</sup>) and the percentage reduction of biosorption capacity.

For the binary, ternary and quaternary systems the extended Langmuir model seems to give the best fitting for the experimental data i.e, highest value of (R<sup>2</sup>). In addition, Combination of Langmuir-Freundlich and Redlich-Peterson models may participate with extended Langmuir model to give the best fit for some systems. The behaviour of an equilibrium isotherm was a favorable type. It can be seen from the figures and related tables, Pb<sup>2+</sup> always adsorbed more favourably onto activated sludge than Hg<sup>2+</sup>, Cr<sup>3+</sup> and As<sup>5+</sup> in the binary, ternary and quaternary systems. The results also indicate that Pb<sup>2+</sup> was the metal that experienced the least displacement in the competitive adsorption process. Hg<sup>2+</sup>, Cr<sup>3+</sup> and As<sup>5+</sup> had little influence on the Pb<sup>2+</sup> adsorption in the presence of activated sludge. Conversely Pb<sup>2+</sup> significantly inhibited the retention of Hg<sup>2+</sup>, Cr<sup>3+</sup> and As<sup>5+</sup> while As<sup>5+</sup> was most affected in the competitive adsorption. From the figures it is clear that at low concentrations, the amount adsorbed for both/all metal ions increased with increasing equilibrium concentration of metal ion in solution due to the abundant adsorption sites on activated sludge. As the concentration of both/all metal ions species increased further, the adsorption sites were also available to both/all adsorbed species which were occupied to an increasing extent by the more strongly adsorbed species, resulting in a decrease in the amount of the more weakly adsorbed species. Furthermore, when metals are competing for the same type of adsorbent, metals with greater affinity (strongly adsorbed species) will displace others with a lower affinity (weakly adsorbed species). Among the four metal ions, As<sup>5+</sup> was the weakest adsorbed ion, therefore when the stronger competitive species Pb<sup>2+</sup> in solution compete with the weakest adsorbed species As<sup>5+</sup>, this may undergo displacement. Compared with their sorption in single component systems, an individual biosorption capacity of all four metals showed obvious decrease in the binary (11-51%), ternary (53-88%) and quaternary systems (79-94%). The biosorption capacity decreased more in the quaternary system as compared with binary and ternary systems. Since in a binary, ternary and quaternary systems the vacant (unoccupied adsorption sites) will be reduce and that in turn affecting the sorption capacity in these systems.

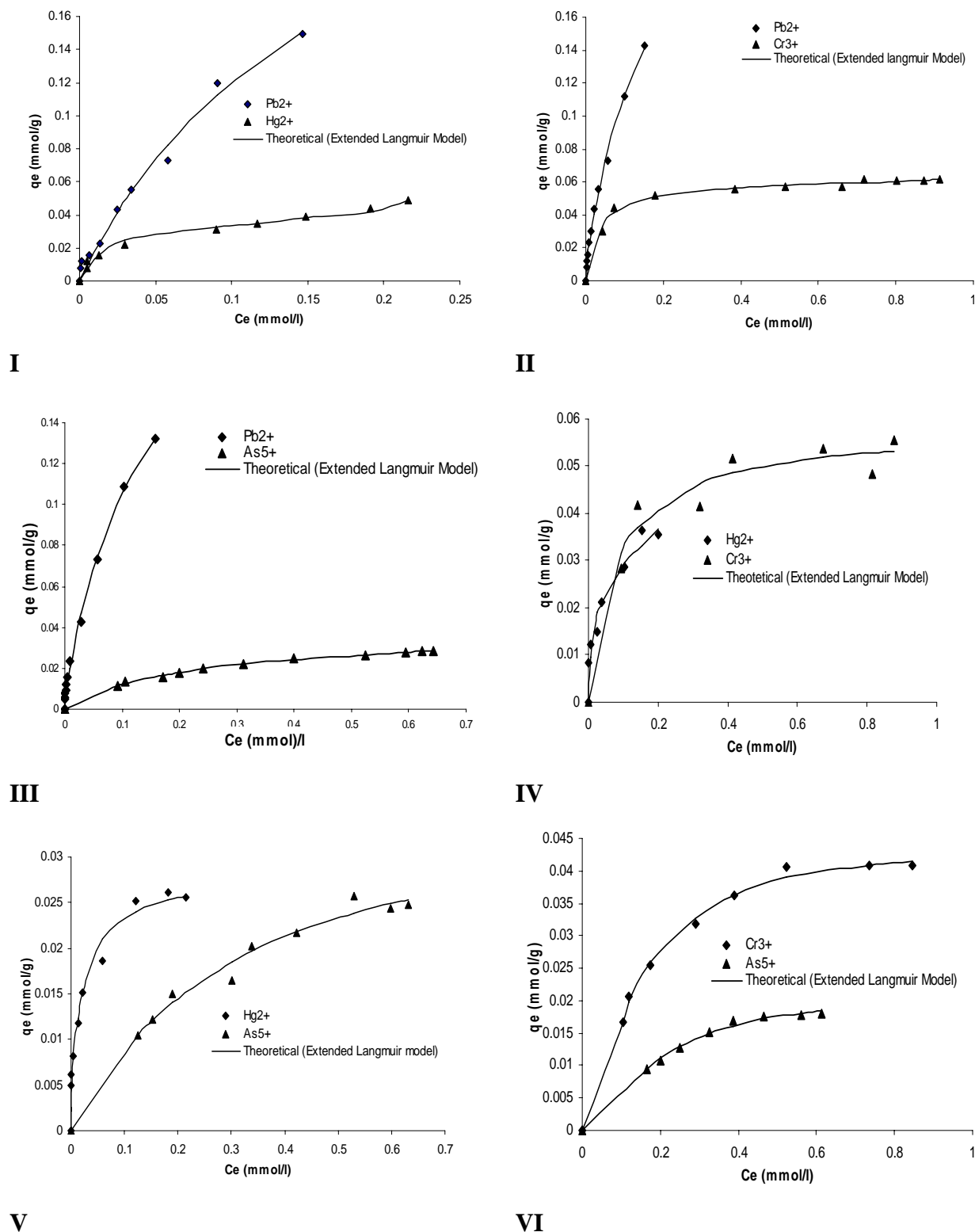


Figure 3. Biosorption isotherm for a binary components system onto DAS at 298 K.  $C_0=50$  mg/l for each component. (I).  $Pb^{2+}$ -  $Hg^{3+}$ , (II).  $Pb^{2+}$ -  $Cr^{3+}$ , (III).  $Pb^{2+}$ - $As^{5+}$ , (IV).  $Hg^{2+}$ - $Cr^{3+}$ , (V).  $Hg^{2+}$ - $As^{5+}$ , (VI). $Cr^{3+}$ - $As^{5+}$

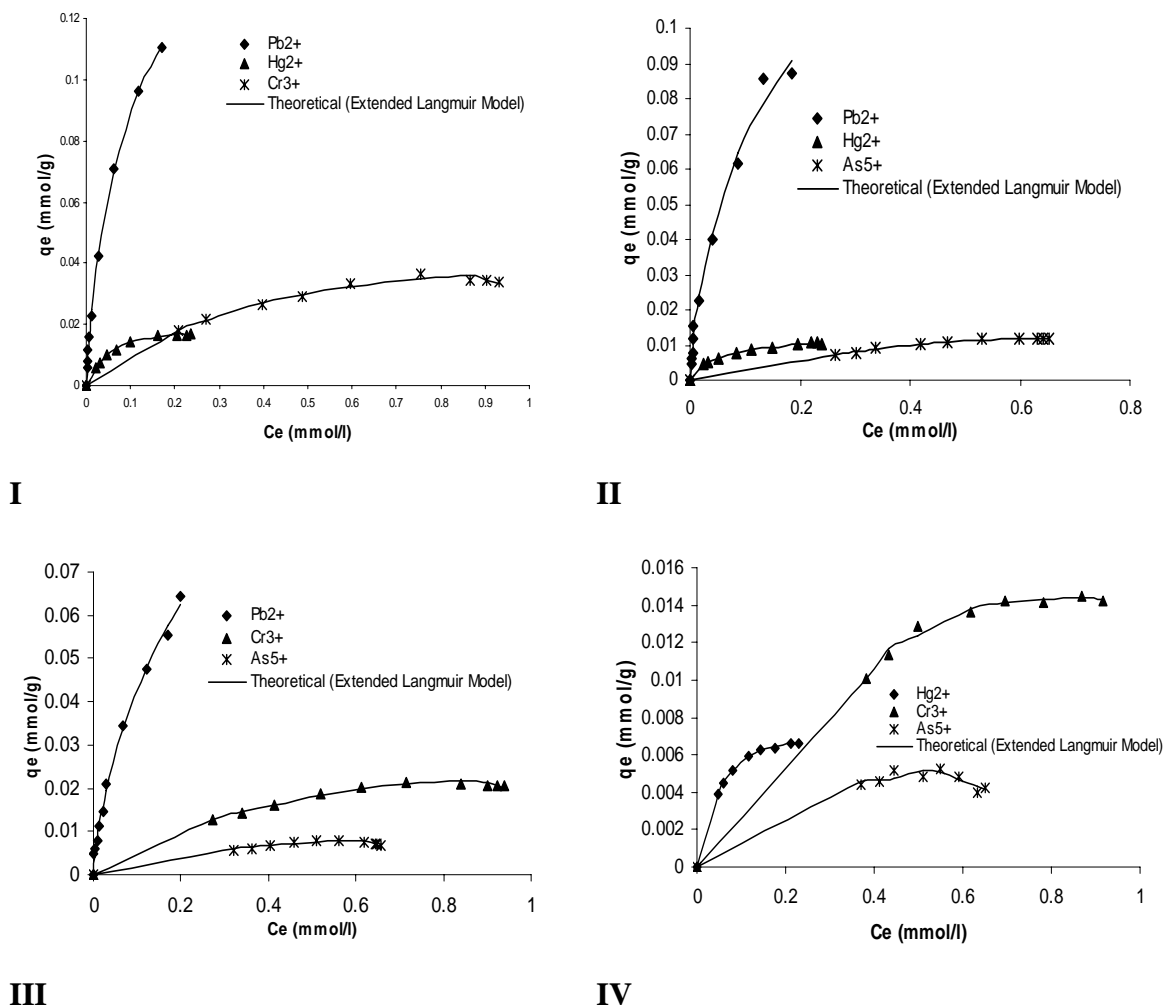


Figure 4. Biosorption isotherm for a ternary components systems onto DAS at 298 K.  $C_o=50$  mg/l for each component. (I).  $Pb^{2+}$ - $Hg^{2+}$ - $Cr^{3+}$ , (II).  $Pb^{2+}$ -  $Hg^{2+}$ - $As^{5+}$ , (III).  $Pb^{2+}$ - $Cr^{3+}$ - $As^{5+}$ , (IV).  $Hg^{2+}$ - $Cr^{3+}$ - $As^{5+}$

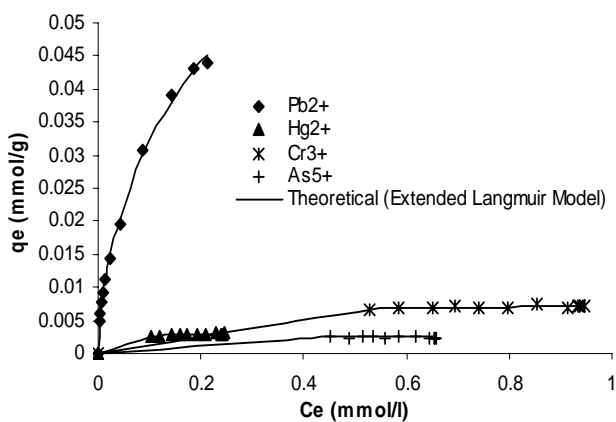


Figure 5. Biosorption isotherm for a quaternary components systems onto DAS at 298 K.  $C_o=50$  mg/l for each component

**Table 5. Biosorption isotherm models and parameters of binary solute isotherm for Pb<sup>2+</sup>, Hg<sup>2+</sup>, Cr<sup>3+</sup> and As<sup>5+</sup>**

| Model  | Parameters     | (Pb <sup>2+</sup> -Hg <sup>3+</sup> ) |                  | (Pb <sup>2+</sup> -Cr <sup>3+</sup> ) |                     | (Pb <sup>2+</sup> -As <sup>5+</sup> ) |                  | (Hg <sup>2+</sup> -Cr <sup>3+</sup> ) |                     | (Hg <sup>2+</sup> -As <sup>5+</sup> ) |                  | (Cr <sup>3+</sup> -As <sup>5+</sup> ) |                  |
|--|----------------|---------------------------------------|------------------|---------------------------------------|---------------------|---------------------------------------|------------------|---------------------------------------|---------------------|---------------------------------------|------------------|---------------------------------------|------------------|
|  |                | Pb <sup>2+</sup>                      | Hg <sup>2+</sup> | Pb <sup>2+</sup>                      | Cr <sup>3+</sup>    | Pb <sup>2+</sup>                      | As <sup>5+</sup> | Hg <sup>2+</sup>                      | Cr <sup>3+</sup>    | Hg <sup>2+</sup>                      | As <sup>5+</sup> | Cr <sup>3+</sup>                      | As <sup>5+</sup> |
| Extended   | q <sub>m</sub> | 0.3318                                | 0.0397           | 0.3087                                | 0.0620              | 0.2680                                | 0.0269           | 0.0368                                | 0.0574              | 0.0306                                | 0.0214           | 0.0515                                | 0.0186           |
| Langmuir   | b              | 5.7394                                | 52.276           | 13.116                                | 26.135              | 15.146                                | 4.7349           | 35.345                                | 12.995              | 48.545                                | 27.428           | 5.0076                                | 17.831           |
| (Weber & Walt, 1979)   | R <sup>2</sup> | 0.9875                                | 0.9873           | 0.9953                                | 0.9952              | 0.9956                                | 0.9963           | 0.9417                                | 0.9606              | 0.9609                                | 0.9836           | 0.9974                                | 0.9964           |
| $q_{e,i} = \frac{q_{m,i} b_i C_{e,i}}{1 + \sum_{K=1}^N b_K C_{e,K}}$ Reduction in biosorption capacity % |                | 11.28                                 | 26.16            | 17.45                                 | 30.54               | 28.33                                 | 28.8             | 31.57                                 | 35.68               | 43.08                                 | 43.34            | 42.28                                 | 50.83            |
|  |                |                                       |                  |                                       |                     |                                       |                  |                                       |                     |                                       |                  |                                       |                  |
| Combination of Langmuir-Freundlich   | q <sub>m</sub> | 0.1918                                | 0.1039           | 0.7534                                | 0.0575              | 0.2409                                | 0.0463           | 0.0123                                | 0.0182              | 0.0247                                | 0.0175           | 0.0162                                | 0.0134           |
| (Fahmi & Munther, 2003)  | b              | 0.0850                                | 0.0006           | 0.0057                                | 0.0042              | 462.76                                | 2.1192           | 0.4554                                | 0.0001              | 0.00004                               | 0.1462           | 0.0037                                | 7.3166           |
|  | n              | 0.5769                                | 3.2046           | 1.7014                                | 1.1663              | 0.8187                                | 1.0967           | 1.7191                                | 5.7095              | 4.3890                                | 0.8604           | 2.1725                                | 0.7560           |
| $q_{e,i} = \frac{q_{m,i} b_i C_{e,i}^{1/n_i}}{1 + \sum_{i=1}^N b_i C_{e,i}^{1/n_i}}$ R <sup>2</sup>      |                | 0.9784                                | 0.9871           | 0.9949                                | 0.9942              | 0.9953                                | 0.9960           | 0.9413                                | 0.9603              | 0.9605                                | 0.9829           | 0.9974                                | 0.9950           |
|  |                |                                       |                  |                                       |                     |                                       |                  |                                       |                     |                                       |                  |                                       |                  |
| Redlich-Peterson   | K <sub>R</sub> | 2.9900                                | 1.5098           | 1424.4                                | 1.0687              | 44.694                                | 6.8170           | 40.501                                | 0.7392              | 36.240                                | 0.1137           | 0.7707                                | 0.4090           |
| (Fahmi & Munther, 2003)  | b <sub>R</sub> | 4.2992                                | 21.783           | 3470.0                                | 183.75              | 0.0404                                | 165.10           | 2239.8                                | 13.171              | 973.46                                | 7.1167           | 14.913                                | 16.314           |
| $q_{e,j} = \frac{K_{Ri}(b_{Ri})C_{e,i}}{1 + \sum_{k=1}^N b_{R,k}(C_{e,k})^{m_{R,k}}}$ m <sub>R</sub>     |                | 0.5052                                | 0.7517           | 0.2225                                | 0.9465              | 0.0221                                | 0.4916           | 0.9121                                | 1.0219              | 0.6997                                | 1.1640           | 1.1447                                | 0.6025           |
|  | R <sup>2</sup> | 0.9783                                | 0.9853           | 0.9951                                | 0.9951              | 0.9552                                | 0.9946           | 0.9415                                | 0.9601              | 0.9603                                | 0.9836           | 0.9970                                | 0.9867           |
| Harkins-Jura   | A              | 0.0045                                | 0.0010           | 0.0040                                | 0.0078              | 0.0034                                | 0.0006           | 0.0009                                | 0.0050              | 0.0005                                | 0.0004           | 0.0016                                | 0.0003           |
| (Nabais et al., 2006)  | B              | 3.6047                                | 4.1656           | 3.6241                                | 5.8477              | 3.6607                                | 4.5064           | 4.2695                                | 5.4726              | 4.4378                                | 4.3936           | 4.6102                                | 4.5431           |
| $\frac{1}{q_e^2} = \frac{B'}{A'} - \frac{1}{A'} \log C_e$ R <sup>2</sup>                                 |                | 0.8444                                | 0.941            | 0.8412                                | 0.8427              | 0.8472                                | 0.922            | 0.9197                                | 0.7222              | 0.8797                                | 0.8829           | 0.8086                                | 0.8343           |
|  |                |                                       |                  |                                       |                     |                                       |                  |                                       |                     |                                       |                  |                                       |                  |
| Halsey-Henderson   | K              | 2.0651                                | 453.58           | 3.0353                                | 9.8x10 <sup>6</sup> | 4.7047                                | 2424.6           | 5301.7                                | 0.7x10 <sup>6</sup> | 78671                                 | 788.61           | 4584                                  | 3173             |
| (Abdul-Hameed, 2009)   | n              | -1.4090                               | -2.4887          | -1.5477                               | -5.8439             | -1.6899                               | -2.3261          | -3.0757                               | -4.6877             | -3.5525                               | -1.954           | -2.754                                | -2.1616          |
| $q_e = \frac{K^{1/n}}{C_e^{1/n}}$ R <sup>2</sup>   |                | 0.9872                                | 0.9871           | 0.9947                                | 0.8980              | 0.9955                                | 0.9828           | 0.9410                                | 0.773               | 0.9602                                | 0.9534           | 0.9200                                | 0.9227           |
|  |                |                                       |                  |                                       |                     |                                       |                  |                                       |                     |                                       |                  |                                       |                  |

**Table 6. Parameters of ternary solute isotherm for Pb<sup>2+</sup>, Hg<sup>2+</sup>, Cr<sup>3+</sup> and As<sup>5+</sup>**

| Model                                 | Parameters                                   | Pb <sup>2+</sup> -Hg <sup>2+</sup> -Cr <sup>3+</sup> |                  |                  | Pb <sup>2+</sup> -Hg <sup>2+</sup> -As <sup>5+</sup> |                  |                  | Pb <sup>2+</sup> -Cr <sup>3+</sup> -As <sup>5+</sup> |                  |                     | Hg <sup>2+</sup> -Cr <sup>3+</sup> -As <sup>5+</sup> |                     |                      |
|---------------------------------------|--|--|------------------|------------------|--|------------------|------------------|--|------------------|---------------------|--|---------------------|----------------------|
|                                       |  | Pb <sup>2+</sup>                                     | Hg <sup>2+</sup> | Cr <sup>3+</sup> | Pb <sup>2+</sup>                                     | Hg <sup>2+</sup> | As <sup>5+</sup> | Pb <sup>2+</sup>                                     | Cr <sup>3+</sup> | As <sup>5+</sup>    | Hg <sup>2+</sup>                                     | Cr <sup>3+</sup>    | As <sup>5+</sup>     |
| Extended<br>Langmuir                  | q <sub>m</sub>                               | 0.1753   | 0.0180           | 0.0357           | 0.1617   | 0.0190           | 0.0131           | 0.1318   | 0.0220           | 0.0082              | 0.0080   | 0.0132              | 0.0046               |
|                                       | b  | 17.964   | 1.3039           | 2.0644           | 4.2269   | 85.9772          | 10.137           | 6.568  | 0.6708           | 2.0228              | 1489.7   | 97.188              | 671.08               |
|                                       | R <sup>2</sup>                               | 0.9986   | 0.9982           | 0.9945           | 0.9912   | 0.9986           | 0.9941           | 0.9941   | 0.9949           | 0.0895              | 0.9994   | 0.9960              | 0.9809               |
|                                       | Reduction<br>in<br>Biosorption<br>Capacity % | 53.11  | 66.57            | 60               | 56.76  | 64.59            | 65.32            | 64.76  | 75.29            | 78.29               | 85.16  | 85.21               | 87.70                |
| Combination of<br>Langmuir-Freundlich | q <sub>m</sub>                               | 0.2192   | 0.0171           | 0.0122           | 0.0145   | 0.0108           | 0.0083           | 0.0717   | 0.0274           | 0.0015              | 0.0071   | 0.0144              | 0.0018               |
|                                       | b  | 0.0055   | 77919            | 0.0352           | 0.0971   | 18.857           | 30.288           | 0.0167   | 6.4077           | 0.0388              | 5.2139   | 2.3x10 <sup>7</sup> | 31.975               |
|                                       | n  | 2.1118   | 0.3054           | 1.0002           | 6.1606   | 0.4458           | 0.3386           | 3.7702   | 0.4613           | 1.0843              | 0.6160   | 0.1966              | 0.6854               |
|                                       | R <sup>2</sup>                               | 0.9986   | 0.9979           | 0.9945           | 0.9910   | 0.9985           | 0.9926           | 0.9941   | 0.9949           | 0.9895              | 0.9993   | 0.9968              | 0.9804               |
| Redlich-Peterson                      | K <sub>R</sub>                               | 17.138   | 2.7058           | 0.7902           | 3.6639   | 2.5075           | 0.1160           | 3.5719   | 0.2912           | 0.7618              | 0.6675   | 0.3344              | 0.5580               |
|                                       | b <sub>R</sub>                               | 88.077   | 101.95           | 13.454           | 0.4337   | 137.10           | 12.972           | 34.719   | 78.733           | 39.191              | 135.69   | 79.572              | 247.88               |
|                                       | m <sub>R</sub>                               | 0.8069   | 0.9579           | 0.4224           | 0.0483   | 0.9782           | 1.0175           | 0.1872   | 0.5426           | 0.8377              | 1.0750   | 1.1083              | 0.9874               |
|                                       | R <sup>2</sup>                               | 0.9981   | 0.9959           | 0.9935           | 0.9609   | 0.9979           | 0.9939           | 0.9939   | 0.9947           | 0.9890              | 0.9992   | 0.9968              | 0.9801               |
| Harkins-Jura                          | A  | 0.003  | 0.0002           | 0.0012           | 0.0021   | 0.0009           | 0.0001           | 0.0009   | 0.0004           | 0.0087              | 0.00006  | 0.0003              | 0.0001               |
|                                       | B  | 3.7850   | 4.6028           | 4.7556           | 3.8818   | 4.6719           | 4.6290           | 3.9190   | 4.9633           | 6.029               | 4.9939   | 5.0288              | 1.4448               |
|                                       | R <sup>2</sup>                               | 0.8151   | 0.8355           | 0.8298           | 0.7919   | 0.9176           | 0.8450           | 0.8825   | 0.7929           | 0.3084              | 0.8707   | 0.7888              | 0.0578               |
| Halsey-Henderson                      | K  | 6.7701   | 12080            | 4322             | 11.238   | 85061            | 4513             | 17.403   | 45247            | 1.6x10 <sup>9</sup> | 3.3x10 <sup>6</sup>                                  | 166679              | 5.2x10 <sup>12</sup> |
|                                       | n  | -1.7044  | -2.6805          | -2.5434          | -1.7373  | -2.8223          | -2.0075          | -1.6218  | -2.8126          | -4.4050             | -3.3125  | -2.8808             | -9.1731              |
|                                       | R <sup>2</sup>                               | 0.9911   | 0.9354           | 0.9082           | 0.9833   | 0.9819           | 0.9075           | 0.9931   | 0.8632           | 0.3410              | 0.9360   | 0.9421              | 0.0637               |

**Table 7. Parameters of quaternary solute isotherm for Pb<sup>2+</sup>, Hg<sup>2+</sup>, Cr<sup>3+</sup> and As<sup>5+</sup>**

| Model                              | Parameters                          | Pb <sup>2+</sup> -Hg <sup>2+</sup> -Cr <sup>3+</sup> -As <sup>5+</sup> Solution |                      |                      |                      |
|------------------------------------|-------------------------------------|---|----------------------|----------------------|----------------------|
|                                    |                                     | Pb <sup>2+</sup>  | Hg <sup>2+</sup>     | Cr <sup>3+</sup>     | As <sup>5+</sup>     |
| Extended<br>Langmuir               | q <sub>m</sub>                      | 0.0783  | 0.0106               | 0.0072               | 0.0024               |
|                                    | b                                   | 8.5366  | 109.75               | 166.68               | 2900.9               |
|                                    | R <sup>2</sup>                      | 0.9983  | 0.9988               | 0.9979               | 0.9946               |
|                                    | Reduction in Biosorption Capacity % | 79.05   | 80.30                | 91.93                | 93.64                |
| Combination of Langmuir-Freundlich | q <sub>m</sub>                      | 0.0683  | 0.0055               | 0.0085               | 0.0503               |
|                                    | b                                   | 3.0317  | 1.5022               | 0.1310               | 7.1235               |
|                                    | n                                   | 0.9178  | 0.9178               | 0.9149               | 0.6733               |
|                                    | R <sup>2</sup>                      | 0.9980  | 0.9980               | 0.9988               | 0.9963               |
| Redlich-Peterson                   | K <sub>R</sub>                      | 18.855  | 1.0798               | 0.9597               | 0.8290               |
|                                    | b <sub>R</sub>                      | 374.84  | 158.21               | 93.087               | 238.31               |
|                                    | m <sub>R</sub>                      | 1.3288  | 0.9686               | 1.0708               | 1.1252               |
|                                    | R <sup>2</sup>                      | 0.9983  | 0.9983               | 0.9988               | 0.9948               |
| Harkins-Jura                       | A                                   | 0.0006  | 0.00002              | 0.0002               | 0.00004              |
|                                    | B                                   | 4.0533  | 6.2491               | 7.2834               | 8.9022               |
|                                    | R <sup>2</sup>                      | 0.8609  | 0.9045               | 0.6133               | 0.5885               |
| Halsey-Henderson                   | K                                   | 82.213  | 7.3x10 <sup>11</sup> | 1.3x10 <sup>13</sup> | 1.5x10 <sup>20</sup> |
|                                    | n                                   | -1.9347   | -5.3218              | -7.2207              | -9.2260              |
|                                    | R <sup>2</sup>                      | 0.9951  | 0.9225               | 0.6173               | 0.5044               |

### 3.5 Removal Efficiency

The removal efficiency of biosorption represents the ability of biosorbent to reduce or/and remove the adsorbates from the solution. The removal efficiency was calculated by using

equation (2).

The values of the percentage removal are tabulated in table 8 which gave the maximum removal percentage achieved for highest mass of activated sludge for the single, binary, ternary and quaternary systems for all pollutants.

$Pb^{2+}$  gives the maximum percentage removal rather than  $Hg^{2+}$ ,  $Cr^{3+}$  and  $As^{5+}$ . This may due to the physical and chemical properties of  $Pb^{2+}$  to be more favorable to be adsorbed than  $Hg^{2+}$ ,  $Cr^{3+}$  and  $As^{5+}$ , these factors were mentioned previously.

For binary, ternary and quaternary systems and for all pollutants, there was a reduction in the percentage of removal. This reduction increases more for quaternary system comparing for the ternary, binary and single systems. This is due to the presence of more than one pollutant within the same adsorbent which will enhance the competition and the struggling race of each pollutant to occupy an adsorbent site and hence, an occupied sites will be a mixture of two and three or more adsorbed species. Therefore reducing the percentage removal of the adsorbate as they are in their single state.

Table 8. Maximum removal efficiency for each pollutant

|            | Pollutants System  | RE %  |
|------------|--|-------|
| Single     | $Pb^{2+}$  | 99.75 |
|            | $Hg^{2+}$  | 99.71 |
|            | $Cr^{3+}$  | 95.87 |
|            | $As^{5+}$  | 95.92 |
| Binary     | $Pb^{2+}$ in ( $Pb^{2+}$ - $Hg^{2+}$ )                         | 99.75 |
|            | $Hg^{2+}$ in ( $Pb^{2+}$ - $Hg^{2+}$ )                         | 98.08 |
|            | $Pb^{2+}$ in ( $Pb^{2+}$ - $Cr^{3+}$ )                         | 99.36 |
|            | $Cr^{3+}$ in ( $Pb^{2+}$ - $Cr^{3+}$ )                         | 95.51 |
|            | $Hg^{2+}$ in ( $Hg^{2+}$ - $Cr^{3+}$ )                         | 99.71 |
|            | $Cr^{3+}$ in ( $Hg^{2+}$ - $Cr^{3+}$ )                         | 90.27 |
|            | $Pb^{2+}$ in ( $Pb^{2+}$ - $As^{5+}$ )                         | 99.74 |
|            | $As^{5+}$ in ( $Pb^{2+}$ - $As^{5+}$ )                         | 86.17 |
|            | $Hg^{2+}$ in ( $Hg^{2+}$ - $As^{5+}$ )                         | 99.71 |
|            | $As^{5+}$ in ( $Hg^{2+}$ - $As^{5+}$ )                         | 81.29 |
|            | $Cr^{3+}$ in ( $Cr^{3+}$ - $As^{5+}$ )                         | 89.20 |
|            | $As^{5+}$ in ( $Cr^{3+}$ - $As^{5+}$ )                         | 75.02 |
| Ternary    | $Pb^{2+}$ in ( $Pb^{2+}$ - $Hg^{2+}$ - $Cr^{3+}$ )             | 98.20 |
|            | $Hg^{2+}$ in ( $Pb^{2+}$ - $Hg^{2+}$ - $Cr^{3+}$ )             | 91.49 |
|            | $Cr^{3+}$ in ( $Pb^{2+}$ - $Hg^{2+}$ - $Cr^{3+}$ )             | 78.30 |
|            | $Pb^{2+}$ in ( $Pb^{2+}$ - $Hg^{2+}$ - $As^{5+}$ )             | 97.23 |
|            | $Hg^{2+}$ in ( $Pb^{2+}$ - $Hg^{2+}$ - $As^{5+}$ )             | 89.82 |
|            | $As^{5+}$ in ( $Pb^{2+}$ - $Hg^{2+}$ - $As^{5+}$ )             | 60.39 |
|            | $Hg^{2+}$ in ( $Hg^{2+}$ - $Cr^{3+}$ - $As^{5+}$ )             | 81.39 |
|            | $Cr^{3+}$ in ( $Hg^{2+}$ - $Cr^{3+}$ - $As^{5+}$ )             | 60.18 |
|            | $As^{5+}$ in ( $Hg^{2+}$ - $Cr^{3+}$ - $As^{5+}$ )             | 44.37 |
|            | $Pb^{2+}$ in ( $Pb^{2+}$ - $Cr^{3+}$ - $As^{5+}$ )             | 96.26 |
|            | $Cr^{3+}$ in ( $Pb^{2+}$ - $Cr^{3+}$ - $As^{5+}$ )             | 71.83 |
|            | $As^{5+}$ in ( $Pb^{2+}$ - $Cr^{3+}$ - $As^{5+}$ )             | 52.03 |
| Quaternary | $Pb^{2+}$ in ( $Pb^{2+}$ - $Hg^{2+}$ - $Cr^{3+}$ - $As^{5+}$ ) | 95.67 |
|            | $Hg^{2+}$ in ( $Pb^{2+}$ - $Hg^{2+}$ - $Cr^{3+}$ - $As^{5+}$ ) | 58.63 |
|            | $Cr^{3+}$ in ( $Pb^{2+}$ - $Hg^{2+}$ - $Cr^{3+}$ - $As^{5+}$ ) | 44.93 |
|            | $As^{5+}$ in ( $Pb^{2+}$ - $Hg^{2+}$ - $Cr^{3+}$ - $As^{5+}$ ) | 32.39 |



### 3.6 Kinetic Studies

Biosorption Kinetics was obtained by plotting the mole of the solute adsorbed per unit weight of activated sludge against time. The experimental data was fitted to the various kinetic models listed in table 7 and the models parameters were found by linear regression.

Comparisons of the kinetic results are depicted in figure 6 and table 9. The pseudo second-order kinetic model was more suitable for explanation of biosorption process mechanism, due to the highest value of correlation coefficient.

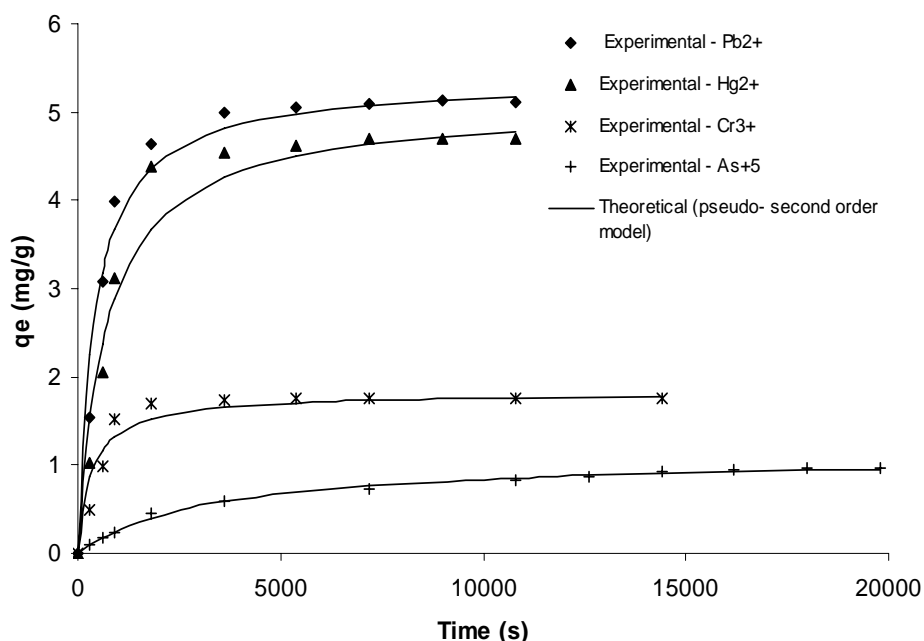


Figure 6. Biosorption kinetics for Pb<sup>2+</sup>, Hg<sup>2+</sup>, Cr<sup>3+</sup> and As<sup>5+</sup> onto DAS

## 4. Conclusion

Results showed that dried activated sludge was suitable for the removal of lead, mercuric, chromium and arsenic ions from aqueous solution. The Langmuir isotherm model was well described the sorption of single component systems onto dried activated sludge, while for multi-component systems, extended Langmuir model was well fitted the equilibrium isotherms. The maximum biosorption uptake of the studied metal ions in single, binary, ternary and quaternary systems by activated sludge showed the following order Pb<sup>2+</sup> > Cr<sup>3+</sup> > Hg<sup>2+</sup> > As<sup>5+</sup>. FT-IR analysis showed that carboxylic acid, amide, and amine groups played the most important role in binding lead, chromium, mercury and arsenic cations onto DAS. The pseudo second-order kinetic model was fitted well with the experimental data.

Dried activated sludge may be used as a low cost natural abundant source for the removal of heavy metals ions and it may be an alternative to more costly materials such as activated carbon.

Table 9. Kinetic models and parameters for the biosorption of  $Pb^{2+}$ ,  $Hg^{2+}$ ,  $Cr^{3+}$  and  $As^{5+}$  onto DAS

| Model   | Parameters | $Pb^{2+}$               | $Hg^{2+}$               | $Cr^{3+}$               | $As^{5+}$               |
|---|------------|-------------------------|-------------------------|-------------------------|-------------------------|
| Pseudo-first order (Lagergren, 1989)<br>$\log(q_{eq} - q_t) = \log q_{eq} - \left(\frac{k_L t}{2.303}\right)$ | $q_e$      | 5.0823                  | 4.7080                  | 1.7684                  | 0.9523                  |
|   | $K_1$      | $1.4968 \times 10^{-3}$ | $1.0912 \times 10^{-3}$ | $1.5408 \times 10^{-3}$ | $2.7052 \times 10^{-4}$ |
|   | $R^2$      | 0.9946                  | 0.9908                  | 0.9804                  | 0.9871                  |
| Pseudo-second order (Ho & McKay, 1999)<br>$\frac{t}{q_t} = \frac{1}{k_s q_{eq}^2} + \frac{t}{q_{eq}}$         | $q_e$      | 5.3676                  | 5.0839                  | 1.8100                  | 1.1095                  |
|   | $K_2$      | $4.4749 \times 10^{-4}$ | $2.8607 \times 10^{-4}$ | $1.6680 \times 10^{-3}$ | $2.8531 \times 10^{-4}$ |
|   | $R^2$      | 0.9985                  | 0.9950                  | 0.9979                  | 0.9986                  |
| Intra-particle diffusion (Weber & Morris, 1963)<br>$q_t = k_{id} t^{1/2} + C$                                 | $K_{id}$   | $3.1500 \times 10^{-2}$ | $3.5800 \times 10^{-2}$ | $1.2539 \times 10^{-2}$ | $6.00 \times 10^{-3}$   |
|   | $C$        | 2.4341                  | 1.6367                  | 0.6481                  | 0.1242                  |
|   | $R^2$      | 0.7216                  | 0.7711                  | 0.6051                  | 0.9406                  |
| Elovich (Cheung et al., 2003)<br>$q_t = \frac{1}{b} \ln ab + \frac{1}{b} \ln t$                               | $a$        | $4.592 \times 10^{-2}$  | 0.2623                  | 0.1562                  | $2.824 \times 10^{-2}$  |
|   | $b$        | 1.1357                  | 0.5035                  | 1.7787                  | 2.3180                  |
|   | $R^2$      | 0.8365                  | 0.8929                  | 0.7117                  | 0.9930                  |

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## Symbols

|          |  |
|----------|--|
| $A'$     | Harkins-Jura model parameter, $(\text{mmol/g})^2$                          |
| $A$      | Elovich model parameter, $(\text{mg/g.s})$                                 |
| $a_K$    | Khan model parameter   |
| $a_t$    | Toth model parameter, $(\text{mmol/l})$                                    |
| $A_R$    | Reddlich-Peterson model parameter, $(\text{l/g})$                          |
| $B$      | BET model parameter, $(\text{l/mmol})$                                     |
| $B$      | Elovich model parameter, $(\text{g/mg})$                                   |
| $B'$     | Harkins-Jura model parameter   |
| $B_1$    | Temkin isotherm constant, $(\text{kJ/mole})$                               |
| $B_D$    | Dubin-Radsukevch model parameter, $(\text{mole/J})$                        |
| $b_K$    | Khan model parameter, $(\text{l/mmol})$                                    |
| $B_R$    | Reddlich-Peterson model parameter, $(\text{l/mmol})^m$                     |
| $b$      | Langmuir constant, $(\text{l/mmol})$                                       |
| $C$      | Parameter in intra-particle diffusion model, $(\text{mg/g})$               |
| $C_e$    | Equilibrium concentration, $(\text{mmol/l})$                               |
| $C_{ei}$ | Equilibrium concentration of component $i$ , $(\text{mmol/l})$             |
| $C_o$    | Initial solute concentration, $(\text{mg/l})$                              |
| $E_o$    | Characteristic adsorption energy, $(\text{kJ/mol})$                        |
| $F_{RP}$ | Radke-Praunsitz model parameter, $(\text{l}^N \text{mmol}^{1-N}/\text{g})$ |
| $K$      | Freundlich equilibrium parameter, $(\text{mmol/g})(\text{l/mmol})^{1/n}$   |
| $K_1$    | Rate constant of pseudo first-order adsorption, $(\text{1/s})$             |
| $K_2$    | Rate constant of pseudo second-order adsorption, $(\text{g/mg.s})$         |
| $K_h$    | Harkins-Henderson model parameter, $(\text{mmol/g})^n(\text{mmol/l})$      |
| $K_{id}$ | Rate constant of intra-particle diffusion model, $(\text{mg/g.s}^{0.5})$   |
| $K_{RP}$ | Radke- Praunsitz model parameter, $(\text{l/g})$                           |
| $K_T$    | Equilibrium binding constant in Temkin model, $(\text{l/mmol})$            |
| $m_R$    | Reddlich-Peterson model parameter  |
| $n$      | Freundlich equilibrium parameter and Seps model parameter                  |

**Symbols**

|           |   |
|-----------|---|
| $A'$      | Harkins-Jura model parameter, (mmol/g) <sup>2</sup>                   |
| $A$       | Elovich model parameter, (mg/g.s)                                     |
| $a_K$     | Khan model parameter  |
| $a_t$     | Toth model parameter, (mmol/l)  |
| $A_R$     | Reddlich-Peterson model parameter, (l/g)                              |
| $B$       | BET model parameter, (l/mmol)   |
| $B'$      | Elovich model parameter, (g/mg)                                       |
| $B'$      | Harkins-Jura model parameter  |
| $B_1$     | Temkin isotherm constant, (kJ/mole)                                   |
| $B_D$     | Dubinin-Radsukevch model parameter, (mole/J)                          |
| $b_K$     | Khan model parameter, (l/mmol)  |
| $n_h$     | Harkins-Henderson model parameter,                                    |
| $N_{RP}$  | Radke-Praunsitz model parameter                                       |
| $Q$       | BET model parameter, (mmol/g)   |
| $Q_{max}$ | Khan model parameter, (mmol/g)  |
| $q_D$     | Dubinin-Radsukevch model parameter, (mmol/g)                          |
| $q_e$     | Internal concentration of solute in particle at equilibrium, (mmol/g) |
| $q_{ei}$  | Amount of adsorbate adsorbed per mass of adsorbent of species $i$     |
| $q_m$     | Adsorption capacity defined by Langmuir equation, (mmol/g)            |
| $q_{mi}$  | Adsorption capacity for species $i$                                   |
| $R$       | Universal gas constant (=8.314 kJ/mol.K)                              |
| $R_p$     | Radius of particle, (mm)  |
| $R_s$     | separation factor   |
| $T$       | Absolute temperature, (K)   |
| $t$       | Toth model parameter  |
| $V_f$     | Final Volume of solution, (ml)  |
| $V_i$     | Initial Volume of solution, (ml)                                      |
| $W$       | Mass of activated sludge, (g)   |

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