

## BIOSORPTION OF ORGANIC AND INORGANIC POLLUTANTS FROM SIMULATED WASTEWATER BY USING EQUISETUM HORSETAIL

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### ABSTRACT

Through easy and environmental friendly processes, equisetum horsetail was used to produce biosorbent materials. This equisetum based biosorbent was investigated for the removal of  $\text{Hg}^{2+}$  and furfural from simulated waste water using granule equisetum horsetail. Many isotherm models were used for single component and binary system. Langmuir model gave the best fitting for the single system ( $R^2_{\text{Fu}} = 0.9946$  and  $R^2_{\text{Hg}^{2+}} = 0.9935$ ), while the binary system was fitted successfully with extended Langmuir model ( $R^2_{\text{Fu}} = 0.9977$  and  $R^2_{\text{Hg}^{2+}} = 0.9969$ ). For kinetic study, Pseudo-first order, pseudo-second order, intra-particle diffusion and Elovich were chosen. From the results, the pseudo-second order model was well fitted for  $\text{Hg}^{2+}$  and furfural ( $R^2_{\text{Fu}} = 0.9942$  and  $R^2_{\text{Hg}^{2+}} = 0.9910$ ). The biosorption thermodynamic indicated that the biosorption of furfural and  $\text{Hg}^{2+}$  on biosorbent was exothermic reaction. Desorption of  $\text{Hg}^{2+}$  and furfural from simulated wastewater was obtained when using 0.1M NaOH and HCl.

**KEYWORDS:** Granule Equisetum Horsetail, Isotherm, Single System, Langmuir Model, Desorption

### INTRODUCTION

Various types of technology are available for removing furfural and mercury from water and wastewater. These include chemical precipitation, conventional coagulation, lime softening; reverse osmosis, ion-exchange and activated carbon adsorption [1]. The search for new technologies involving the removal of toxic metals from wastewater has directed the attention to biosorption, based on metal binding capacities of various biological materials. Biosorption can be defined as the ability of biological materials to accumulate heavy metals from wastewater through metabolically mediated or physico-chemical pathways of uptake [2]. Biosorption is generally used for the treatment of heavy metal pollutants in wastewater. Application of biosorption for organic and other pollutants could also be used for the treatment of wastewater [3]. Algae, bacteria, fungi and yeasts have proved to be potential metal/organic biosorbents [4]. The major advantages of biosorption over conventional treatment methods include [5]:

- **Cost Effective:** The cost for biosorbents is low since often they are made from abundant natural source or waste biosorbent from industry.
- **Metal/Organic Selective:** The metal/organic sorption capacity of different types of biosorbents can be more or less selective on different metals/organics. This depends on various factors, such as type of biosorbent, mixture in the solution, type of biosorbent preparation, and physico-chemical environment.

- **Regenerative:** Biosorbents can be reused after the metal/organic is recycled. Some types of biosorbent are immobilized in a synthetic polymer matrix to obtain the required mechanical properties for repeated reuse.
- **Minimization of Sludge Generation:** No secondary problems with sludge occur with biosorption, as is the case with many other techniques such as precipitation.
- **Metal/Organic Recovery Possible:** Metal/organic can be recovered after being sorbed from the solution by desorbing solutions such as acid/base and chelate agents (elutants).
- **Competitive Performance:** Biosorption is capable of a performance comparable to the most similar technique such as ion exchange treatment.

The biosorption process involves a solid phase (sorber or biosorbent; biological material) and a liquid phase (solvent, normally water) containing a dissolved species to be sorbed (sorbate). Due to higher affinity of the sorber for the sorbate species. The process continues till equilibrium is established between the amount of solid-bound sorbate species and its portion remaining in the solution. The degree of sorber affinity for the sorbate determines its distribution between the solid and liquid phases[6]. In this aspect, an agricultural equisetum such as horsetail has been used as biosorbent for the biosorption process. Equisetum horsetail is readily available, low cost and cheap and finally environment friendly bio-materials. Many steps were taken for preparing the biosorbents from horsetail for the removal of mercury and furfural from wastewater. The aim of this study was to prepare and characterize the biosorbent then investigate the sorption capacity, removal efficiency and kinetics of mercury and furfural from simulated wastewater as single and binary system onto granular equisetum horsetail.

## MATERIALS AND METHODS

### Biosorbent Granule Equisetum Horsetail (GEHT)

Granule equisetum horsetail was used as a biosorbent. It was obtained from market of Basrah city, Iraq. The equisetum horsetail was washed several times with distilled water to remove undesired solid materials and to dissolve heavy metals. Then, it dried under sun light and again it dried in oven at 60°C until having constant weight (24 h). The dry equisetum was crushed by jaw crusher and sieved by successive sieves, and then the biosorbent was kept in desiccators until the time of use. The physical and chemical properties were listed in Table (1)[7].

**Table 1: Physical and Chemical Properties of GEHT**

| Physical Properties                 | GEHT  | Chemical Properties | GEHT |
|-------------------------------------|-------|---------------------|------|
| Actual density, kg/m <sup>3</sup>   | 1537  | PH                  | 7.78 |
| Apparent density, kg/m <sup>3</sup> | 630   | Ash content, (%)    | 14   |
| Particle porosity                   | 0.554 | Cation Exchange     | -    |
| Bed porosity                        | 0.45  |                     |      |
| Pore volume, cm <sup>3</sup> /g     | 0.43  |                     |      |
| Particle size, mm                   | 0.41  |                     |      |
| Particle size, mm                   | 0.501 |                     |      |

### Adsorbate

1000 mg/l of stock solution of Hg<sup>2+</sup> ion and furfural (Fu) prepared by dissolving, Hg (NO<sub>3</sub>)<sub>2</sub>

1/2H<sub>2</sub>O and furfural respectively in distilled water. A solution of ions concentration of 50 mg/l was prepared by dilution of stock solution. The chemicals were annular grade produced by Fluka and BDH[7].

## Methods

The initial pH of furfural and mercury solutions was measured using Orion pH meter. The biosorption of metals and organics decrease at low pH values because of competition for binding sites between cations 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 biosorption sites on the surface of the GEHT. Therefore the optimum pH was found around 6 [7,8,9]. So, pH was adjusted with the range of (6) for all single and binary systems by adding the 0.1N HNO<sub>3</sub> and 0.1N NaOH for acidic and basic pH respectively.

The equilibrium biosorption isotherm, a sample of (100 ml) of each solution is placed in bottles of (250 ml), containing (0.1, 0.2,... 1.4 g) of GEHT. Then the bottles were placed on a shaker and agitated continuously at 150 rpm and 303K for (6 h). After (6 h) of agitation which was enough to reach equilibrium [7]. Concentration mercury was measured using atomic absorption spectrophotometer (model VGP-210), while spectrophotometer (model UV PD-303) was used for furfural.

JASCO FTIR 4200 spectrum system was used for FT-IR analysis of GEHT.

The kinetic experiments were obtained by using 2 liter Pyrex beaker fitted with a variable speed mixer. The beaker was filled with 1 liter of known concentration solution and agitation started before adding the GEHT. At time zero, the accurate weight of GEHT was added. The necessary dosage of GEHT to reach equilibrium related concentration of  $C_e/C_0$  equal 0.05, were calculated by using eq. (1). [7]. The adsorbed amount was calculated using the following equation:

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

The biosorption performance was evaluated in the removal efficiency as RE (%) [7].

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

In order to determine if the biosorption process is a physical or chemical, many experiments were carried out at the temperature ranged of (298-328 K). Thermodynamic parameters were obtained by varying the temperature and keeping the concentration of Fu and Hg<sup>2+</sup> at 50 mg/l. Four gram of GEHT and 100 ml of Fu/Hg<sup>2+</sup> solution at pH= 6 were added to each glass bottles. Then, the biosorption mixture was left in a thermostat shaker to maintain the desired temperature for 6h. The thermodynamic parameters such as  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  which describing Fu and Hg<sup>2+</sup> uptake by GEHT was calculated using the following relationships [8]

$$\Delta G^\circ = -RT \ln(K_e) \quad (3)$$

$$K_e = \frac{C_{ad./bio.}}{C_e} \quad (4)$$

$$\Delta H^\circ = \Delta G^\circ + T \Delta S^\circ \quad (5)$$

The optimum agitating speed for batch adsorbed to reach the needed equilibrium concentration of Fu and  $\text{Hg}^{2+}$  was obtained by using 2 liter Pyrex beaker fitted with a variable speed mixer (150,300,450, 600 and 750 rpm). The beaker was filled with 1(L) of known concentration solution and agitation started before adding the GEHT. At time zero, an accurate weight of GEHT was added. Samples were taken every 5 min. The necessary doses of GEHT to reach equilibrium related concentration of  $C_e/C_o$  equal 0.05 were calculated by using Eq. (1)[7].

Desorption experiments were performed in order to demonstrate the ability of spent GEHT for regeneration and reuse. Desorption experiments were performed by adding 0.5 gm of GEHT to four glass bottles. The desorption procedure was the same as that previously described for biosorption process. The loaded GEHT with Fu and  $\text{Hg}^{2+}$  was washed with deionized water and dried at 383K for 24 h after equilibrium experiments. Then, the GEHT was contacted with 50 ml of 0.1M elutant for 6 h to allow Fu/ $\text{Hg}^{2+}$  to be released from the GEHT. Four elutants have been examined (EDTA,  $\text{Na}_2\text{CO}_3$ , NaOH and HCl).

## RESULTS AND DISCUSSIONS

### Single System

The equilibrium isotherm for the investigated solutes (Fu and  $\text{Hg}^{2+}$ ) onto GEHT using multi-component Langmuir model are presented in Figure (1). The Langmuir model parameters ( $q_m$  and  $b$ ) were estimated by non-linear regression method using STATISTICA version-16 software. The correlation coefficient ( $R^2$ ) between the experimental data and the theoretical model is 0.9923 and 0.9963 for furfural and mercury respectively. The Langmuir parameters are as follows:

- **Fu:**  $q_m = 43.04751 \text{ mg/g}$ ,  $b = 0.0631 \text{ l/mg}$ ,  $R^2 = 0.9946$ .
- **$\text{Hg}^{2+}$ :**  $q_m = 7.1428 \text{ mg/g}$ ,  $b = 0.12211 \text{ /mg}$ ,  $R^2 = 0.9935$ .

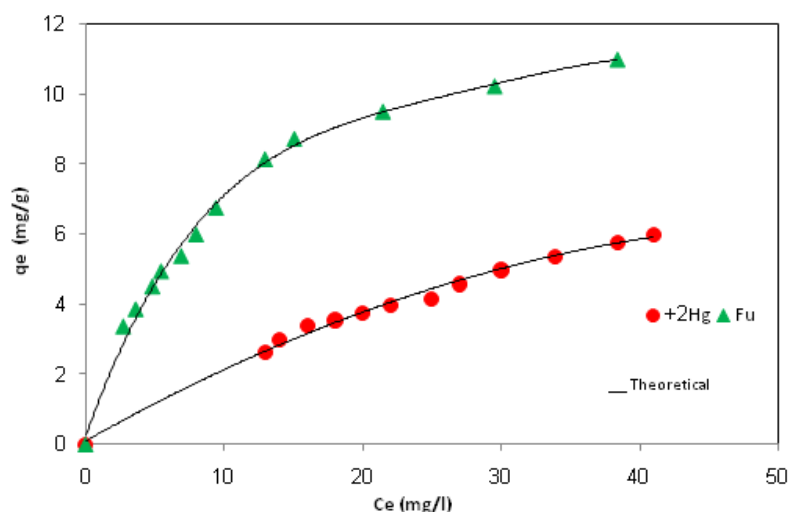


Figure 1: Biosorption of Furfural and Mercury onto GEHT in Single System at 303 K

Table 2: Biosorption Isotherm Models and Parameters of Single Solute Isotherm for Fu and  $\text{Hg}^{2+}$  [7]

| Model              | Parameters                           | GEHT   |                  |
|--------------------|--------------------------------------|--------|------------------|
|                    |                                      | Fu     | $\text{Hg}^{2+}$ |
| Freundlich[10]     | $K (\text{mg/g})(\text{l/mg})^{1/n}$ | 1.5345 | 0.7783           |
| $q_e = KC_e^{1/n}$ | n                                    | 2.0170 | 3.3222           |
|                    | $R^2$                                | 0.9929 | 0.9879           |

Table 2: Contd.,

|  |   |   |   |
|--|---|---|---|
| Langmuir[11]<br>$q_e = \frac{q_m b C_e}{1 + b C_e}$  | $q_m$ (mg/g)<br>$b$ (l/mg)<br>$R^2$<br>$R_s$<br>$E_{ad.}$ (%)           | 43.04751<br>0.0631<br>0.9946<br>0.2405<br>94.5601 | 7.1428<br>0.1221<br>0.9935<br>0.1407<br>74.1421 |
| Toth[12]<br>$q_e = \frac{K_t C_e}{(a_t + C_e)^{1/t}}$  | $K_t$ (mg/g)<br>$a_t$<br>$t$<br>$R^2$                                   | 7.2508<br>6.1209<br>2.6707<br>0.9943              | 257.0531<br>9.5218<br>0.7323<br>0.9929          |
| Combination of Langmuir-Freundlich[13]<br>$q_e = \frac{b q_m C_e^{1/n}}{1 + b C_e^{1/n}}$                | $q_m$ (mg/g)<br>$b$ (l/mg) <sup>1/n</sup><br>$n$<br>$R^2$               | 100.2984<br>0.0425<br>1.4475<br>0.9958            | 16.8006<br>0.1864<br>1.6905<br>0.9935           |
| Khan [14]<br>$q_e = \frac{Q_{max} b_k C_e}{(1 + b_k C_e)^{a_k}}$   | $Q_{max}$ (mg/g)<br>$b_K$ (l/mg)<br>$a_K$<br>$R^2$                      | 2.0337<br>6.0558<br>0.4300<br>0.9967              | 52.6538<br>0.0625<br>1.5047<br>0.9929           |
| Temkin[15]<br>$q_e = \frac{RT}{b} \ln(K_T C_e)$  | $B_1$ (KJ/mole)<br>$K_T$ (l/mg)<br>$R^2$                                | 0.8427<br>1.0125<br>0.8924                        | 0.4786<br>0.8292<br>0.9572                      |
| BET [16]<br>$q_e = \frac{B Q C_e}{(C_s - C_e)[1 + (B-1)(C_e/C_s)]}$                                      | $B$ (l/mg)<br>$Q$ (mg/g)<br>$R^2$                                       | 6.50661<br>34.8066<br>0.9789                      | 83.6195<br>23.0814<br>0.8152                    |
| Harkins - Henderson [17]<br>$q_e = \frac{K_h^{1/n_h}}{C_e^{1/n_h}}$                                      | $K_h$ (mg/g)(mg/l) <sup>1/n<sub>h</sub></sup><br>$n_h$<br>$R^2$         | 0.0339<br>1.2813<br>0.9678                        | 0.3171<br>-1.2926<br>0.9329                     |
| Redlich-Peterson[18]<br>$q_e = \frac{A_R C_e}{1 + B_R C_e^{m_R}}$  | $A_R$ (l/mg)<br>$B_R$ (l/mg) <sup>m<sub>R</sub></sup><br>$m_R$<br>$R^2$ | 2.2573<br>1.9171<br>0.8936<br>0.9954              | 0.4233<br>1.8800<br>1.9729<br>0.9898            |
| Radke-Praunszitz[19]<br>$q_e = \frac{K_{RP} C_e}{1 + \left(\frac{K_{RP}}{F_{RP}}\right) C_e^{1-N_{RP}}}$ | $K_{RP}$ (l/mg)<br>$F_{RP}$<br>$N_{RP}$<br>$R^2$                        | 2.1036<br>10.3343<br>0.7155<br>0.9954             | 0.3591<br>104.8074<br>-0.2901<br>0.9934         |

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

In order to find out which functional groups were responsible for the Fu and Hg<sup>2+</sup> biosorption, FT-IR analysis of raw and loaded GEHT was carried out. Infrared spectra of GEHT samples before and after furfural and mercury binding were shown in Figure (2) and listed in Table 3. Spectra analysis of FT-IR spectrum after cations adsorption showed that there was a substantial decrease in the wave number and adsorption intensity of GEHT. Furfural can be adsorbed by means of electrostatic attraction between negatively charge furfural and positively charged binding sites. In this case positive groups such as amine (-NH<sub>2</sub><sup>+</sup>) at 3449.62cm<sup>-1</sup> and alkane (-CH<sup>+</sup>) at 1639.49 cm<sup>-1</sup> considered to be responsible for this attraction. Physical adsorption was the main mechanism to adsorb furfural and mercury biosorption depended mainly on the electrostatic attraction by negatively charge functional groups (-OH<sup>-</sup>) at 1436.47 cm<sup>-1</sup>.

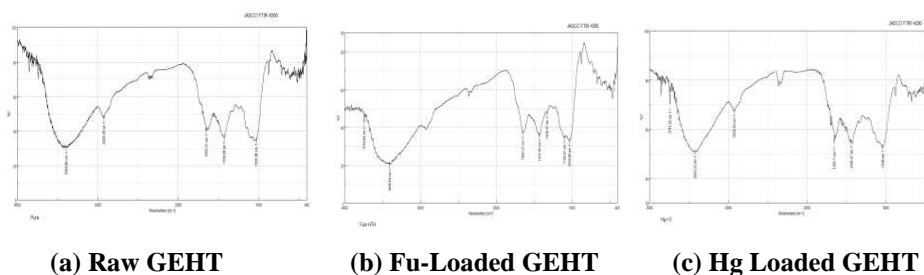


Figure 2: FT-IR Analysis for Granular Horsetail

Table 3: FT-IR Analysis for Raw and Loaded GEHT

| Functional Group              | Type of Bond                            | Wave Number, $\text{cm}^{-1}$                                       | Tr (%) before Adsorption | Tr (%) after Adsorption |                  |
|-------------------------------|---|---|--------------------------|-------------------------|------------------|
|                               |   |   |                          | Fu                      | $\text{Hg}^{2+}$ |
| Carboxylic acid               | -OH                                     | 3749.62   | 75                       | 55                      | 87               |
| Carboxylic acid               | -OH                                     | 3549.02   | 60                       | 73                      | 68               |
| Carboxylic acid, Amide, Amine | -OH, -NH, -NH <sub>2</sub> <sup>+</sup> | 3393.68   | 57                       | 71                      | 45               |
| Carboxylic acid, Amide, Amine | -OH, -NH, -NH <sub>2</sub> <sup>+</sup> | 3417.86   | 54                       | 60                      | 62               |
| Carboxylic acid               | -OH                                     | 2928.38   | 68                       | 48                      | 68               |
| Alkane                        | -CH <sup>+</sup>                        | 2360.87   | 61                       | 91                      | 68               |
| Alkane                        | -CH <sup>+</sup>                        | 1652.21   | 66                       | 90                      | 55               |
| Alkane                        | -CH <sup>+</sup>                        | 1430.68   | 64                       | 94                      | 56               |
| Carboxylic acid               | -OH                                     | 1543.05   | 67                       | 89                      | 51               |
| Carboxylic acid               | -OH                                     | 1430.68   | 65                       | 99                      | 80               |
| Carboxylic acid               | -C=O                                    | 1034.38   | 70                       | 86                      | 73               |
| Alkyl halides                 | -C-Br                                   | 613.36  | 68                       | 98                      | 69               |
|                               |   | Sum of difference in peaks absorption %, (after -before) adsorption |                          | 954                     | 782              |

### Binary System

Four isotherm models were used to fit the experimental data. The isotherms were shown in Figure (3) and listed in Table 4 which represents the values of the parameters of each model. For the binary system the extended Langmuir model seems to give the best fitting for the experimental data i.e, highest value of ( $R^2$ ). In addition, Redlich-Peterson and extended Freundlich models may participate with extended Langmuir model to give the best fit for binary system. The behavior of an equilibrium isotherm was a favorable type. It can be seen from the figure and the related tables, Fu always adsorbed more favorably onto GEHT than  $\text{Hg}^{2+}$ .

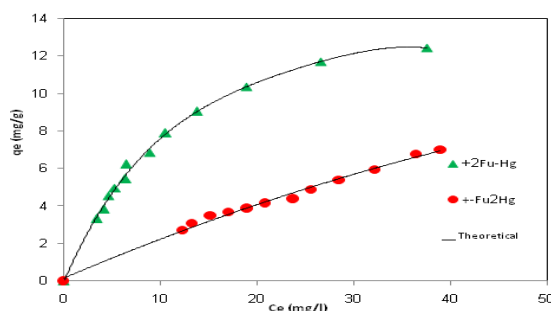


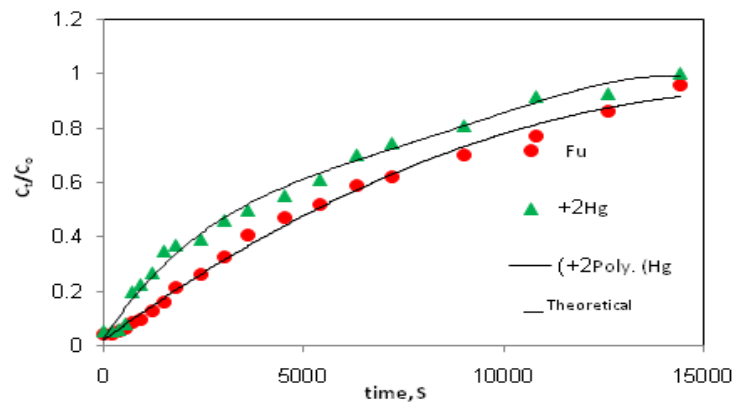
Figure 3: Biosorption of Furfural and Mercury onto GEHT in Binary System at 303 K

**Table 4: Biosorption Isotherm Models and Parameters of Binary Solute Isotherm for Fu and Hg<sup>2+</sup>[7]**

| Model  | Parameters  | GEHT<br>(Fu-Hg <sup>2+</sup> ) Solution   |   |
|--|---|---|---|
|  |   | Fu  | Hg <sup>2+</sup>  |
|  |   | Extended Langmuir[20]<br>$q_{e,i} = \frac{q_{m,i} b_i C_{e,i}}{1 + \sum_{k=1}^N b_k C_{e,k}}$ | q <sub>m</sub> (mg/g)<br>b(l/mg)<br>R <sup>2</sup><br>R <sub>s</sub><br>E <sub>bio.</sub> (%) |
| Combination of Langmuir-Freundlich[21]<br>$q_{e,i} = \frac{q_{m,i} b_i C_{e,i}^{1/n_i}}{1 + \sum_{i=1}^N b_i C_{e,i}^{1/n_i}}$ | q <sub>m</sub> (mg/g)<br>b<br>n<br>R <sup>2</sup>   | 42.0180<br>0.1383<br>6.8332<br>0.9967   | 0.7498<br>6.7330<br>4.0191<br>0.9852  |
| Redlich-Peterson[21]<br>$q_{e,i} = \frac{K_{Ri} (b_{Ri}) C_{e,i}}{1 + \sum_{k=1}^N b_{R,k} (C_{e,k})^{m_{R,k}}}$               | K <sub>R</sub> (l/mg)<br>b <sub>R</sub> (l/mg) <sup>m<sub>R</sub></sup><br>m <sub>R</sub><br>R <sup>2</sup> | 6.2425<br>1.3004<br>0.7249<br>0.9978  | 1.0450<br>0.0189<br>0.6649<br>0.9875  |
| Extended Freundlich[22]<br>$q_{e,i} = \frac{K_i C_{e,i}^{n_i+n_i}}{C_{e,i}^{n_i} + \sum_{j=1}^N K_j C_{e,j}^{n_j}}$            | K<br>(mg/g)(l/mg) <sup>1/n</sup><br>n<br>R <sup>2</sup>   | 10.9800<br>0.0592<br>0.9953   | 2.7762<br>0.1520<br>0.9875  |

**Kinetic Studies**

The experimental data was fitted to the various kinetic models as shown in Figure (4) and there parameters were listed in Table 5. The model parameters were found by linear regression. The pseudo-second order was the most fitted model to the experimental data. The external mass transfer was very fast. The value of constant (C) in the intra-particle diffusion model is not equal to zero, suggesting that biosorption proceeds from boundary layers mass transfer across the interfaces to the intra-particle diffusion within the pores of biosorbent. This indicates that, the mechanisms of furfural and mercury biosorption are complex and both the surface biosorption as well as intra-particle diffusion contribute to the rate determining step. Elovich model shows high value of correlation coefficient (R<sup>2</sup>) for biosorption of furfural and mercury. This indicates that, the biosorption is heterogeneous process (i.e., physical, chemical, electrostatic, and other mechanisms). However, physical biosorption stay play a great role in the process, this approved previously in determining heat of biosorption.



**Figure 4: Biosorption Kinetics for Furfural and Mercury**

Table 5: The Kinetic Constants for the Biosorption of Fu and Hg<sup>2+</sup>[7]

| Model  | Parameters                              | GEHT  |   |
|--|---|---|---|
|  |   | Fu  | Hg <sup>2+</sup>                            |
| Pseudo-first order[23]<br>$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303t}$      | $q_e$ (mg/g)<br>$K_1$ (l/s)<br>$R^2$    | 6.6116<br>$3.4348 \times 10^{-4}$<br>0.9634 | 7.1030<br>$2.9078 \times 10^{-4}$<br>0.9085 |
| Pseudo-second order[24]<br>$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$ | $q_e$ (mg/g)<br>$K_2$ (g/mg.s)<br>$R^2$ | 7.8260<br>$4.0501 \times 10^{-5}$<br>0.9942 | 9.5643<br>$2.1262 \times 10^{-5}$<br>0.9910 |
| Intra-particle diffusion[25]<br>$q_t = K_{id} t^{1/2} + C$                       | $K_{id}$<br>$C$<br>$R^2$                | $1.6451 \times 10^{-3}$<br>0.8875<br>0.9187 | $0.9108 \times 10^{-3}$<br>0.3961<br>0.9485 |
| Elovich[26]<br>$q_t = \frac{1}{b} \ln a \bar{b} + \frac{1}{b} \ln t$             | $a$<br>$b$<br>$R^2$                     | $1.0301 \times 10^{-2}$<br>0.4753<br>0.9824 | $0.9273 \times 10^{-2}$<br>0.4423<br>0.9813 |

### Thermodynamic Parameters

The biosorption of Fu and Hg<sup>2+</sup> for various temperatures (298-328 K) at 6 h of contact time were shown in Figure (5). The heat of biosorption ( $\Delta H^0$ ) was found to be (15.176, 7.428) for furfural and mercury respectively. However, these values are less than 40 KJ/mole which indicate that, the process was exothermic reaction and that physical mechanism play a major role in the biosorption processes [8].

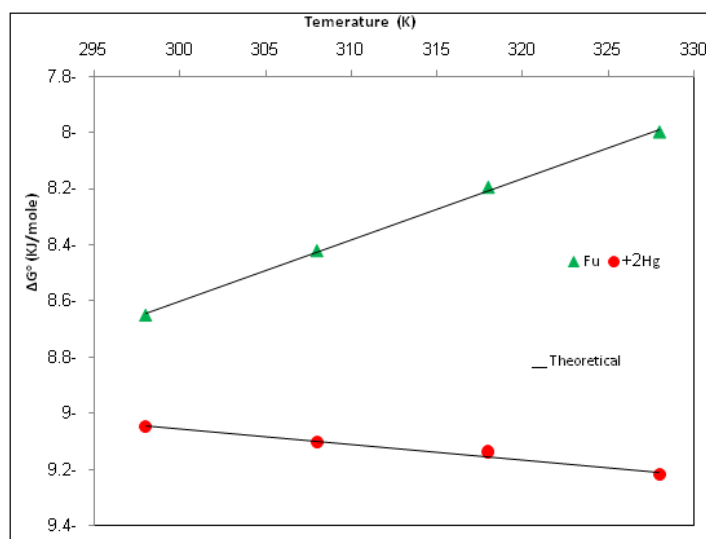


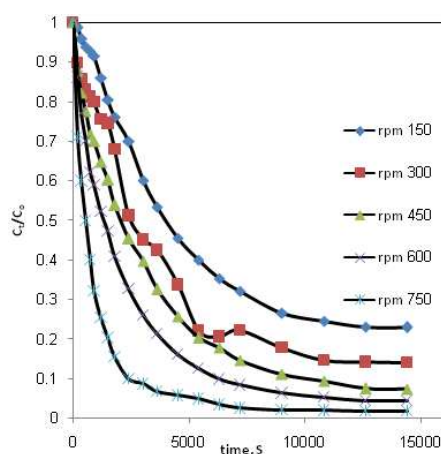
Figure 5: Free Energy Change for Furfural and Mercury Biosorption

### Optimum Agitation Speed

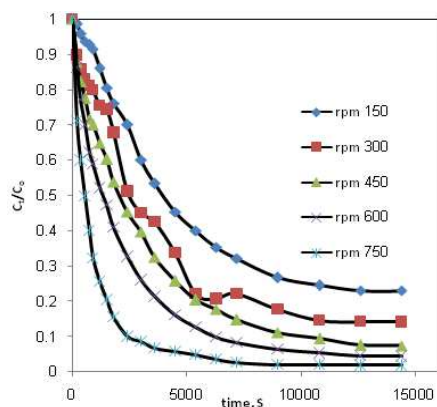
The concentration decay curves of solutes were shown in Figure (6, 7) for Fu and Hg<sup>2+</sup> respectively at different agitation speeds of (150, 300, 450, 600 and 750 rpm). The effluent concentration which equal to 5% of inlet concentration was taken as the breakthrough point. The optimum agitation speed needed to achieve  $C_e/C_o=0.05$  was found to be 600 rpm. These Figure show that, if the speed is above 600 rpm, the equilibrium relative concentration was less than 0.05, with possible pulverization of GEHT at high speed, and in this case the work was ended with powdered rather than granular GEHT.



The effect of increasing the agitating rate was to decrease the film resistance to mass transfer surrounding the biosorbent particles[8].



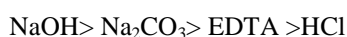
**Figure 6: Concentration-Time Decay Curves for Furfural Biosorption onto GEHT at Different Agitation Speed**



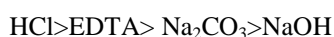
**Figure 7: Concentration-Time Decay Curves for Mercury Biosorption onto GEHT at Different Agitation Speed**

### Desorption and Regeneration Studies

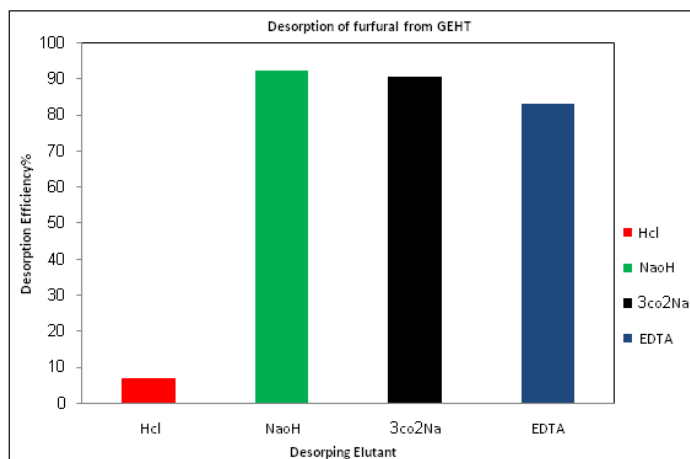
The desorption efficiencies using different desorbing elutants from GEHT are shown in figures (8, 9). It is clear from the previous figures, the elution tendency as a percentage recovery of furfural followed the sequence as:



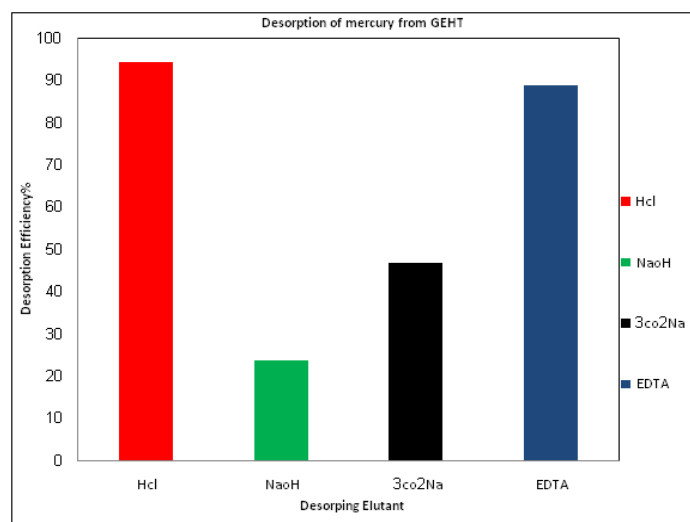
This observed trend may be due to affinity between hydroxyl group present in furfural and NaOH. Sodium hydroxide is considered one of the chelating agents which interact with furfural through molecular attraction through covalent bond, which is stronger than that responsible to bind furfural to functional groups onto GEHT surface. However, for mercury the process is reverse and followed the following sequence:



This is due to the ionic attraction between mercury cation and negative groups present in acid elutants such as  $\text{Cl}^-$  and  $\text{CO}_3^{2-}$ . Therefore, NaOH and HCl were selected as an effective desorbing elutants for furfural and mercury respectively and used in biosorption-desorption-regeneration cycle.



**Figure 8: Desorption Efficiency of Furfural from GEHT**



**Figure 9: Desorption Efficiency of Mercury from GEHT**

## CONCLUSIONS

Based upon the experimental results and theoretical application models in batch systems, the following remarks can be made about this work:

- GEHT was more efficient in biosorption of furfural than mercury.
- Functional groups of GEHT responsible for biosorption for furfural exceed that for mercury.
- The equilibrium isotherm for each component Fu and Hg<sup>2+</sup> onto GEHT were of favorable type. In addition to the familiar Langmuir model. While for binary system, extended Langmuir model was well fitted the equilibrium isotherms.
- The biosorption capacity in single and binary (Fu and Hg<sup>2+</sup>) systems onto GEHT is: Fu > Hg<sup>2+</sup> onto GEHT. This difference in behavior due to high affinity between Fu GEHT.
- Thermodynamic parameters including the Gibbs free energy and enthalpy changes indicated that the biosorption of furfural and Hg<sup>2+</sup> ions onto biosorbent was feasible, spontaneous and exothermic reactions.

- Pseudo-second order kinetic model was found to be more suitable for biosorption of furfural and mercury. This was due to higher correlation coefficients as compared with other models.
- The optimum agitation speed needed to achieve  $C_e/C_0=0.05$  was found to be 600 rpm.
- NaOH and HCl were selected as an effective desorbing elutants for furfural and mercury respectively and used in biosorption-desorption-regeneration cycle.

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## APPENDICES

### Nomenclatures

Table 6

| Symbol          | Description   | Units                       |
|-----------------|---|-----------------------------|
| a               | Elovich model parameter                                   | mg/g.s                      |
| a <sub>K</sub>  | Khan model parameter                                      | -                           |
| a <sub>t</sub>  | Toth model parameter                                      | -                           |
| A <sub>R</sub>  | Reddlich-Peterson model parameter                         | l/mg                        |
| B               | BET model parameter                                       | l/mg                        |
| B <sub>1</sub>  | Temkin isotherm constant                                  | kJ/gm                       |
| b               | Elovich model parameter                                   | (g/mg)                      |
| b <sub>K</sub>  | Khan model parameter                                      | l/mg                        |
| C               | Parameter in intra-particle diffusion model               | mg/g                        |
| C <sub>e</sub>  | Equilibrium concentration                                 | mg/l                        |
| C <sub>ei</sub> | Equilibrium concentration of component i                  | mg/l                        |
| C <sub>0</sub>  | Initial solute concentration                              | mg/l                        |
| F <sub>RP</sub> | Radke-Praunsitz model parameter                           | -                           |
| K               | Freundlich equilibrium parameter                          | (mg/g)(l/mg) <sup>1/n</sup> |
| K <sub>1</sub>  | Rate constant of pseudo first-order adsorption            | 1/s                         |
| K <sub>2</sub>  | Rate constant of pseudo second-order adsorption           | (g/mg.s)                    |
| K <sub>h</sub>  | Harkins-Henderson model parameter                         | (mg/g) <sup>n</sup> (mg/l)  |
| K <sub>id</sub> | Rate constant of intra-particle diffusion model           | (mg/g.s <sup>0.5</sup> )    |
| K <sub>R</sub>  | Reddlich-Peterson model parameter system)                 | l/mg                        |
| K <sub>RP</sub> | Radke- Praunsitz model parameter                          | l/g                         |
| K <sub>T</sub>  | Equilibrium binding constant in Temkin model              | l/mg                        |
| m <sub>R</sub>  | Reddlich-Peterson model parameter                         |                             |
| n               | Freundlich equilibrium parameter and Sips model parameter |                             |
| n <sub>h</sub>  | Harkins-Henderson model parameter                         |                             |

Table 6: Contd.,

|                    |   |                                 |
|--------------------|---|---------------------------------|
| $N_{RP}$           | Radke-Praunsitz model parameter                                 |                                 |
| Q                  | BET model parameter   | mg/g                            |
| $Q_{max}$          | Khan model parameter  | mg/g                            |
| $q_e$              | Internal concentration of solute in particle at equilibrium     | mg/g                            |
| $q_{ei}$           | Amount of adsorbate adsorbed per mass of adsorbent of species i | $g \cdot g^{-1} \cdot min^{-1}$ |
| $q_m$              | Adsorption capacity defined by Langmuir equation                | mg/g                            |
| $q_{mi}$           | Adsorption capacity for species i                               |                                 |
| R                  | Universal gas constant  | 8.314 kJ/mol.K                  |
| $R_s$              | 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 granular equisetum horsetail                            | g                               |
| $(\Delta G^\circ)$ | Gibbs free energy   | KJ/mol                          |
| $(\Delta H^\circ)$ | Enthalpy change   | J/mol                           |
| $(\Delta S^\circ)$ | Entropy change  | J/mol. K                        |

