



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

Abbas H. Sulaymon and Hayfa'a L. Swadi*

Power Engineering Department, College of engineering, University of Baghdad, Iraq

Chemical Engineering Department, College of Engineering, University of Basrah, Iraq

ABSTRACT

Equisetum horsetail was used to produce bioadsorbent through easy and environmental friendly processes. This equisetum based biosorbent was evaluated for removal of Hg^{2+} and furfural from simulated wastewater using granule equisetum horsetail was investigated. Batch type experiments were carried out to find the equilibrium isotherm data for single and binary system. 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 $R_2 \text{Hg}^{2+} = 0.9969$). Pseudo-first order, pseudo-second order, intra-particle diffusion and Elovich choose for kinetic study. Pseudo-second order model was well fitted for Hg^{2+} and furfural ($R_2 \text{ Fu} = 0.9942$ and $R_2 \text{Hg}^{2+} = 0.9910$). Thermodynamic parameters including the Gibbs free energy and enthalpy changes indicated that the biosorption of furfural and Hg^{2+} ions onto biosorbent was feasible, spontaneous and exothermic reactions. Significant desorption of Hg^{2+} and furfural from simulated wastewater were obtained when using 0.1M NaOH and HCl.

Keywords: *Granule equisetum horsetail, Isotherm, Single system, Langmuir model*

© 2013 IJCPS. All rights reserved

* Corresponding author.

E-mail addresses: hayfaa_swadi@yahoo.com (Hayfaa L. Swadi)

© 2013 IJCPS. All rights reserved.

1. INTRODUCTION

Mercury pollution results from metallurgical industries, chemical manufacturing and metal finishing industries [1, 2]. Mercury in the liquid form is not dangerous and it is used in a number of industries. In the vapor form mercury becomes very poisonous. It attacks the lungs, kidneys and the brain. The vapor crosses the blood-brain and blood stream [3]. Furfural is used as a solvent in industries [4]. Furfural solvent has high capability for separation a component of multi-components and especially in petroleum combinations to separate sulfur and carbonaceous compounds. This substance is used to remove aromatics in refinery of industrial lubricant oils [5]. Direct contact with this substance should be avoided since this substance causes sensitivity in the skin, eye, mucous membranes, even the destruction of the liver, kidney and osteoporosis [6]. 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 [7]. The search for new technologies involving the removal of toxic metals from wastewater has directed attention to biosorption, based on metal binding capacities of various biological materials. Biosorption can be defined as the passive uptake of toxicants by dead/inactive biological materials or by materials derived from biological sources. The major advantages of biosorption over conventional treatment methods include low cost, high efficiency of metal removal from dilute solution, minimization of chemical and/or biological sludge, no additional nutrient requirement and regeneration of biosorbent and the possibility of metal recovery [8, 9, 10]. Actual wastewater treatment systems often have to deal with a mixture of heavy metals. The presence of inorganic (especially heavy metals) and organic compounds in the environment can be detrimental to a variety of living species including humans. While many studies have been carried out on the removal of single species of metal ions and organic species by wastewater treatment methods, little attention seems to have been given to the study of organic-metal ion mixtures. In this aspect, an agricultural equisetum such as horsetail has been used as biosorbent for the biosorption. Equisetum horsetail is readily available, low cost and cheap, environment friendly bio-materials. A step was taken for preparing biosorbents from horsetail for removal of mercury and furfural from wastewater. The aim of this study was to prepare biosorbent and characterization and investigate the sorption capacity, removal efficiency and kinetics of mercury and furfural from simulated wastewater as single and binary system onto granular equisetum horsetail.

2. MATERIALS AND METHODS

2.1 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 dissolved heavy metals, dried under sun light, then 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, then after which the biosorbent was kept in a desiccators for use. The physical and chemical properties were listed in Table.1.

Tab.1. Physical and chemical properties of GHTH.

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

2.2 ADSORBATE

1000 mg/l of stock solution of Hg²⁺ ion and furfural (Fu) prepared by dissolving, Hg (NO₃)₂·1/2H₂O and furfural respectively in distilled water. A solution of ions concentration of 50 mg/l was prepared by dilution of stock solution. Chemicals were annular grade produced by Fluka and BDH.

2.3 METHODS

The biosorption of Hg²⁺ ion and furfural (Fu) decreases at low pH values 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 biosorption processes. Therefore the optimum pH was found around 6. pH was adjusted with the range of (6) for all single and binary system by adding the 0.1N HNO₃ and 0.1N NaOH. For determination of 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. The bottles were then 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 [11], 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 for mercury metal, while for furfural (model UV PD-303) spectrophotometer, and computed from the calibration curves.

The functional groups of GEHT were detected by FT-IR analysis before and after biosorption. The proportion of GEHT biomass/KBr was 1/100. The background was obtained from the scan of pure KBr. JASCO FTIR 4200 spectrum system was used for FT-IR analysis of GEHT. Kinetic experiments were carried out for understanding of the biosorption dynamics of Hg²⁺ and furfural onto GEHT. A 2000 ml Pyrex beaker was filled with 1000 ml of 50 mg/l solution of Hg²⁺ and agitation was started before adding the biosorbent. At zero time, an accurate weight of biosorbent was added. The suspensions were agitated at 450 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 GEHT biosorption was evaluated in terms of its removal efficiency as RE (%).

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

To decide if the biosorption process is a physical or chemical, the experiments were carried out at the temperature ranged (298-328 K). Thermodynamic parameters were obtained by varying the temperature and keeping concentration of 50 mg/l for Fu and Hg^{2+} . Four gram of GEHT was introduced to each glass bottles employed and 100 ml of Fu/ Hg^{2+} solution at pH= 6 were added to the bottles. The biosorption mixture was then left in a thermostat shaker to maintain the desired temperature for 6 h. The thermodynamic parameters such as ΔG° , ΔH° and ΔS° , describing Fu and Hg^{2+} uptake by GEHT was calculated using the following relationships [12]

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

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

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

Estimating the optimum agitating speed for batch adsorbed to reach the needed equilibrium concentration of Fu and Hg^{2+} was obtained by using 2 liter Pyrex beaker fitted with a variable speed mixer (150,300,450 and 600,750 rpm). The beaker was filled with 1(L) of known concentration solution and agitation started before adding the GEHT. At time zero, the 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_0 equal 0.05 were calculated by using Eq. (1).

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 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/ Hg^{2+} to be released from the GEHT. Four elutants have been examined (EDTA, Na_2CO_3 , NaOH and HCl).

3. RESULTS AND DISCUSSION

3.1 SINGLE SYSTEM

The biosorption isotherm was obtained by plotting the weight of the solute adsorbed per unit weight of GEHT (q_e) against the equilibrium concentration of the solute in the solution (C_e) at constant temperature [13]. For a single system of Hg^{2+} and Fu, the equilibrium isotherms were conducted at (303 K) with initial concentration of each component, $C_0=50$ mg/l. The isotherm is shown in Fig.1. Ten isotherm models were used to fit the experimental data. Isotherm models were given in Table 2.

The model parameters were evaluated by non-linear curve fitting method using STATISTICA version 16 and EXCEL-2007 software. Table.2 represents the parameters of each model, the correlation coefficients (R^2) and the percentage reduction of biosorption. It is clear from Fig.(1) and Table 2, that the equilibrium isotherm for each single component was of favourable type, since $0 < R_s < 1$ ($R_s = 0.2405$ and 0.14071) for Fu and Hg^{2+} onto GEHT. The experimental data for

furfural and mercury described successfully with Langmuir model with correlation coefficient 0.9946 and 0.9935 on to GEHT. It was found that the maximum metal uptake q_m (mg/g) for Fu was greater than that for Hg^{2+} on to GEHT (q_m , $Fu=43.04751$ and $q_m, Hg^{2+}=7.1428$) respectively.

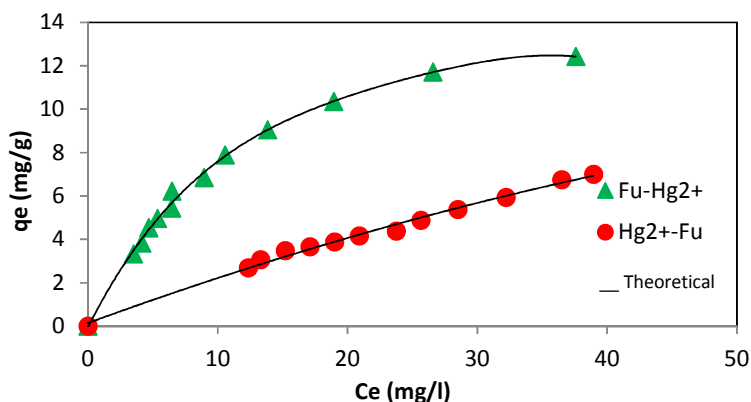


Fig. 1. Biosorption of furfural and mercury onto GEHT in binary system at 303 K.

Table.2. Biosorption isotherm models and parameters of single solute isotherm for Fu and Hg^{2+} .

Model	Parameters	GEHT	
		Fu	Hg^{2+}
Freundlich[14]	$K (mg/g)(l/mg)^{1/n}$	1.5345	0.7783
$q_e = KC_e^{1/n}$	n	2.0170	3.3222
	R^2	0.9929	0.9879
Langmuir [15]	$q_m (mg/g)$	43.04751	7.1428
$q_e = \frac{q_m b C_e}{1 + b C_e}$	b (l/mg)	0.0631	0.1221
	R^2	0.9946	0.9935
Toth[16]	$K_t (mg/g)$	7.2508	257.0531
$q_e = \frac{K_t C_e}{(a_t + C_e)^{1/t}}$	a_t	6.1209	9.5218
	t	2.6707	0.7323
Combination of Langmuir	$q_m (mg/g)$	100.2984	16.8006
Freundlich[17]	$b (l/mg)^{1/n}$	0.0425	0.1864
$bq_m C_e^{1/n}$	n	1.4475	1.6905

Khan [18]	$Q_{\max}$ (mg/g)	2.0337	52.6538
$q_e = \frac{Q_{\max} b_k C_e}{(1 + b_k C_e)^{a_k}}$	b_k (l/mg)	6.0558	0.0625
	a_k	0.4300	1.5047
Temkin[19]	B_1 (KJ/mole)	0.8427	0.4786
$q_e = \frac{RT}{BET [20]} \ln(K_T C_e)$	K_T (l/mg)	1.0125	0.8292
	B (l/mg)	6.50661	83.6195
$q_e = \frac{BQ C_e}{(C_s - C_e)[1 + (B-1)C]}$	Q (mg/g)	34.8066	23.0814
	R^2	0.9789	0.8152
Harkins - Henderson [21]	$K_h(\text{mg/g})(\text{mg/l})^{1/n_h}$	0.0339	0.3171
$q_e = \frac{K_h^{1/n_h}}{C_e^{1/n_h}}$	n_h	1.2813	-1.2926
	R^2	0.9678	0.9329
Redlich-Peterson[22]	A_R (l/mg)	2.2573	0.4233
$q_e = \frac{A_R C_e}{1 + B_R C_e^{m_R}}$	B_R (l/mg) m_R	1.9171	1.8800
	m_R	0.8936	1.9729
Radke-Praunsitz [23]	K_{RP} (l/mg)	2.1036	0.3591
$q_e = \frac{K_{RP} C_e}{1 + (\frac{K_{RP}}{F_{RP}}) C_e^{1-N}}$	F_{RP}	10.3343	104.8074
	N_{RP}	0.7155	-0.2901
	R^2	0.9954	0.9934

3.2 Fourier-Transform Infrared Analysis (FT-IR)

In order to find out which functional groups were responsible for the Fu and Hg^{2+} 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 Fig.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 ($-\text{NH}_2^+$) at 3449.62cm^{-1} and alkane ($-\text{CH}^+$) at 1639.49cm^{-1} considered to be responsible for this attraction. Physical adsorption was the main mechanisms to adsorb furfural and mercury biosorption depended mainly on the electrostatic attraction by negatively charge functional groups ($-\text{OH}^-$) at 1436.47cm^{-1} .

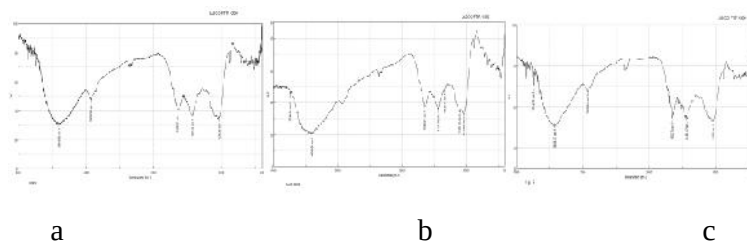


Fig.2.FT-IR analysis for granular horsetail (a) raw GEHT, (b) Fu-loaded GEHT and (c) Hg loaded GEHT.

Table.3.FT-IR analysis for raw and loaded GEHT.

Wavenumber,cm ⁻¹	Type of bond	Functional group	Tr (%) before adsorption	Tr (%)	
				Fu	Hg ²⁺
3749.62	-OH ⁺	Carboxylic acid	75	55	87
3549.02	-OH ⁺	Carboxylic acid	60	73	68
3393.68	-OH ⁺ , -	Carboxylic acid,	57	71	45
3417.86	-OH ⁺ , -	Carboxylic acid,	54	60	62
2928.38	-OH ⁺	Carboxylic acid	68	48	68
2360.87	-CH ⁺	Alkane	61	91	68
1652.21	-CH ⁺	Alkane	66	90	55
1430.68	-CH ⁺	Alkane	64	94	56
1543.05	-OH ⁺	Carboxylic acid	67	89	51
1430.68	-OH ⁺	Carboxylic acid	65	99	80
1034.38	-C=O ⁺	Carboxylic acid	70	86	73
613.36	-C-Br ⁻	Alkyl halides	68	98	69
Sum of difference in				954	782

3.3 BINARY SYSTEM

For a binary system of Hg²⁺ and furfural the equilibrium isotherms were conducted at (303 K) with initial concentration of each component, C₀=50 mg/l the isotherm was shown in Fig.3. Four isotherm models were used to fit the experimental data. The isotherm models were listed in Table 4 which represents the values of the parameters of each model, the correlation coefficients (R²) and the percentage reduction of biosorption capacity. For the binary system the extended Langmuir model seems to give the best fitting for the experimental data i.e, highest value of (R²). 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 related tables, Fu always adsorbed more favorably onto GEHT than Hg²⁺.

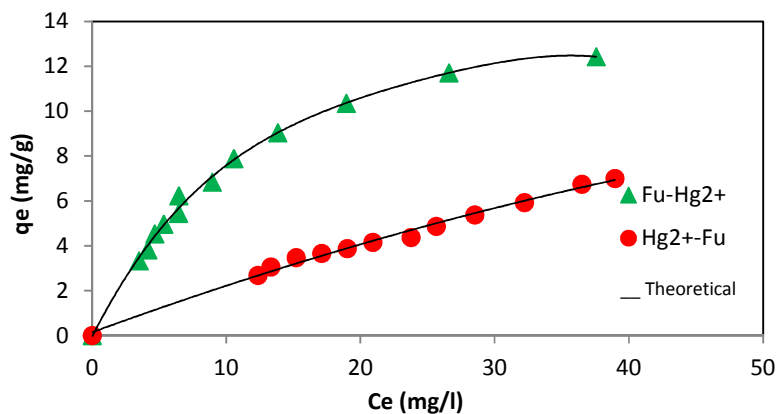


Fig.3.Biosorption of furfural and mercury onto GEHT in binary system at 303 K.

Table.4.Biosorption isotherm models and parameters of binary solute isotherm for Fu and Hg^{2+} .

Model	Parameters	GEHT (Fu- Hg^{2+}) Solution	
		Fu	Hg^{2+}
Extended Langmuir[24]	q_m (mg/g)	35.6240	1.4874
$q_{e,i} = \frac{q_{m,i} b_i C_{e,i}}{1 + \sum_{k=1}^N b_k C_{e,k}}$	b (l/mg)	0.05137	0.3293
	R^2	0.9977	0.9969
	R_s	0.2802	0.0572
	F_{max} (%)	93.0304	51.2601
Combination of Langmuir-Freundlich[25]	q_m (mg/g)	42.0180	0.7498
$q_{e,i} = \frac{q_{m,i} b_i C_{e,i}^{1/n_i}}{1 + \sum_{i=1}^N b_i C_{e,i}^{1/n_i}}$	b	0.1383	6.7330
	n	6.8332	4.0191
	R^2	0.9967	0.9852
Redlich-Peterson[25]	K_R (l/mg)	6.2425	1.0450
$q_{e,i} = \frac{K_{Ri} (b_{Ri}) C_{e,i}}{1 + \sum_{k=1}^N b_{R,k} (C_{e,k})^{m_{R,k}}}$	b_R (l/mg) m_R	1.3004	0.0189
	m_R	0.7249	0.6649
	R^2	0.9978	0.9875
Extended Freundlich[26]	K (mg/g)(l/mg) $^{1/n}$	10.9800	2.7762
$q_{e,i} = \frac{K_i C_{e,i}^{n_i+1}}{C_{e,i}^{n_i} + \sum_{j=1}^N K_j C_{e,j}^{n_j}}$	n	0.0592	0.1520
	R^2	0.9953	0.9875

3.4 KINETIC STUDIES

Biosorption kinetics was obtained by plotting the weight of the solute adsorbed per unit weight of GEHT against time Fig.4. The experimental data was fitted to the various kinetic models and their parameters were listed in Table.5. The model parameters were found by linear regression. The pseudo-second order was the most fitted model to 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 the mechanisms of furfural and mercury biosorption is 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^2) 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 may play a great role in the process, this was approved previously in determining heat of biosorption.

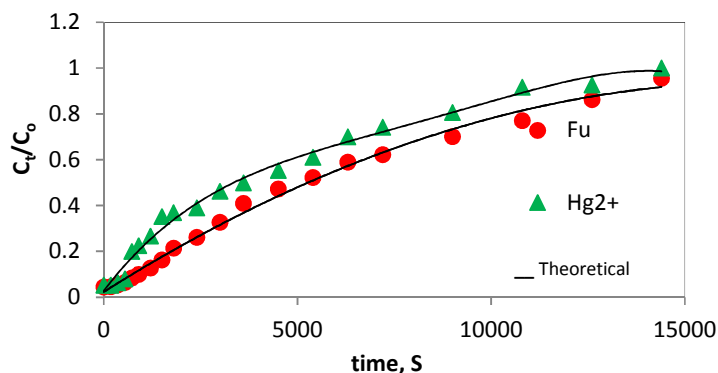


Fig.4. Biosorption kinetics for furfural and mercury.

Table.5. The kinetic constants for the biosorption of Fu and Hg^{2+} .

Model	Parameters	GEHT	
		Fu	Hg^{2+}
Pseudo-first order[27]	q_e (mg/g)	6.6116	7.1030
$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303t}$	K_1 (l/s)	3.4348 $\times 10^{-4}$	2.9078×10^{-4}
	R^2		0.9085
Pseudo-second order[28]	q_e (mg/g)	7.8260	9.5643
$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	K_2 (g/mg.s)	4.0501 $\times 10^{-5}$	2.1262×10^{-5}
	R^2		0.9910
Intra-particle diffusion[29]	K_{id}	1.6451 $\times 10^{-3}$	0.9108×10^{-3}
$qt = K_{id}t^{1/2} + C$	C		0.3961
	R^2	0.8875	0.9485

$E_{\text{lovich}}^{[30]}$	a	1.0301 $\times 10^{-2}$	0.9273×10^{-2}
$q_t = \frac{1}{b} \ln a \bar{b} + \frac{1}{b} \ln t$	b	0.4753	0.4423
	R^2	0.8834	0.9813

3.5 THERMODYNAMIC PARAMETERS

A plot of temperature against ΔG° gave a straight line with slope $-\Delta S^\circ$ and an intercept of ΔH° . The biosorption of Fu and Hg^{2+} for various temperatures (298-328 K) at 6 h of contact time were shown in Fig.5. The heat of biosorption (ΔH°) 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 [31].

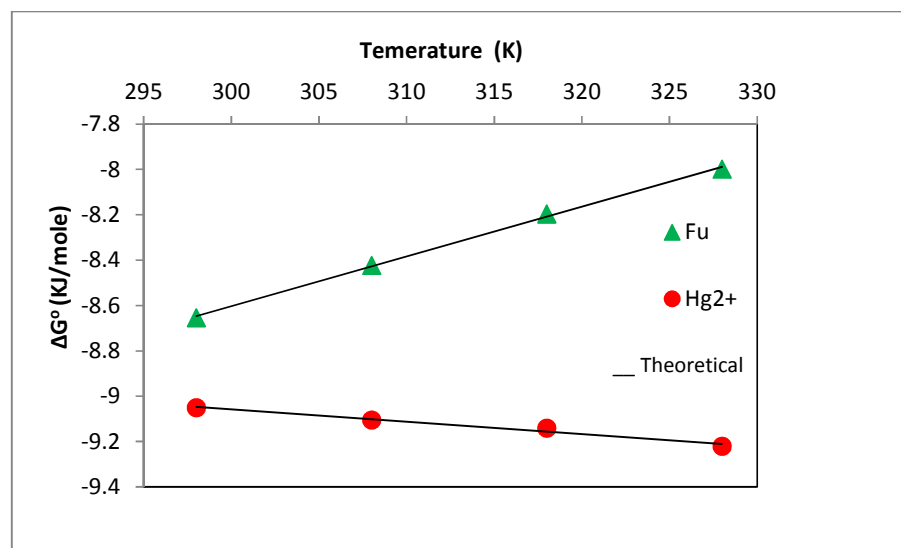


Fig.5. Free energy change for furfural and mercury biosorption.

3.6 OPTIMUM AGITATION SPEED

The concentration decay curves of solutes were shown in Figs.6-7 for Fu and Hg^{2+} respectively at different agitation speeds of (150, 300, 450, 600 and 750 rpm). The effluent concentration 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 Figs. 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.

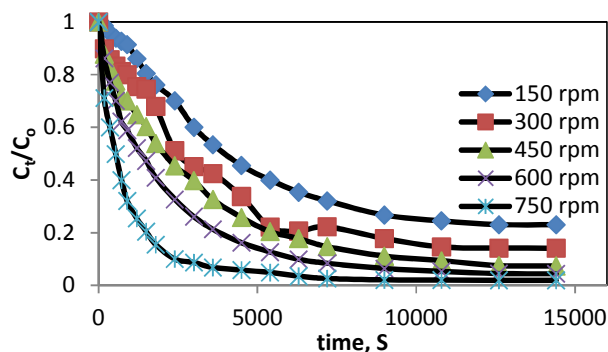


Fig.6.Concentration-time decay curves for furfural biosorption onto GEHT at different agitation speed.

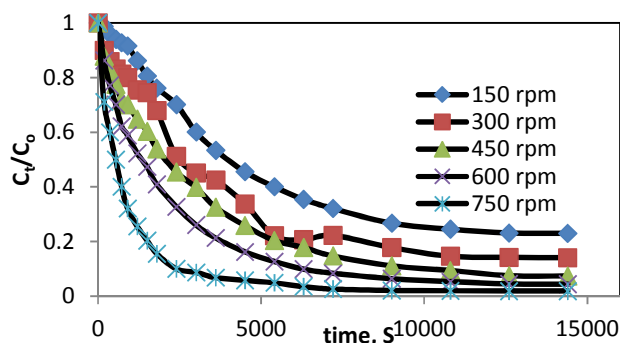
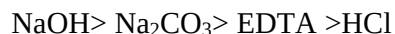


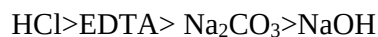
Fig.7.Concentration-time decay curves for mercury biosorption onto GEHT at different agitation speed.

3.7 DESORPTION AND REGENERATION STUDIES

The desorption efficiencies using different desorbing elutants from GEHT are shown in figs.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 Cl^- and 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.

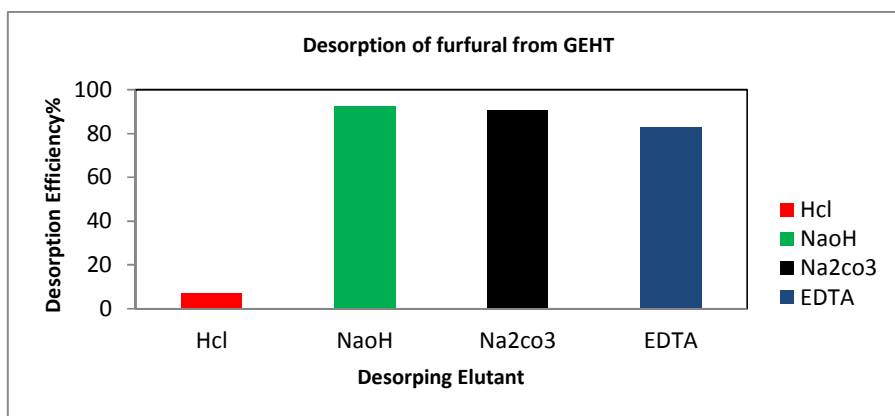


Fig. 8.Desorption efficiency of furfural from GEHT.

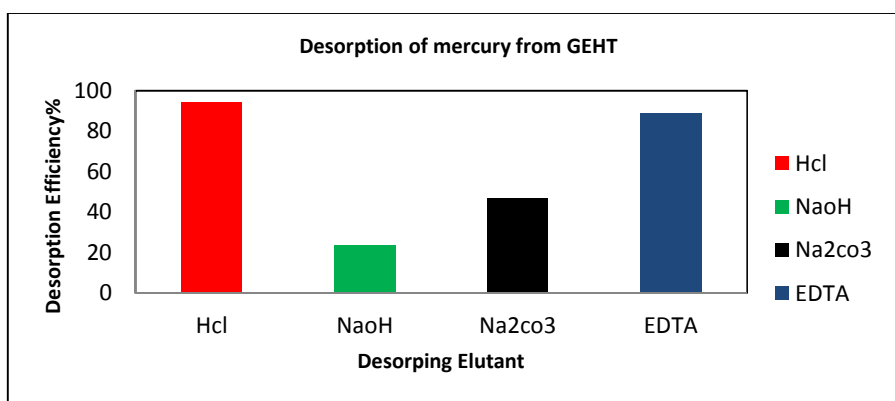


Fig.9.Desorption efficiency of mercury from GEHT.

4. CONCLUSION

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 Hg²⁺ 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 Hg²⁺) systems on to GEHT is: Fu > Hg²⁺ 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 Hg²⁺ 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 $C_e/C_o=0.05$ 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.

6. REFERENCES

- [1] JC Igwe, CU Iroh, AA Abia (2005) *Journal of Environmental. Managt.* (in press).
- [2] AH Sulaymon; AB Abid; JA Al-Najar (2009) *Journal of chemical engineering*, 155, 647-653.
- [3] JC Igwe, AA Abia (2006) *Journal of process Biochemical*, , pp. 1167-1179., Vol. 34, pp. 451-65.
- [4] G Zhang, W Todd French, R Hernandez, E Alley, M Paraschivescu (2011) *Journal of Biomass and Bioenergy*, 35(1): 734-740.
- [5] B Coto, R van Grieken, JL Peña, JJ Espada (2006) *Journal of Chemical Engineering Science*, 61(24): 8028- 8039.
- [6] H Hassan, AG Nima, S Alireza, A Shahram (2012) *Advances in Environmental Biology*, 6(8): 2378-2383, ISSN 1995-0756.
- [7] F Veglio , F Beolchini, A Gasbarro (1997) *Process Biochemistry*, Vol. 2, pp. 99-105.
- [8] B Volesky (1990) Biosorption and biosorbents. In: *Biosorption of heavy metals*. Boston, USA, CRCpress, 3-5.
- [9] B Volesky (2003) *Sorption and Biosorption*, BV, Sorbex, Inc. Montreal, Canada., Section 6.1, pp. 103-116.
- [10] GM Gadd, (1990) Heavy metal accumulation by bacteria and other microorganisms *Experientia*, Vol. 46, pp. 834-8403.
- [11] A. Ajay Kumar, A. Naif, and N. Hilal (2009) Study of Various Parameters in the Biosorption of Heavy Metals on Activated Sludge, *World Applied Sciences Journal* 5 (Special Issue for Environment), pp. 32-40.
- [12] N A Babarinde; O Oyesiku; J Babalola, O Olatunji (2008) *Journal of Applied Sciences Research*, Vol. 4, No. 6, pp. 716-721.
- [13] J.C. Crittenden (1987) Evaluation multicomponent competitive adsorption in fixed-bed, *J. Environmental Engineering*, Vol. 113, No. 6, pp. 1363-1375.
- [14] H. Freundlich (1907) Ueber die adsorption in loesungen. *Z. Phys. Chem.*, 57, 385-470.
- [15] G. Belfort (1980), Adsorption on carbon: theoretical considerations. *Environmental Science and Technology*, 14(8), 910-913.
- [16] J. Toth (1971) State equations of the solid gas interface layer. *Acta. Chem. Acad. Hung*, 69,
- [17] R. Sips (1984) On the structure of a catalyst surface. *J. Chem. Phys.*, 16, 490-495.
- [18] A. Khan, T. Al-Bahri, and A. Al-Haddad (1997) Adsorption of phenol based organic pollutants on activated carbon from multi-component dilute aqueous solutions. *Water Res.*, 31 , 2102-2112 .

- [19] M. Temkin (1934) Die gas adsorption und der nernstschewärmesatz. Acta.Physicochem. URSS, 1, 36-52.
- [20] S. Brunauer,P. Emmet, E. Teller(1938) Journal of Chemical, , 60,309-319.
- [21] W.D Harkins, S Henderson (1952) Journal of Agriculture Engineering, 33 29-4.
- [22] O. Redlich; D.L. Peterson (1959) Journal of Physical and Chemical, 63, 1024-1025.
- [23] W. D. Harkins, and S . Henderson (1952) A basic concept of equilibrium moisture Agriculture Eng. J., 33, 29-41.
- [24] J. R.Weber and J.Walt (1979) Physicochemical Processes for Water Quality Control. NewYork: Wiley-Interscience.
- [25] A. Fahmi, K. Munther (2003) Separation Science and Technology, 38, 483-497.
- [26] F. Pagnanelli, M. Trifoni ,F .Beolchini, A.Esposito, L. Toro, F. Veglio (2001) Journal of Process Biochemistry, Vol. 37, pp. 115–124
- [27] S Lagergren (1989) About the theory of so-called adsorption of soluble substances. Kung Seventeen Hand, 24, 1-39.
- [28] YS Ho, G McKay (1999)Pseudo-second order model for sorption processes. ProcessBiochem.,34, 451-65.
- [29] WJ Weber; J CMorris (1963) Journal of Civil Engineering, 89, 31-59.
- [30] WH Cheung; G Mckay (2003) Journalof Chemical Technology. Biotech. Vol. 78, pp. 562–571.
- [31] N A Babarinde; O Oyesiku; J Babalola, O Olatunji (2008)Journal of Applied Sciences Research, Vol. 4, No. 6, pp. 716-721.