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Performance of adsorption/biosorption for removal of organic and inorganic pollutants

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ABSTRACT

The adsorption/ biosorption of Hg^{+2} *and furfural from simulated water using granule activated carbon and granule dead anaerobic sludge were investigated. Batch type experiments were carried out to find the equilibrium isotherm data for single and binary system. Ten isotherm models were used for single component and four models for binary system. Langmuir model gave the best fitting for the single system, while the binary system was fitted successfully with extended Langmuir model. FT-IR analysis was carried out before and after adsorption/biosorption to determine which functional groups were responsible for binding the* Hg^{+2}*and furfural. Kinetic study showed that pseudo- second order model was well fitted for* Hg^{+2} *and furfural.* R^2 *used to enhance the justification analysis for each used model.*

Key words: Granule dead anaerobic sludge, Batch type experiments, Single system, Binary system, Langmuir model.

INTRODUCTION

Water pollution by toxic metals in industrial wastewater has become a major issue throughout the world. 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]**.Adsorption as a wastewater treatment process has been found to be an economically feasible alternative for metal removal. Activated carbon is one of the most well-known adsorbents**[7,8,9,10,11,12,13]**but the high costs of the process has limited its use. 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 ability of biological materials to accumulate heavy metals from wastewater through metabolically mediated or physico-chemical pathways of uptake**[14]**. 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, regeneration of biosorbent and the possibility of metal recovery**[15, 16, 17]**. Biosorption for the removal of heavy metal ions may provide an attractive alternative to physico-chemical methods**[18]**.

The variety of materials tested includes bark, chitin, lignin, modified wool and seaweeds**[19].** They can be used for the effective removal and recovery of several species from wastewater streams.

Anaerobic sludge was investigated as a substitute for granular activated carbon (GAC), for prepared low cost, available, efficient, economic and practicable biosorbent material in granular dead anaerobic sludge (GDAS) for the treatment of organic and inorganic pollutants. This sludge is a biomass waste 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. Rather than disposing of the sludge, considered use of this waste material seems to be a promising way of turning it into a useful resource. The microorganisms overgrown in such wastewater systems can be utilized for removal of heavy metal as an abundant and cheaper biosorbent.

Sludge wastes generated from wastewater systems considered as heterogeneous microorganisms contents, contain bacteria, fungi, yeast and protozoa. Microorganisms have a high surface area to volume ratio because of their small size and therefore, they can provide a large contact interface, which interact with metals from surrounding environment**[20]**. The cell wall of these microorganisms essentially consists of various organic compounds such as carboxyl, chitin, acidic polysaccharides, lipids, amino acids and other components offer many functional groups which can bind metal ions such as carboxylate, hydroxyl, amine, etc. Potent metal biosorbents under the class of bacteria include genre of Bacillus **[21,22]**, Pseudomonas**[23,24]** and Streptomyces **[25,26]**.

The aim of this study was to investigate the sorption capacity, removal efficiency and kinetics of mercury and furfural from simulated wastewater as single and binary system onto granular activated carbon and granular dead anaerobic sludge.

EXPERIMENTAL SECTION

Adsorbent (Granular Activated Carbon)

Commercial granulated activated carbon was used as an adsorbent. It was supplied by (Unicarbo, Italians) and was bought from the Iraqi markets. The activated carbon was washed before being used with distilled water to remove fine powder and then dried in an oven at 110 ^{0}C for (24 h). The dry activated carbon was crushed by jaw crusher and sieved by successive sieves, then kept in a desiccators for use. The physical properties were tabulated in Table (1).

Biosorbent (Granule Dead Anaerobic Sludge)

Granule dead anaerobic sludge was used as a biosorbent. It was obtained from Hamdan wastewater 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 ^{0}C until having constant weight(24 h). The dry sludge was crushed by jaw crusher and sieved by successive sieves, then after which the biosorbent was kept in a desiccators for use. The physical properties were listed in Table (1).

Table (1) Physical properties of GAC and GDAS

Physical properties	GAC	GDAS
Actual density, kg/m^3	1542	1740.7
Apparent density, kg/m^3	640	608.9
Particle porosity	0.584	0.65
Bed porosity	0.42	0.45
Pore volume, cm^3/g	0.422	0.544
Particle size, mm	0.501	0.501

Adsorbate

1000 mg/l of stock solution of Hg^{+2}ionand furfural (Fu) prepared by dissolving, $Hg(NO3)_2 \cdot 1/2H_2O$ 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.

Methods

The adsorption/biosorption ofHg^{+2} 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 adsorption/biosorption processes. Therefore the optimum pH was found around 4 **[22,28]**. So, pH was adjusted with the range of (4) for all single and binary system by adding the 0.1N HNO_3 and 0.1N NaOH. For determination of equilibrium adsorption/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 GAC/GDAS. The bottles were then placed on a shaker and agitated continuously at 150 rpm and 303K for(6h). After (6 h) of agitation which was enough to reach equilibrium [27] , 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 GAC/GDAS were detected by FT-IR analysis before and after adsorption / biosorption. The proportion of GDAS biomass/KBr was 1/100. The background was obtained from the scan of pure KBr. JASCO FTIR 4200spectrum system was used for FT-IR analysis of GAC/GDAS. Kinetic experiments were carried out for understanding of the adsorption/biosorption dynamics of Hg^{+2} and furfural onto GAC/GDAS. A 2000 ml Pyrex beaker was filled with 1000 ml of 50 mg/l solution of Hg^{+2} and agitation was started before adding the adsorbent /biosorbent. At zero time, an accurate weight of adsorbent /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:

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

The performance of GAC/GDAS adsorption was evaluated in terms of its removal efficiency as RE(%).

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

RESULTS AND DISCUSSION

Single System

The adsorption/biosorption isotherms were obtained by plotting the weight of the solute adsorbed per unit weight of GAC/ GDAS (q_e) against the equilibrium concentration of the solute in the solution (C_e) at constant temperature **[29]**. For a single system ofHg^{+2} and Fu , the equilibrium isotherms were conducted at (303 K) with initial concentration of each component, C_o=50 mg/l. These isotherms are shown in Figs.(1 and 2). 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 adsorption/biosorption. It is clear from Figs.(1 and 2)and Table (2), that the equilibrium isotherm for each single component was of favorable type, since $0 < Rs < 1$ (Rs = 0.2460 and 0.1431) for Fuand Hg^{+2}onto GAC, while (Rs = 0.2732 and 0.1372) for Fuand Hg^{+2}onto GDAS respectively . The experimental data for furfural and mercury described successfully with Langmuir model with correlation coefficient 0.9952and 0.9938 onto GAC 0.9959 and 0.9922onto GDAS respectively. It was found that the maximum metal uptake q_m(mg/g) for Fu was greater than that for Hg^{+2}onto GAC ($q_{m,Fu=}$43.4824and$q_{m,Hg+2}$=14.2857)while it was opposite for GDAS($q_{m,Fu}$=45.8234and$q_{m,Hg+2}$= 48.1370)respectively.

Fourier-Transform Infrared Analysis (FT-IR)

In order to find out which functional groups were responsible for the Fu and Hg^{+2} adsorption/biosorption, FT-IR analysis of raw and loaded GAC/GDAS was carried out. Infrared spectra of GAC/GDAS samples before and after furfural and mercury binding were shown in Figs.(3and4)and listed in Tables (3and 4). Different functional groups listed in Tables (3and4) were detected on the GAC/GDAS surface. Spectra analysis of FT-IR spectrum after cations adsorption showed that there was a substantial decrease in the wave number and adsorption intensity of GAC. 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 ($-NH_2^+$) at 3449.62cm^{-1} and alkane ($-CH^+$) at 1639.49 cm^{-1} considered to be responsible for this attraction. Physical adsorption was the main mechanisms to adsorb furfural. Mercury adsorption depended mainly on the electrostatic attraction by negatively charge functional groups($-OH^-$) at 1543.05 cm^{-1}. While the carboxylic acid, amide and alkyl halides groups at 3414, 2929.95and 1652.88 cm^{-1}were the major groups in biosorption process.

Binary System

For a binary system of Hg^{+2} and furfural the equilibrium isotherms were conducted at (303 K) with initial concentration of each component, C_o=50 mg/l these isotherms were shown in Figs.(5and 6).Four isotherm models were used to fit the experimental data. The isotherm models were listed in Table (5)which represents the values of the parameters of each model, the correlation coefficients (R^2) and the percentage reduction of absorption /biosorption capacity. For the binary systems the extended Langmuir model seems to give the best fitting for the experimental data i.e, highest value of (R^2). In addition, Redlich-Petrson 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 figures and related tables, Hg^{+2} always adsorbed more favorably onto GDAS than Fu .

Removal Efficiency

The removal efficiency of adsorption/ biosorption represents the ability of adsorbent/ biosorbent to reduce or remove the adsorbate from the solution. The removal efficiency was calculated by using equation (2). Percentage removal are tabulated in Table (6) . From this table the removal percentage achieved for highest mass of GAC/GDAS for the single and binary system for all pollutants. Fu gave the maximum percentage removal compared with Hg^{+2} onto GAC ,this may be due to the physical and chemical properties of Fu to be more favorable to be adsorbed than Hg^{+2} .While onto GDAS Hg^{+2} gave the maximum percentage removal. For binary system there was a reduction in the percentage of removal. This is due to the presence of more than one pollutant within the same adsorbent/biosorbent which will enhance the competition and the struggling race of each pollutant to occupy an adsorbent site and hence, occupied sites will be a mixture of two adsorbed species. Therefore reducing the percentage removal of the adsorbate compared with the system.

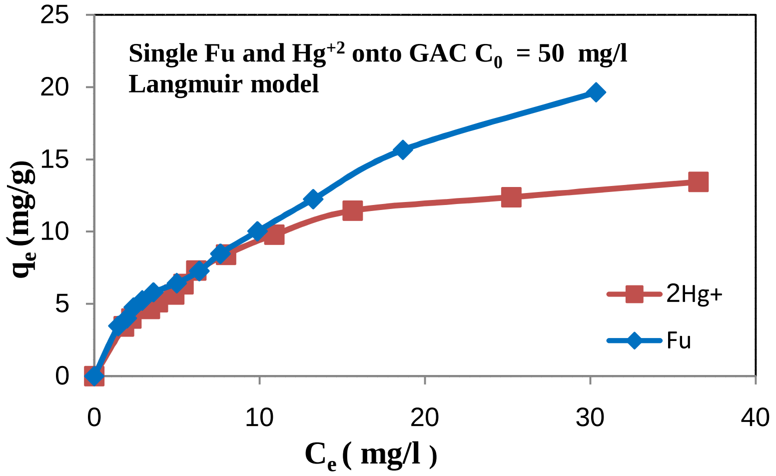


Fig. (1) Adsorption isotherm for single furfural and mercury onto GAC at 303K

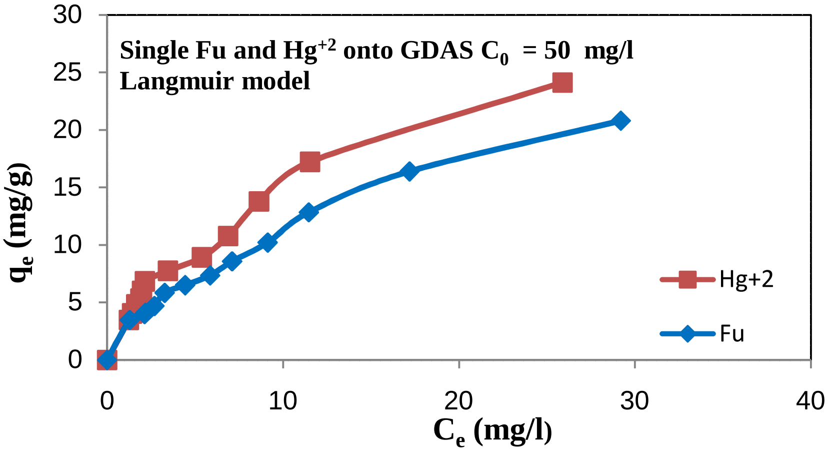
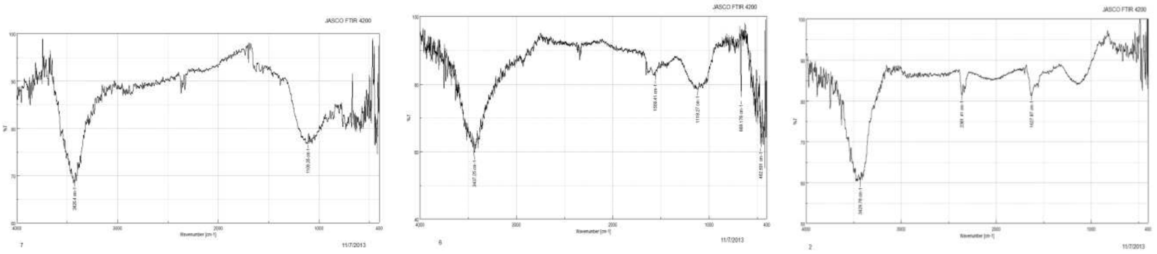


Fig. (2) Biosorption isotherm for single furfural and mercury onto GDAS at 303 K

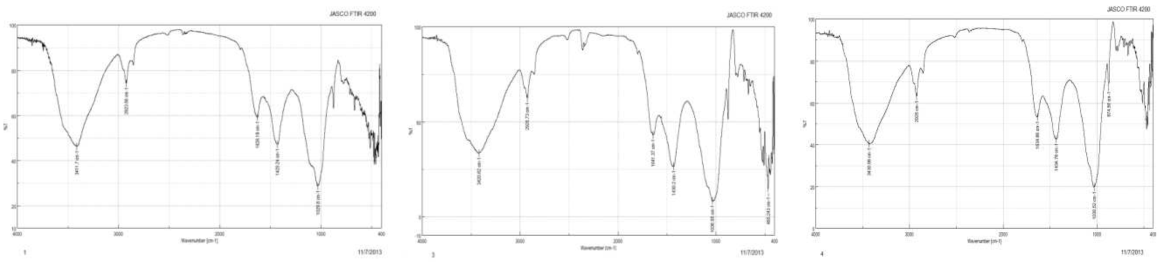
Table (2) Adsorption/Biosorption isotherm models and parameters of single solute isotherm for Fu and Hg^{+2}

Model	Parameters	GAC		GDAS	
		Fu	Hg^{+2}	Fu	Hg^{+2}
Freundlich**[30]** $q_e = KC_e^{1/n}$	K (mg/g)(l/mg)$^{1/n}$ n R^2	1.5508 1.9583 0.9941	1.5567 2.2148 0.9851	1.7184 1.6483 0.9956	2.0332 2.3448 0.9750
Langmuir**[31]** $q_e = \frac{q_m bC_e}{1+bC_e}$	q_m (mg/g) b (l/mg) R^2 R_s $E_{ad.}$ (%)	43.4824 0.0619 0.9952 0.2460 97.0740	14.2857 0.1197 0.9938 0.1431 96.4360	45.8234 0.0590 0.9959 0.2732 97.4403	48.1370 0.1249 0.9922 0.1372 97.5420
Toth**[32]** $q_e = \frac{K_t C_e}{(a_t + C_e)^{1/t}}$	K_t (mg/g) a_t t R^2	7.3241 0.1265 2.6184 0.9948	259.6496 19.1391 0.7180 0.9932	5.8241 0.1068 2.5086 0.9956	262.5796 18.0189 0.6818 0.9922
Combination of Langmuir-Freundlich**[** $q_e = \frac{bq_m C_e^{1/n}}{1+bC_e^{1/n}}$	q_m (mg/g) b (l/mg)$^{1/n}$ n R^2	101.3116 0.0417 1.4192 0.9952	33.6012 0.1243 1.1270 0.9908	103.3115 0.0417 1.3182 0.9959	157.6417 0.1243 0.9776 0.9907
Khan **[34]** $q_e = \frac{Q_{\max} b_k C_e}{(1+b_k C_e)^{a_k}}$	Q_{max} (mg/g) b_K (l/mg) a_K R^2	2.0543 5.9371 0.4216 0.9953	53.1857 0.0613 1.4752 0.9925	2.0343 5.9081 0.4018 0.9956	52.4579 0.0563 1.45587 0.9922
Temkin**[35]** $q_e = \frac{RT}{b}\ln(K_T C_e)$	B_1(KJ/mole) K_T (l/mg) R^2	1.3642 0.9329 0.9047	0.9182 13.321 0.9481	1.3642 0.9329 0.9047	0.9182 13.321 0.9481
BET **[36]** $q_e = \frac{BQC_e}{(C_s - C_e)[1+(B-1)(C_e/}$	B (l/mg) Q (mg/g) R^2	6.5724 34.1201 0.9776	167.2391 15.3876 0.7841	6.5724 34.1201 0.9776	167.2391 15.3876 0.7841
Harkins – Henderson**[37]** $q_e = \frac{K_h^{1/n_h}}{C_e^{1/n_h}}$	K_h(mg/g)(mg/l)$^{1/n_h}$ n_h R^2	0.0357 1.2562 0.9636	0.63421 -0.8328 0.9282	0.0143 -1.8436 0.9689	0.0096 -1.5986 0.9624
Redlich-Peterson **[38]** $q_e = \frac{A_R C_e}{1+B_R C_e^{m_R}}$	A_R (l/mg) B_R (l/mg)^{m_R} m_R R^2	2.3514 1.8769 0.8761 0.9938	0.8467 0.2151 1.3153 0.9906	11.7562 1.8432 6.14738 0.9942	0.5163 0.2841 1.2652 0.9927
Radke-Praunsitzl**[39]** $q_e = \frac{K_{RP} C_e}{1+(\frac{K_{RP}}{F_{RP}}) C_e^{1-N_{RP}}}$	K_{RP} (l/mg) F_{RP} N_{RP} R^2	2.1249 10.1317 0.7015 0.9946	0.7182 69.8716 -0.1934 0.9921	17. 2864 6.7329 0.7829 0.9959	0.5732 56.9483 0.0743 0.9931



a b c

Fig.(3) FT-IR analysis for granular activated carbon (a) raw GAC, (b) Fu-loaded GAC and (c) Hgloaded GAC



d **e** **f**

Fig.(4) FT-IR analysis for granular dead anaerobic sludge (d) raw GDAS, (e) Fu-loaded GDAS and (f) Hg loaded GDAS

Kinetic Studies

Adsorption/biosorption kinetics were obtained by plotting the weight of the solute adsorbed per unit weight of GAC/ GDAS against time Figs.(7 and 8). The experimental data was fitted to the various kinetic models and there parameters were listed in Table (7).The model parameters were found by linear regression. The pseudo second-order kinetic model was more suitable for explanation of adsorption/ biosorption process mechanism, due to the highest value of correlation coefficient.

Table(3) FT-IR analysis for raw and loaded GAC .

Wave number, cm^{-1}	Type of bond	Functional group	Tr (%) before adsorption	Tr (%) after adsorption	
				Fu	Hg^{+2}
3749.62	$-OH^-$	Carboxylic acid	74	82	86
3549.02	$-OH^-$	Carboxylic acid	59.5	70	66
3479.58	$-OH^-$,$-NH^-$, $-NH_2^+$	Carboxylic acid, Amide, Amine	55	68	62
3417.86	$-OH^-$, $-NH^-$,$-NH_2^+$	Carboxylic acid, Amide, Amine	53	59	59
3236.55	$-OH^-$	Carboxylic acid	66	88	78
2360.87	$-CH^+$	Alkane	60.5	90	67
1639.49	$-CH^+$	Alkane	64.5	90	73
1616.35	$-CH^+$	Alkane	63	96	70
1543.05	$-OH^-$	Carboxylic acid	66.5	86	81
1400.32	$-OH^-$	Carboxylic acid	68	95	80
1018.14	$-C=O^-$	Carboxylic acid	69	82	73
613.36	$-C-Br^-$	Alkyl halides	67	100	69

Table (4) FT-IR analysis for raw and loaded GDAS

Wave Number,cm^{-1}	Type of bond	Functional group	Tr (%) before biosorption	Tr (%)after biosorption	
				Fu	Hg^{+2}
3741.90	$-OH^-$	Carboxylic acid	76	95	96
3549.02	$-OH^-$	Carboxylic acid	36	66	63
3475.73	$-OH^-$, $-NH^-$, $-NH_2^+$	Carboxylic acid, Amide, Amine	28	60	58
3414.00	$-OH^-$, $-NH^-$, $-NH_2^+$	Carboxylic acid, Amide, Amine	25	57	57
2954.95	-OH	Carboxylic acid	51	72	74
2920.23	$-CH^+$	Alkane	33	49	56.5
2850.79	$-CH^+$	Alkane	47	66	67
2515.18	$-OH^-$	Carboxylic acid	80	96	90
2360.87	$-CH^+$	Alkane	80	93	103
1797.66	$-C=O^-$	Carboxylic acid	75	93	97
1639.49	$-CH^+$	Alkane	35	59	96
1562.34	$-NH^-$	Amide	38	50	63
1419.61	$-OH^-$	Carboxylic acid	28	41	58
1080.14	-C-O-C-	Alcohol	31	41	57
1029.99	-C-O-C-, OH-	Alcohol, Carboxylic acid	22	31	74
875.68	-CH+	Aromatic	50	75	56.5
797.24	-PH+	Phosphines	58	80	67
713.66	-C-Cl-	Alkyl halides	54	79	90
582.07	-C-l-	Alkyl halides	44	76	103
513.07	-C-Br-	Alkyl halides	32	62	97

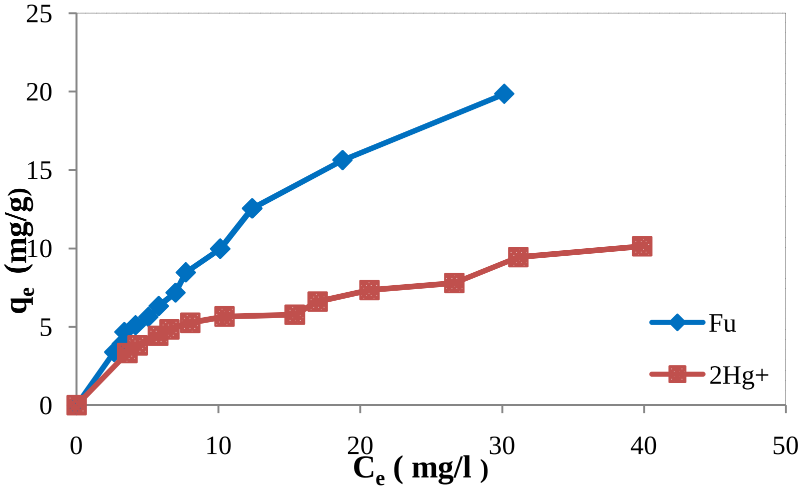


Fig. (5) Adsorption isotherms for (Fu-Hg^{+2}) onto GAC at 303 K

Table(5) Adsorption/Biosorption isotherm models and parameters of binary solute isotherm for Fu and Hg^{+2}

Model	Parameters	GAC		GDAS	
		(Fu-Hg^{+2}) Solution		(Fu-Hg^{+2}) Solution	
		Fu	Hg^{+2}	Fu	Hg^{+2}
Extended Langmuir**[40]** $q_{e,i} = \frac{q_{m,i} b_i C_{e,i}}{1+\sum_{k=1}^{N} b_k C_{e,k}}$	q_m (mg/g) b(l/mg) R^2 R_s $E_{bio.}$ (%)	39.5823 0.0467 0.9987 0.2999 95.356	3.0988 0.2167 0.9963 0.0845 93.084	21.3756 0.0529 0.9973 0.2743 92.020	36.6349 0.0830 0.9962 0.19142 95.780
Combination ofLangmuir-Freundlich**[41]** $q_{e,i} = \frac{q_{m,i} b_i C_{e,i}^{1/n_i}}{1+\sum_{i=1}^{N} b_i C_{e,i}^{1/n_i}}$	q_m (mg/g) b n R^2	46.6867 0.1258 6.2120 0.9958	1.5622 4.4887 2.6794 0.9832	1.8709 4.8381 1.4916 0.9877	6.7560 4.3793 0.0833 0.7979
Redlich-Peterson**[41]** $q_{e,i} = \frac{K_{Ri}(b_{Ri})C_{e,i}}{1+\sum_{k=1}^{N} b_{R,k}(C_{e,k})^{m_{R,k}}}$	K_R (l/mg) b_R(l/mg)$^{m}{}_R$ m_R R^2	6.9362 1.1822 0.6590 0.9987	2.1773 0.0126 0.4433 0.9904	1.4367 11.4763 0.1004 0.9962	11.2354 13.7829 0.7116 0.9944
Extended Freundlich**[42]** $q_{e,i} = \frac{K_i C_{e,i}^{ni+n1}}{C_{e,i}^{n1} + \sum_{j=1}^{N} K_j C_{e,j}^{nj}}$	K (mg/g)(l/mg)$^{1/n}$ n R^2	12.2001 0.0539 0.9923	5.7838 0.1000 0.9775	7.3540 0.1159 0.9895	46.0430 0.6754 0.9921

Table (6)Removal efficiency for each pollutant

	Single				Binary			
	GAC RE%		GDAS RE%		GAC RE%		GDAS RE%	
Weight (g)	Fu	Hg^{+2}	Fu	Hg^{+2}	Fu	Hg^{+2}	Fu	Hg^{+2}
0.1	19.65	36.55	20.8	24.13	19.844	10.14	18.744	25.433
0.2	62.66	49.54	65.63	76.94	62.494	37.724	54.322	69.75
0.3	73.52	68.73	77.08	82.752	75.244	46.732	69.178	80.494
0.4	80.26	78.22	81.76	86.25	79.75	58.692	78.256	85.144
0.5	84.74	84.07	85.8	89.248	84.604	66.026	81.954	85.742
0.6	87.3	87.65	88.3	93.1	86.048	69.248	82.47	87.804
0.7	90.03	89.22	91.14	95.708	88.428	79.136	84.136	89.772
0.8	92.84	90.33	93.47	96.048	89.884	83.978	86.514	91.91
0.9	94.21	92.3	92.43	96.208	91.682	86.902	89.2	92.692
1	95.24	93.26	94.43	96.694	93.282	88.514	89.498	94.44
1.2	96.05	95.53	94.71	97.16	93.634	91.408	91.048	95.598
1.4	97.09	96.43	95.02	97.524	94.724	92.856	91.936	95.792

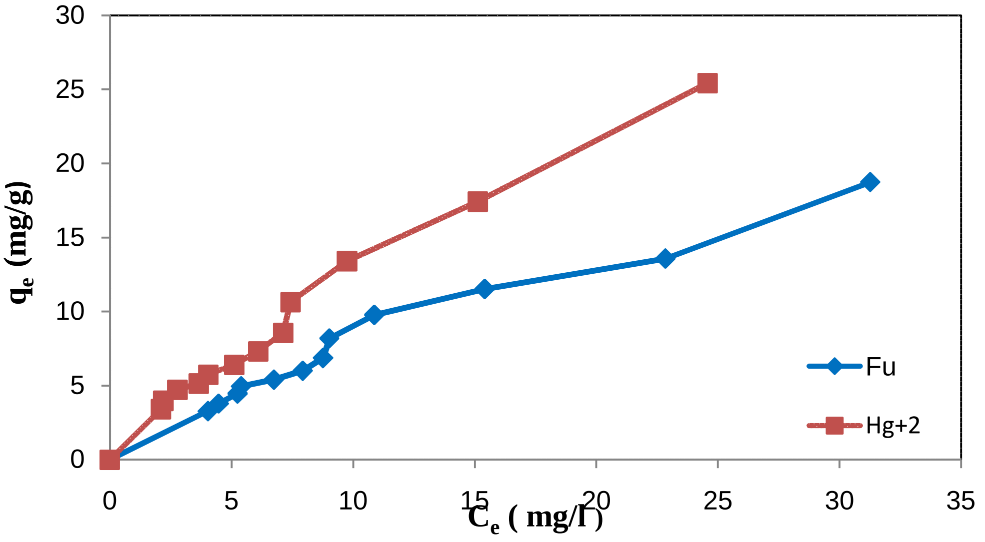


Fig. (6)Biosorption isotherms for (Fu-Hg^{+2}) onto GDAS at 303 K

Table (7)The kinetic constants for the adsorption/biosorption of Fu and Hg^{+2}

Model	Parameters	GAC		GDAS	
		Fu	Hg^{+2}	Fu	Hg^{+2}
Pseudo-first order**[43]** log(qe- qt) =log qe-$\frac{k_1}{2.303t}$	q_e (mg/g)	8.6437	9.2854	7.8235	9.1117
	K_1(l/s)	4.4900×10^{-4}	3.8000×10^{-4}	4.1600×10^{-4}	4.3200×10^{-4}
	R^2	0.9815	0.9277	0.9771	0.9329
Pseudo-second order**[44]** $\frac{t}{q_t} = \frac{1}{k_2 q_e 2} + \frac{t}{q_e}$	q_e(mg/g)	9.6618	10.6270	9.1575	18.2815
	K_2(g/mg.s)	5.0002×10^{-5}	2.6250×10^{-5}	7.4681×10^{-5}	7.8347×10^{-5}
	R^2	0.9985	0.9913	0.9953	0.9983
Intra-particle diffusion**[45]** $q_t = K_{id} t^{1/2} + C$	K_{id}	2.4300×10^{-3}	1.0120×10^{-3}	2.3510×10^{-3}	1.5830×10^{-2}
	C	1.2460	0.4892	1.514	5.2930
	R^2	0.9213	0.9498	0.8905	0.7256
Elovich**[46]** $q_t = \frac{1}{\bar{b}} \ln a\bar{b} + \frac{1}{\bar{b}} \ln t$	a	1.164×10^{-2}	1.0479×10^{-2}	1.237×10^{-2}	1.189×10^{-1}
	b	0.5371	0.4998	0.5781	0.3105
	R^2	0.9824	0.9813	0.9787	0.8963

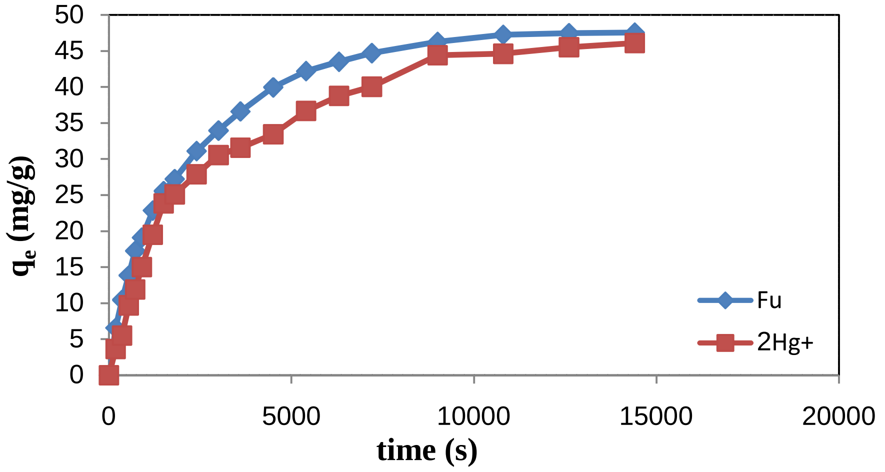


Fig.(7) Adsorption kinetics for Fu and Hg $^{+2}$ onto GAC

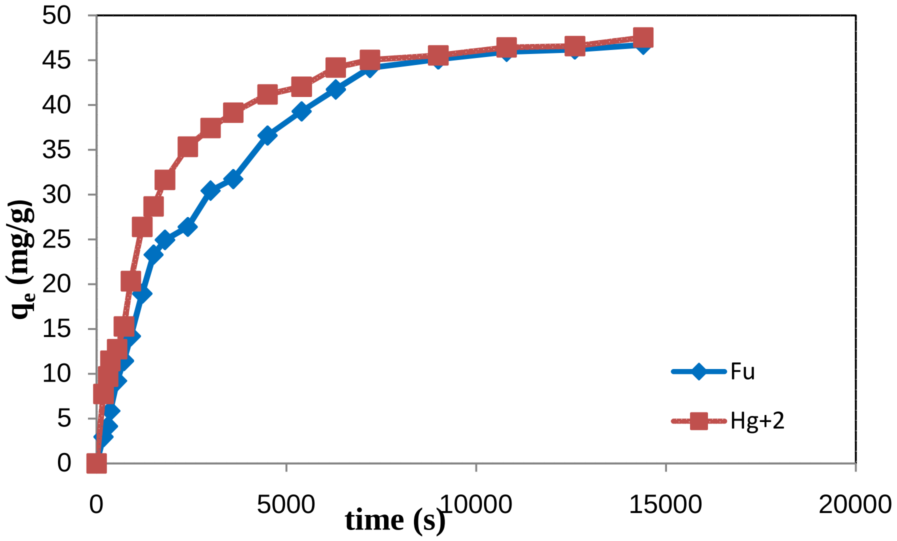


Fig.(8)Biosorption kinetics for Fu and Hg $^{+2}$ onto GDAS

CONCLUSION

GDAS was more efficient than GAC in biosorption of furfural and mercury. Functional groups of GDAS responsible for biosorption process exceeded GAC for furfural and mercury adsorption .The equilibrium isotherm for each component Fu and Hg^{+2} onto GAC/GDAS were favorable type. Langmuir model and extended Langmuir model were well fitted the experimental data for single and binary system respectively. The adsorption/ biosorption capacity in single and binary (Fu and Hg^{+2}) system onto GAC/GDAS are: Fu > Hg^{+2}onto GAC; Hg^{+2}> Fu onto GDAS. This difference in behavior due to high affinity between Fu and GAC and it is opposite for GDAS. Pseudo-second order kinetic model was found to be more suitable for adsorption/biosorption of furfural and mercury. This was due to higher correlation coefficients as compared with other models.

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SYMBOLS

a *Elovich model parameter, (mg/g.s)*
a_K *Khan model parameter*
a_t*Toth model parameter, (mg/l)*
A_R*Reddlich-Peterson model parameter, (l/mg)*
B BET model parameter, (l/mg)
B_1*Temkin isotherm constant, (kJ/gm)*
bElovich model parameter, (g/mg)
b Langmuir equilibrium parameter (l/g)
b_K *Khan model parameter, (l/mg)*
b_R*Reddlich-Peterson model parameter (l/mg)*
C Parameter in intra-particle diffusion model, (mg/g)m_R
C_e *Equilibrium concentration, (mg/l)*
C_{ei} *Equilibrium concentration of component i, (mg/l)*
C_0 *Initial solute concentration, (mg/l)*
F_{RP}*Radke-Praunsitz model parameter*
K Freundlich equilibrium parameter, $(mg/g)(l/mg)^{1/n}$
K_1 *Rate constant of pseudo first-order adsorption, (1/s)*
K_2 *Rate constant of pseudo second-order adsorption, (g/mg.s)*
K_h *Harkins-Henderson model parameter,* $(mg/g)^n(mg/l)$
K_{id}*Rate constant of intra-particle diffusion model,* $(mg/g.s^{0.5})$
K_R *Reddlich-Peterson model parameter (binary system) (l/mg)*
K_{RP}*Radke- Praunsitz model parameter, (l/g)*
K_T *Equilibrium binding constant in Temkin model, (l/mg)*
m_R*Reddlich-Peterson model parameter*
nFreundlich equilibrium parameter and Sips model parameter
n_h *Harkins-Henderson model parameter,*
N_{RP}*Radke-Praunsitz model parameter*
Q BET model parameter, (mg/g)
Q_{max} *Khan mdel 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*
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)
Rs separation factor
T Absolute temperature , (K)
tToth model parameter

V_f *Final Volume of solution, (ml)*
V_i *Initial Volume of solution, (ml)*
W Mass of granular activated carbon /granular dead anaerobic sludge (g)