



Adsorption/biosorption of furfural and mercury onto granular activated carbon/granular dead of anaerobic sludge

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ABSTRACT

The removal of furfural and Hg^{+2} ions pollutant from wastewater by using granular dead of anaerobic sludge (GDAS) and granular activated carbon (GAC) were studied. Batch adsorption/biosorption experiments were carried out as a function of pH, concentration of furfural and Hg^{+2} ions, time, temperature and adsorbent dose. Maximum removal was found around pH =4. It was found that the maximum uptake for furfural was greater than mercury onto GAC, while it was the opposite for GDAS. Thermodynamic parameters including the Gibbs free energy and enthalpy changes indicated that the adsorption/biosorption of furfural and Hg^{+2} ions onto adsorbent/biosorbent were feasible, spontaneous and exothermic reactions.

Key words: Batch adsorption/biosorption, Activated Carbon, Dead of anaerobic sludge, Thermodynamic, Mercury removal.

INTRODUCTION

Water pollution by toxic metallic, organic and metal-organic compounds is an important economic and environmental issue in numerous parts of the world [1]. Due to the rapid increase in metal concentration as well as increase in awareness of the toxicological effects of metals released into environment, a number of studies for metal recovery and removal for solutions have been done. Conventional methods for metal removal include chemical precipitation, lime coagulation, ion exchange, reverse osmosis and solvent extraction [2]. These are conventional methods for the removal of heavy metals from wastewater, however, cost prohibitive having inadequate efficiencies at low metal concentrations, particularly in the range of 1–100 mg/l. Furthermore, generate toxic sludge, the disposal of which is a burden on the techno-economic feasibility of treatment procedures [3].

Adsorption using commercial granular activated carbon (GAC) is an effective purification and separation techniques used in industry especially in water and wastewater treatment that can remove heavy metals from wastewater [4–11]. Activated carbon suffers from a number of disadvantages. It is quite expensive and the higher the quality, the greater the cost. Both chemical and thermal regeneration of spent carbon is expensive and impractical on a large scale, which produces additional effluent, and results in considerable loss of the adsorbent. Also, it is susceptible to blocking of its pores by large organic hydrocarbons of low solubility [12,13].

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]. According to the literature, biosorption can be divided into two main processes: adsorption of the ions on cell surface and bioaccumulation within the cell [19]. Anaerobic sludge (AS) was investigated as a substitute for granular activated carbon, to prepared low cost, available, efficient, economic and practicable biosorbent material granular dead anaerobic sludge 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 [20]. Sludge wastes generated from waste water systems considered as heterogeneous microorganism's contents, contain bacteria, fungi, yeast and protozoa. 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[21]. 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.

The main aims of this study were utilize granular dead anaerobic sludge (GDAS) biosorbents. Also investigation the potentiality of biosorbents for removing single pollutants of furfural and mercury then comparing with granular activated carbon (GAC) adsorption capacity. The effect of pH, temperature, duration of contact, concentration of pollutants and dose of sorbent on the adsorption/biosorption was studied. Also, the thermodynamic parameters of furfural and mercury adsorption /biosorption were evaluated.

EXPERIMENTAL SECTION

Adsorbent (Granular Activated Carbon)

Commercial granulated activated carbon GAC 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 °C for (24 h). The dry activated carbon was crushed by jaw crusher and sieved by successive sieves, then after which the GAC is kept in a desiccators for use. The physical and chemical properties were tabulated in Table (1).

Biosorbent(Granule Dead Anaerobic Sludge)

Granule dead anaerobic sludge GDAS 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 °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 and chemical properties of GAC / GDAS were listed in Table (1).

Table (1): Physical and chemical properties of GAC / 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
Chemical properties		
PH	7.84	7.5
Ash content, (%)	5	13
Cation Exchange Capacity, CEC (meq/100 g)	-	51.153

Adsorbate

1000 mg/l of stock solution of each metal ion of Hg^{+2} and furfural (Fu) prepared by dissolving, $\text{Hg}(\text{NO}_3)_2 \cdot 1/2\text{H}_2\text{O}$ and furfural respectively in distilled water. A solution of ions concentration of 25, 50, 100, 150, 200, 250 mg/l was prepared by dilution of the stock solution. The using chemicals were annular grade produced by Fluka and BDH.

Methods

Solutions of fixed volume (100 ml) with varying concentrations 25, 50, 100, 150, 200 and 250 mg/l in (100 ml) were placed into conical flasks and thoroughly mixed with 2 g of adsorbent (GAC) /biosorbent(GDAS) dose at 30°C and (150 rpm) shaking speed for (6 h). Six hours of period for sorption experiment were used to ensure equilibrium [22]. The pH was adjusted from 2-12 by using 0.1N HNO_3 and 0.1N NaOH solutions. The flasks were placed on a shaker with constant speed (150 rpm). After 6 h the flasks were removed and the solution was separated from the (GAC)/(GDAS) by filtration through filter paper (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 metals, while for furfural (model UV PD-303) spectrophotometer, then the concentration computed from the calibration curves.

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

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

To decide if the adsorption/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} . Two gram of GAC/GDAS was introduced to each glass bottles employed and 100 ml of Fu/ Hg^{+2} solutions at pH= 4 were added to the bottles. The adsorption 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} uptakes by GAC and GDAS were calculated using the following relationships [23].

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

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

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

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 rpm). The beaker was filled with 1(L) of known concentration solution and agitation started before adding the (GAC)/(GDAS). At time zero, the accurate weight of (GAC)/(GDAS) were added. Samples were taken every 5 min. The necessary doses of (GAC)/(GDAS) to reach equilibrium related concentration of C_e/C_0 equal 0.05, were calculated by using Eq. (1).

RESULTS AND DISCUSSION**Effect of the pH**

pH is one of the most important parameter which controls the surface properties of adsorbent/biosorbent, functional groups and ionic state of metal's species. The adsorption/biosorption of metal and organic 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 process and do not bind to the adsorption sites on the surface of the GAC/GDAS. Therefore the optimum pH was found around 4

[24, 25]. So, pH was adjusted with the range of (4) for all single system by adding the 0.1N HNO₃ and 0.1N NaOH for acidic and basic pH respectively. The experimental data were presented in Figs.(1and 2).

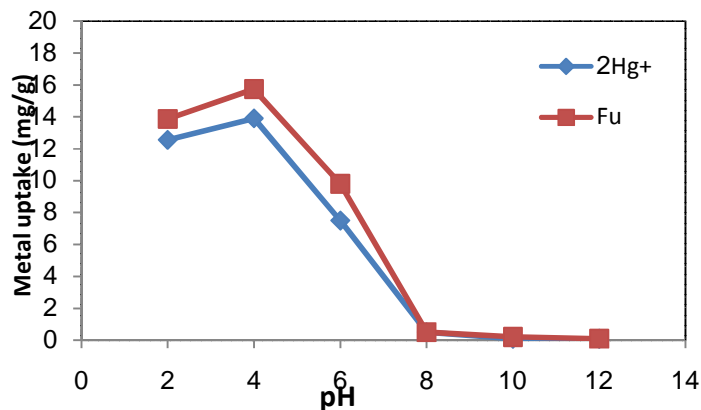


Fig. (1) Effect of pH onto GAC

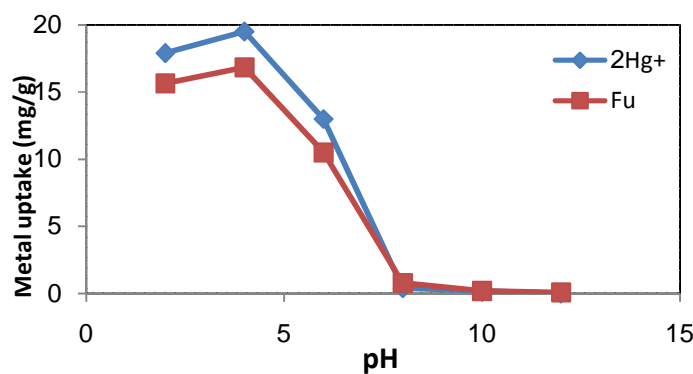


Fig.(2) Effect of pH onto GDAS

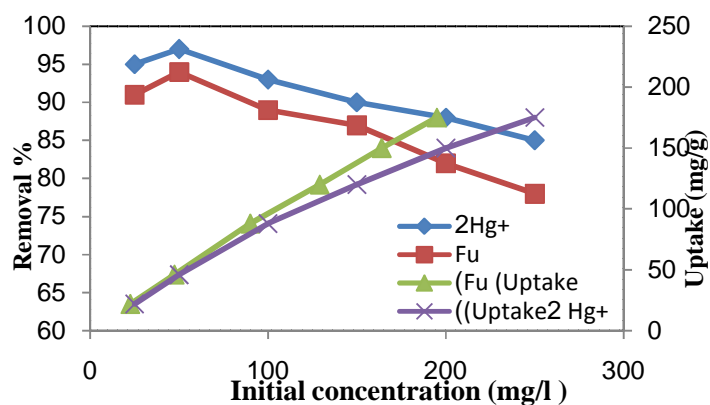


Fig.(3) Effect of initial concentration on Fu/Hg²⁺ removal and uptake capacity(GAC)

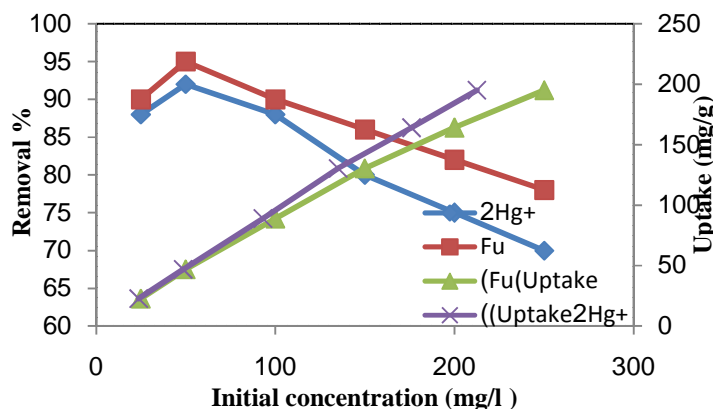


Fig.(4) Effect of initial concentration on Fu and Hg⁺² removal and uptake capacity(GDAS)

Effect of initial concentration

The effect of initial concentration of Fu/Hg⁺² were investigated by conducting different sets of experiments at different initial concentrations (25, 50, 100, 150,200and 250) ppm . Other parameters were kept constant. Such as, temperature, pH (4), agitation speed (150 rpm), particle size (0.501mm) and adsorbent dose (2g).Percentage adsorption/biosorption and the uptake versus initial concentration were plotted Figs(3and 4) respectively. It was found that the percentage adsorption/biosorption decreased with the increase in initial concentration of the adsorbate. But the uptake capacity increased with the increase in initial concentration. The higher initial adsorbate concentration provided higher driving force to overcome mass transfer resistances of the Fu/Hg⁺² from the aqueous to the solid phase resulting in higher probability of collision between metal ions and active sites[26].

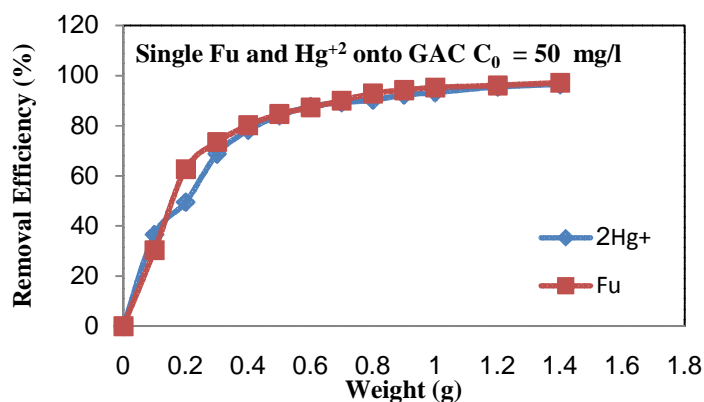


Fig.(5) Effect of GAC dose on the adsorption of furfural and mercury

Effect of adsorbant/ biosorbent doses

Effect of adsorbant/ biosorbent doses on adsorption/biosorption of Fu and Hg⁺²were studied by changing the adsorbent / biosorbent doses from 0.1 to 1.4g and there is no change in other parameters. Figs.(5and6) show an increase in percentage as doses of adsorbent/biosorbent increased until steady the adsorption/ biosorption. This is because of the availability of more binding sites in the surface of the adsorbent / biosorbent for complexation of Fu and Hg⁺² [27, 28].

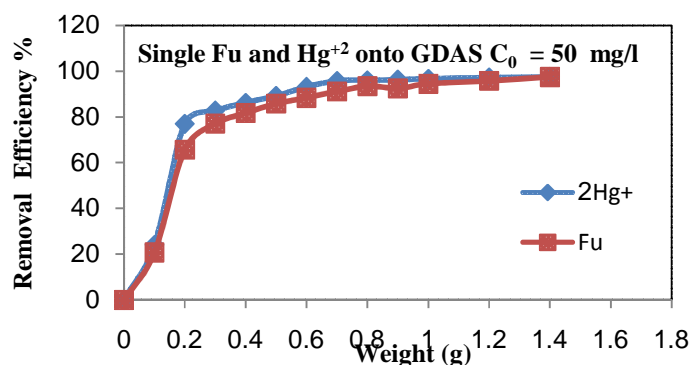


Fig.(6) Effect of GDAS dose on the biosorption of furfural and mercury

Effect of contact time

The effect of contact time on adsorption/biosorption of Fu and Hg^{+2} for a solution of 50 mg/l was shown in Fig.(7). This figure indicated that the rate of adsorption/ biosorption was very rapid during first 180 min, and thereafter, the rate of pollutants removal remained stable. There were no significant increases found after 360, 390 min for Hg^{+2} and Fu respectively onto GAC while 240, 390 min onto GDAS were needed to achieve equilibrium and the adsorption / biosorption decreases significantly with further increase of contact time. Eventually it was the equilibrium time [28]. Initially, there were a large number of vacant active binding sites available at the beginning of the experiment and a large amount of Fu/ Hg^{+2} were bound rapidly onto the GAC/GDAS at a faster adsorption /biosorption rate. The binding site was shortly become limited and the remaining vacant surface sites were difficult to be occupied by Fu/ Hg^{+2} due to the formation of repulsive forces between the Fu/ Hg^{+2} on the solid surface and the liquid phase [27].

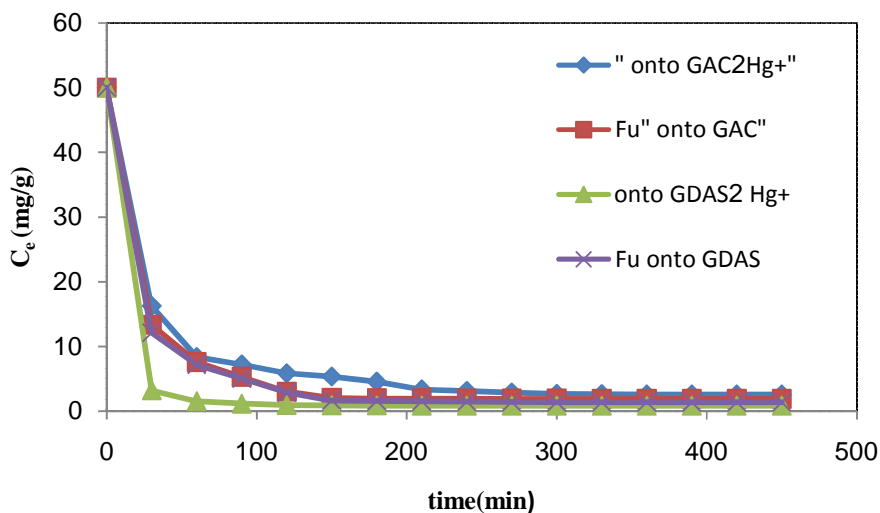


Fig.(7) Effect of contact time

Thermodynamic Parameters

A plot of temperature against ΔG° gave a straight line with slope $-\Delta S^{\circ}$ and an intercept of ΔH° . The adsorption/biosorption of Fu and Hg^{+2} for various temperatures (298-328 K) at 6 h of contact time were shown in Figs.(8 and 9). The heat of adsorption/biosorption (ΔH°) was found to be (9.5077, 9.0561, 7.2026 and 8.0203) 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 adsorption/biosorption processes [22].

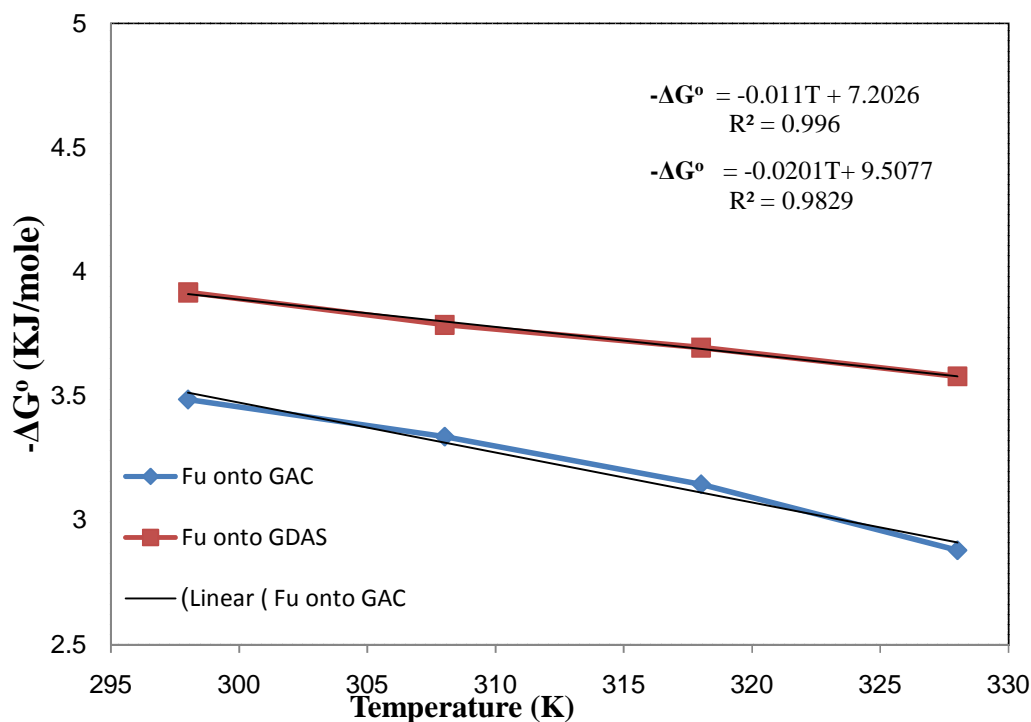


Fig. (8) Free energy change for furfural adsorption/biosorption

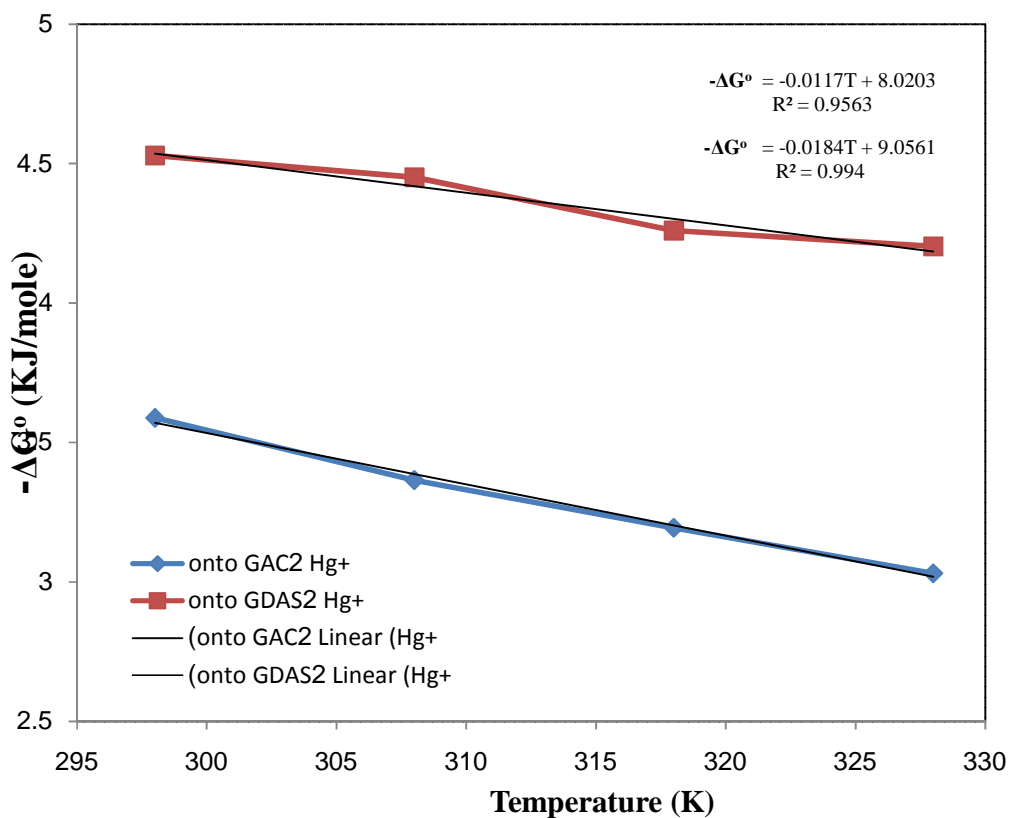


Fig. (9) Free energy change for mercury adsorption/biosorption

Optimum agitation speed

The concentration decay curves of solutes were shown in Figs.(12, 13,14and15) for Fu and Hg^{+2} respectively at different agitation speeds of (150, 300, 450 and 600 rpm). The effluent concentration equal to 5% of inlet concentration was taken as the breakthrough point. The optimum agitation speed needed to achieve $C_t/C_o=0.05$ was found to be 450 rpm. These Figs. Show that, if the speed is above 450 rpm, the equilibrium relative concentration was less than 0.05, with possible pulverization of GAC/GDAS at high speed, and in this case the work was ended with powdered rather than granular GAC/GDAS. The effect of increasing the agitating rate was to decrease the film resistance to mass transfer surrounding the adsorbent/biosorbent particles.

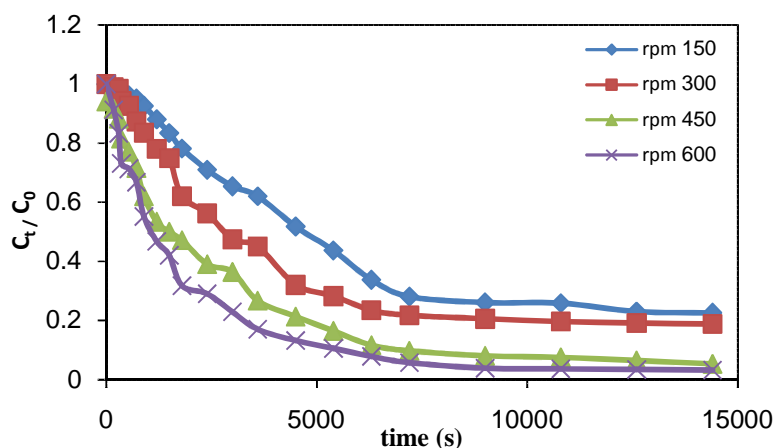


Fig. (10) Concentration-time decay curves for furfural adsorption onto GAC at different agitation speed

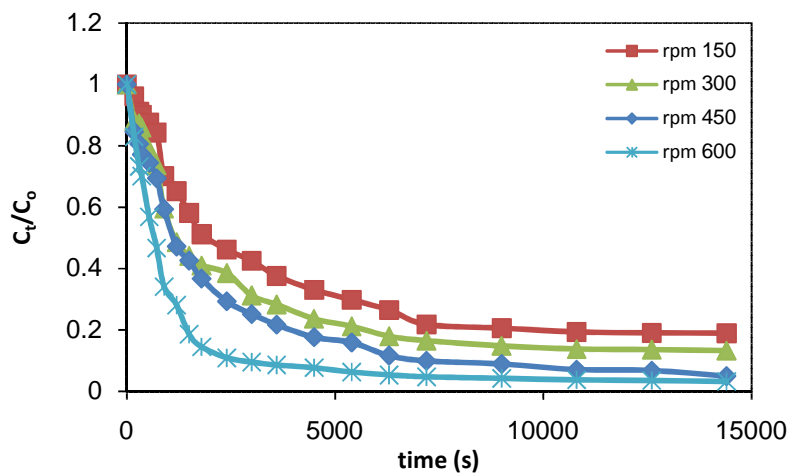


Fig.(11) Concentration-time decay curves for mercury adsorption onto GAC at different agitation speed

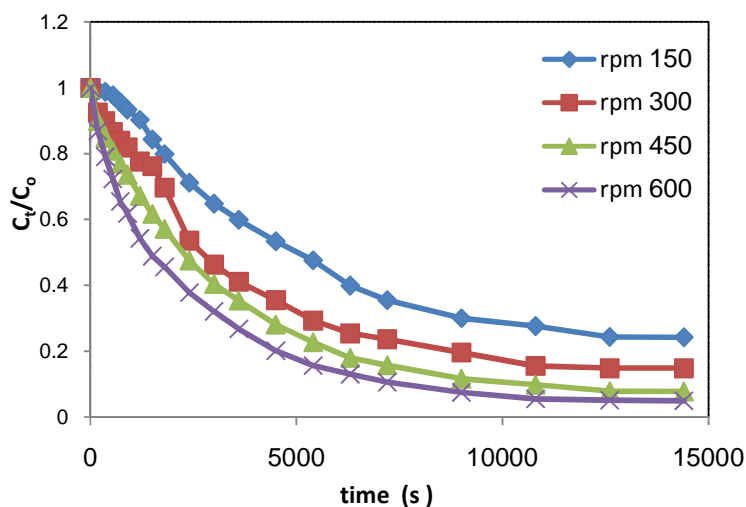


Fig. (12) Concentration-time decay curves for furfural biosorption onto GDAS at different agitation speed

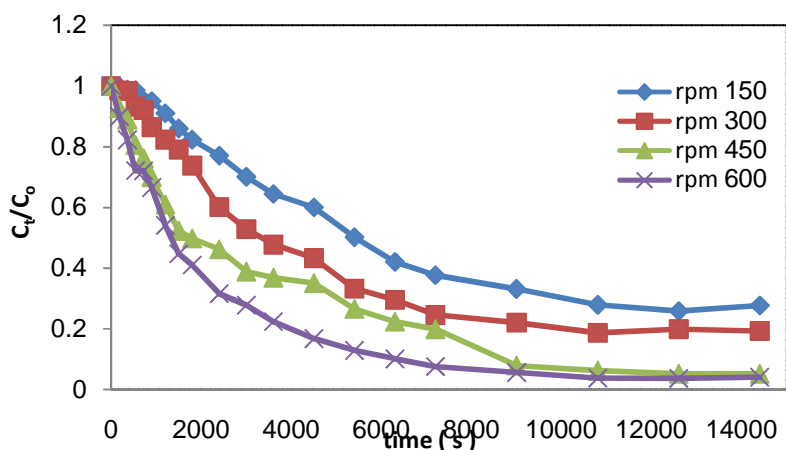


Fig.(15) Concentration-time decay curves for mercury biosorption onto GDAS at different agitation speed

CONCLUSION

The maximum adsorption/biosorption of Fu and Hg^{+2} at pH=4. The percent adsorption/biosorption of Fu/ Hg^{+2} increased with increasing the adsorbent dose. GAC/GDAS had proved to be an efficient for the removal of Fu/ Hg^{+2} from aqueous solutions with low concentrations (50) mg /l. The optimum agitating speed for adsorption/biosorption were found about (450 rpm). The maximum adsorption/biosorption capacity of the GAC and GDAS were found to decrease as temperature increase. This indicates that adsorption/biosorption was an exothermic process. However, the heat of adsorption/biosorption was found to be less than 40 KJ/mol, which showed that the two processes coincide with physical mechanisms.

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SYMBOLS

- Ce Equilibrium concentration, (mg/l)
- Co Initial solute concentration, (mg/l)
- K_c Equilibrium constant
- q_e Internal concentration of solute in particle at equilibrium, (mg/g)
- R Universal gas constant (=8.314 kJ/mol.K)
- T Absolute temperature, (K)
- Vf Final Volume of solution, (ml)
- Vi Initial Volume of solution, (ml)
- W Mass of activated carbon /granular dead anaerobic sludge (g)
- (ΔG°) Gibbs free energy J/mol
- (ΔH°) Enthalpy change J/mol
- (ΔS°) Entropy change J/mol.K