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A comparative adsorption/biosorption for the removal of phenol and lead onto granular activated carbon and dried anaerobic sludge

Abbas H. Sulaymon[a], Dheyaa W. Abbood[b], Ahmed H. Ali[b,*]

[a]*Department of Environmental Engineering, University of Baghdad, Baghdad, Iraq*
[b]*Department of Environmental Engineering, University of Al-Mustansirria, Bagdad, Iraq*
Tel. +96 47711010491; email: ahmedhassoon_2021@yahoo.com

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ABSTRACT

The potential use of dried anaerobic granular sludge (DAGS) as a substitute for granular activated carbon (GAC) for removing phenol and lead from aqueous solution was examined in a batch system. To make the comparison between adsorption/biosorption process fair, the working sorption pH, temperature, mixing speed and contact time were fixed at 4, 30°C, 250 rpm and 24 h, respectively for both the sorbents. Adsorption/biosorption isotherms were developed for both the single and binary component systems and expressed by four models. Model parameters were estimated by the nonlinear regression method using STATISTICA version 6 and EXCEL 2007 software. The maximum loading capacity (q_m) of the phenol was 66.8234 and 37.0370 mg/g for lead onto GAC, while it was 70.0183 mg/g for phenol and 89.8783 mg/g for lead onto DAGS in single system. However, in binary system, the loading capacity decreased because of competition between compounds to binding sites of adsorbent/biosorbent.

Keywords: Adsorption; GAC; Biosorption; DAGS; Phenol; Lead; Adsorption isotherms

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1. Introduction

The removal of toxic contaminants such as heavy-metal ions and organic pollutants from industrial wastewaters is one of the most important environmental issues to be solved today. Lead (II) has been found together with a variety of aromatic compounds including phenol, naphthalene and trichloroethylene at high concentrations in a number of contaminated sites. Lead (II) and its organic co-pollutants often originate from industrial sources such as the iron-steel, cook, petroleum, pesticides, paints, solvent, pharmaceuticals and wood preserving chemicals. Phenol-containing water, when chlorinated during disinfection of water, results in the formation of chlorophenol [1–3].

Adsorption is a well-established and powerful technique for treating domestic and industrial effluents. Activated carbon is the most widely and effectively used adsorbent. A typical activated carbon particle, whether in a powdered or granular form, has a porous structure consisting of a network of interconnected macropores, mesopores and micropores that provide a good capacity for the adsorption of organic molecules due to high surface area. The surface chemistry of activated carbon and the chemical characteristics of adsorbate, such as polarity, ionic nature, functional groups and solubility, determine the nature of bonding mechanisms as well as the extent and strength of adsorption. A variety of physicochemical mechanisms/forces, such as van der Waals, H-binding, dipole–dipole interactions, ion

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*Corresponding author.

exchange, covalent bonding, cation bridging and water bridging, can be responsible for the adsorption of organic compounds in activated carbon. In spite of these characteristics, 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 regenerations of spent carbon are expensive and impractical on a large scale, produce additional effluent and result in considerable loss of the adsorbent [4–6].

Biosorption (binding to active sites on cell surface) 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. Anaerobic sludge is a well-known biomass used for the purification of some industrial effluents and domestic wastes. Part of the micro-organisms overgrown in such wastewater systems can be separated and utilized for the removal of heavy-metal ions as an abundant and cheaper biosorbent. Due to the adsorptive capacity of cells for heavy-metal ions, the biomass can be also successfully used as a sorbing agent for organics. Anaerobic sludge from wastewater systems contains bacteria, fungi, protozoa, yeast, etc. The cell wall of micro-organisms essentially consisting of various organic compounds such as chitin, acidic polysaccharides, lipids, amino acids and other cellular components could provide a passive uptake of metal ions and phenolic compounds in a manner of surface adsorption, complexation, chelation, ion exchange, precipitation, etc. Several functional groups are present on the micro-organisms cell wall, including carboxyl and phosphonate, as they are negatively charged and abundantly available, carboxyl groups actively participate in the binding of metal cations. Also, amine groups are very effective in removing anionic species such as phenol via electrostatic interaction or hydrogen bonding [7–10].

While much research has been carried out on the uptake of single species of metal ions and organic species by activated carbon, little attention seems to have been given to the study of organic—metal ion mixtures. Despite the fact that not only single toxic metallic species but organic components also exist in wastewaters and the presence of a multiplicity of metals and organics often gives rise to interactive effects, insufficient attention seems to have been paid to this problem. Examining the effects of metal ions and organics in various combinations is more representative, of the actual environmental problems faced by treatment technologies, than are single metal or organic studies [11,12].

2. Experimental materials and procedure

2.1. Adsorbate

The 50 mg/l standard stock solution of Phenol and lead (II) were prepared by dissolving Ph and Pb $(NO_3)_2$ in distilled water.

2.2. Adsorbent/Biosorbent

2.2.1. Granular activated carbon

Commercial granulated activated carbon (GAC) was used as an adsorbent in the present work. It was supplied by (Unicarbo, Italians) and was bought from the Iraqi markets. The physical and chemical properties were measured at the laboratories of the Ministry of Industry and Minerals (Ibn Sina State Company), Ministry of Oil (Petroleum Development and Research Center), Al-Mustansirria University (Collage of engineering, Environmental Department) and according to the data from the supplier. The physical and chemical properties of GAC are listed in Table 2. A sample of GAC used in the present work and SEM image are shown in Plates 1 and 2.

2.2.2. Dried anaerobic granular sludge

The anaerobic sludge used in the present work was collected as slurry from sewage sludge collection system (Al-Rustamiyah sewage treatment plant, the old project, Baghdad, Iraq). There were 14 drying beds each one has a dimension of (300 m × 25 m × 1 m).This means that, the volume of sludge produced by each drying bed is about (7,500 m^3).

The sludge was collected from about 20 cm depth of drying bed surface where anaerobic conditions are predominate. The observation of methane gas bubbles during collection of sludge proved this fact. The steps in the preparation of dried anaerobic granular sludge (DAGS) were as follows:

Plate 1. Sample of GAC.

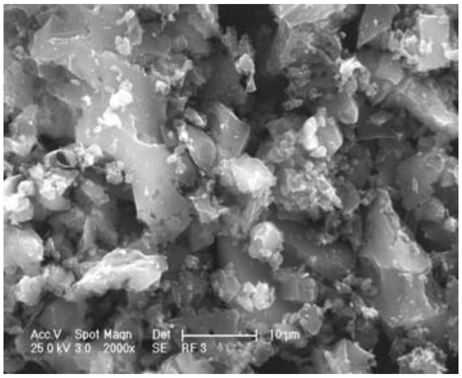

Plate 2. SEM image of GAC shows amorphous structures.

- Drying of anaerobic sludge at dry climate condition (temperature 30 ± 5°C and relative humidity of 45%) for 2 days.
- Formation of flocks of dried anaerobic sludge (DAS).
- Grinding the flocks by used agate mortar.
- Sieving the resulting biosorbent with two sieves of 20/30 mesh number, respectively.
- The DAGS was washed thoroughly using distilled water to remove any coarse impurities, and the washing process was continued until the filtrate contains no lead ions or/and phenol pollutants. This can be confirmed by taking a random sample and analyzed by using AAS and GC.
- After washing, DAGS was dried using electrical oven for 24 h at 60°C to avoid the alteration of functional groups.

The physical, chemical and biological tests of anaerobic sludge were conducted at the same laborites and are listed in Table 1. Plates 3–6 show the stages in preparation of DAGS.

2.3. FT-IR analysis of GAC and DAGS

The functional groups of GAC and DAGS were detected by FT-IR analysis. The proportion of GAC, DAGS or KBr is 1/100. The background is obtained from the scan of pure KBr. FT-IR spectrophotometer, IRPRESTIGE-21, SHIMADZU, Japan, was used for analysis.

2.4. Procedure

The initial pH of Phenol and lead solutions was measured by pH meter, (ORION 3 STAR, Thermo, US), and it is found to be 5.45 and 4.40, respectively. The adsorption of metals and organics decreases at low pH values because of competition for binding sites between cations and protons, while at pH higher than 5.5, solubility of metal complexes decreases sufficiently allowing precipitation, which may complicate the sorption process and do not bind to the adsorption sites on the surface of the GAC/DAGS. Therefore, the optimum pH was found around four [13,14]. So, pH was adjusted with the range of (4) for all single and binary systems by adding the 0.1 N HNO_3 and 0.1 N NaOH for acidic and basic pH, respectively. A sample of 100 mg/l initial concentration and (100 ml) of each solution was placed in bottles of (250 ml) in volume, containing (from 0.05, 0.1, 0.15 to 0.6 g) of GAC/DAGS. The bottles were then placed on a shaker and agitated continuously at 250 rpm to provide good mixing for 24 h which is more than the ample time to reach equilibrium according to pervious work at 30°C [15]. Then, the solution was filtrated using filter paper type (Wattmann No. 4), and a sample of (20 ml) from each bottles was taken for analysis to measure phenol and lead concentration, respectively, using (GC 1000, Italia) and (AAS, Buck, Accusys 211, USA). The adsorbed amount was calculated using the following equation [16]:

$$q_e = \frac{V_L(C_o - C_e)}{W} \tag{1}$$

The adsorption efficiency was calculated by the difference in the initial and equilibrium concentration of each pollutant by the following relationship:

$$E_{\mathrm{ad./bio.}} = \frac{(C_0 - C_e)}{C_o} \times 100 \tag{2}$$

All the experiments were carried out in duplicates, and the average values were used for further calculations.

3. Adsorption isotherm models

3.1. Single-component isotherm models

Four models for single system have been tested in the present work and they are:

3.1.1. Freundlich model (Freundlich, 1907)

The first mathematical fit to an isotherm was published by Freundlich and Kuster in 1907. Freundlich showed that adsorption from solution could be expressed by empirical formula [17]:

$$q_e = k_F C_e^{1/n_F} \tag{3}$$

Table 1
Properties of GAG and DAGS

Property	GAC		DAGS	
Physical properties				
BET Surface area, m^2/g	751.965		94.53	
Particle porosity	0.584		0.65	
Average particle diameter, mm	0.775		0.775	
Pore volume, cm^3/g	0.422		0	
Chemical properties				
pH	10.2–10.6		7.5	
Ash content,%	3–5		12	
CEC, meq/100 g	0		51.153	
Species of Bacteria		CFU/ml	Gram-Positive	Gram-Negative
Pseudomonas aeruginosa		3.5×10^6		–
Escherichia coli		4.3×10^6		–
Bacillus subtilis		2.4×10^4	+	
Proteus mirabilis		5.0×10^5		–
Enterobacter cloacae		3.0×10^5		–
Salmonella sp.		20×10^6		–
Shigella dysenteria		25×10^5		–
Staphylococcus xylosus		1.36×10^5	+	
Aeromonas caviae		2.22×10^4		–
Klebsiella pneumonia		4.3×10^4		–
Species of Yeast				
Candida albicans		17,200		
Species of protozoa				
Entamoeba				
Guardig lambilig				
Ova of worm				
Species of Fungi				
Penicillium chrysogenum				

Plate 3. Anaerobic sludge during drying.

Plate 4. Flocks of drying anaerobic sludge.

3.1.2. Langmuir model (Langmuir, 1916)

In 1916, Irving Langmuir published a new model isotherm for gas or liquid adsorbed on solid, which retained his name. The Langmuir adsorption model is valid for single-layer adsorption. It is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, that the energy of adsorption is constant, and that there is no transmigration of

Plate 5. A sample of prepared DAGS.

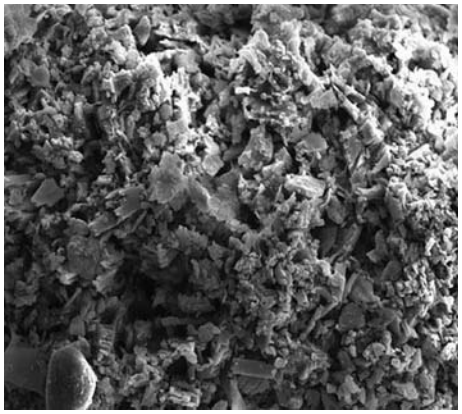

Plate 6. SEM image of DAGS shows the amorphous structures.

adsorbate in the plane of the surface. The Langmuir isotherm equation is [18]:

$$q_e = \frac{q_m b C_e}{1 + bC_e} \tag{4}$$

The essential characteristics of a Langmuir isotherm equation could be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, "R_s" which is defined by the following equation:

$$R_s = \frac{1}{1 + bC_0} \tag{5}$$

This separation factor yields the type of isotherm which was described by Weber and Chakravorti (1974) as shown in Table 2 [19]:

Table 2
Values of separation factor and type of isotherm

Values of R_s	Type of isotherm
$R_s > 1$	Unfavorable
$R_s = 1$	Linear
$0 < R_s < 1$	Favorable
$R_s = 0$	Irreversible

3.1.3. Redlich-Peterson model (Redlich and Peterson, 1959)

The Redlich–Peterson model expressed by the following equation [20]:

$$q_e = \frac{A_R C_e}{1 + B_R C_e^{m_R}} \tag{6}$$

This model expresses the adsorption process when dealing with a certain pollutants at high concentration.

3.1.4. Combination of Langmuir–Freundlich model (Sips, 1984)

This model referred as (Sips model) is widely used for a single-component adsorption, when a single-component adsorption process obeys Langmuir isotherm in some condition and turned to obey Freundlich isotherm or vise-versa. The Sips model can be expressed as [21]:

$$q_e = \frac{b q_m C_e^{1/n_F}}{1 + bC_e^{1/n_F}} \tag{7}$$

The properties of each previously mentioned isotherm with characteristics are summarized in Table 3.

3.2. Multi-component isotherm models

The experimental measurement of multicomponent adsorption isotherm is time-consuming because of large number of variables involved. Thus, the problem of predicting multicomponent adsorption isotherm from single-component adsorption data has attracted a lot of attention. Several isotherms have been proposed to describe the competitive adsorption. Most of these isotherms are based on single-component isotherm parameters and correction factors extracted from the experimental competitive data [22]. Four of these models are as follows:

3.2.1. Extended Langmuir model

The Langmuir isotherm can be extended for multicomponent system to give the following form:

$$q_{e,i} = \frac{q_{m,i} b_i C_{e,i}}{1 + \sum_{k=1}^{N} b_k C_{e,k}} \tag{8}$$

Table 3
Adsorption isotherm models characteristics [21]

Isotherm	Equation	Advantages	Disadvantages
Langmuir	$q_\mathrm{e} = \frac{q_\mathrm{m} b C_\mathrm{e}}{1+bC_\mathrm{e}}$	Interpretable parameters	Not structured, monolayer-sorption
Freundlich	$q_\mathrm{e} = K\,C_\mathrm{e}^{1/n_\mathrm{F}}$	Simple expression	Not structured, not leveling off
Redlich and Peterson	$q_\mathrm{e} = \frac{A_\mathrm{R} C_\mathrm{e}}{1+B_\mathrm{R} C_\mathrm{e}^{m_\mathrm{R}}}$	Approach Freundlich high concentration	No special advantages
Combination (Langmuir and Freundlich)	$q_\mathrm{e} = \frac{b q_\mathrm{m} C_\mathrm{e}^{1/n_\mathrm{F}}}{1+bC_\mathrm{e}^{1/n_\mathrm{F}}}$	Combination of above	Unnecessarily complicated

This model is applicable when each single component obeys the Langmuir model in a single-component system [23].

3.2.2. Combination of Langmuir–Freundlich model

The competitive Sips model related to the individual isotherm parameters is expressed in the following equation [24]:

$$q_{\mathrm{e},i} = \frac{q_{\mathrm{m},i} b_i C_{\mathrm{e},i}^{1/nFi}}{1+\sum_{i=1}^{N} b_i C_{\mathrm{e},i}^{1/nFi}} \tag{9}$$

3.2.3. Extended Freundlich model

The empirical extended form of the Freundlich model restricted to binary mixtures can be given by following equation [25]:

$$q_{\mathrm{e},i} = \frac{K_\mathrm{Fi} C_{\mathrm{e},i}^{n_\mathrm{Fi}+n1}}{C_{\mathrm{e},i}^{n1} + \sum_{j=1}^{N} b_j C_{\mathrm{e},j}^{n_\mathrm{Fj}}} \tag{10}$$

3.2.4. Redlich–Peterson model

The competitive Redlich–Peterson model related to the individual isotherm parameters is given by the following equation [25]:

$$q_{\mathrm{e},i} = \frac{K_\mathrm{Ri}(b_\mathrm{Ri}) C_{\mathrm{e},i}}{1+\sum_{k=1}^{N} b_{\mathrm{R},k} (C_{\mathrm{e},k})^{m_{\mathrm{R},k}}} \tag{11}$$

4. Results and discussion

4.1. FT-IR analysis of GAC and DAGS

The FT-IR analysis of GAC and DAGS is shown in Figs. 1 and 2. According to FT-IR DAGS figure, the band between 3,741 and 3,414 cm^{-1} indicates the presence of OH, NH and $\mathrm{NH_2}$ groups. A 2,954.95 cm^{-1} asymmetric vibration of CH, 2,920 cm^{-1} symmetric vibration of CH and 2,850 cm^{-1} symmetric vibration of CH. 2,515.18, 2,360.87 and 1,797.66 cm^{-1} vibration of carboxylic acids are indicated. 1,639.49 cm^{-1} and 1,562.34 cm^{-1} stretching vibration of C=O and NH peptidic bond of proteins. A 1,419.61 cm^{-1} of phenolic OH and CO stretching. The 1,080.14 cm^{-1} band is vibration of C–O–C polysaccharides. A 1,029 cm^{-1} band is vibration of C–O–C and OH groups. The < 1,000 cm^{-1} is finger print zone which are phosphate and alkyl halides groups [26].

Results of FT-IR spectra show that DAGS has different functional groups responsible for biosorption process. The anaerobic sludge biosorbent is known as a rich organic mass and composes of micro-organisms (bacteria, yeast, fungi and protozoa) as has been identified. The biochemical compositions of these organic mass are protein, lipid extra cellular polysaccharides, nucleic acids, cell wall compositions and other cellular compounds of the micro-organisms. FT-IR result showed that DAGS biosorbents have characteristic bands of proteins, lipids, polymeric compounds and carboxylic, amine and amide groups which are able to react with functional groups of phenol and lead molecules in aqueous solution. Similar characteristics are shown in literature for polymetric materials of activated sludge by Gulnaz et al. [27]

On the other hand, the FT-IR spectra of GAC in the range of 400–4,000 cm^{-1} shows less intensity in functional groups that are responsible for adsorption process compared to DAGS. From the results shown in Fig. 2, it can be concluded that the C=O stretching of carbonyl in carbonized acid is at 1,700 cm^{-1}, C=C stretching of the aromatic compound and alcohol at 1,500 cm^{-1}, and C–O stretching of carboxylic acid at 1,200 cm^{-1} and other groups [28].

4.2. Adsorption isotherms

4.2.1. Adsorption isotherms constants for single-component systems

The adsorption isotherms for single-component system of Ph and $\mathrm{Pb^{2+}}$ onto GAC are shown in Figs. 3

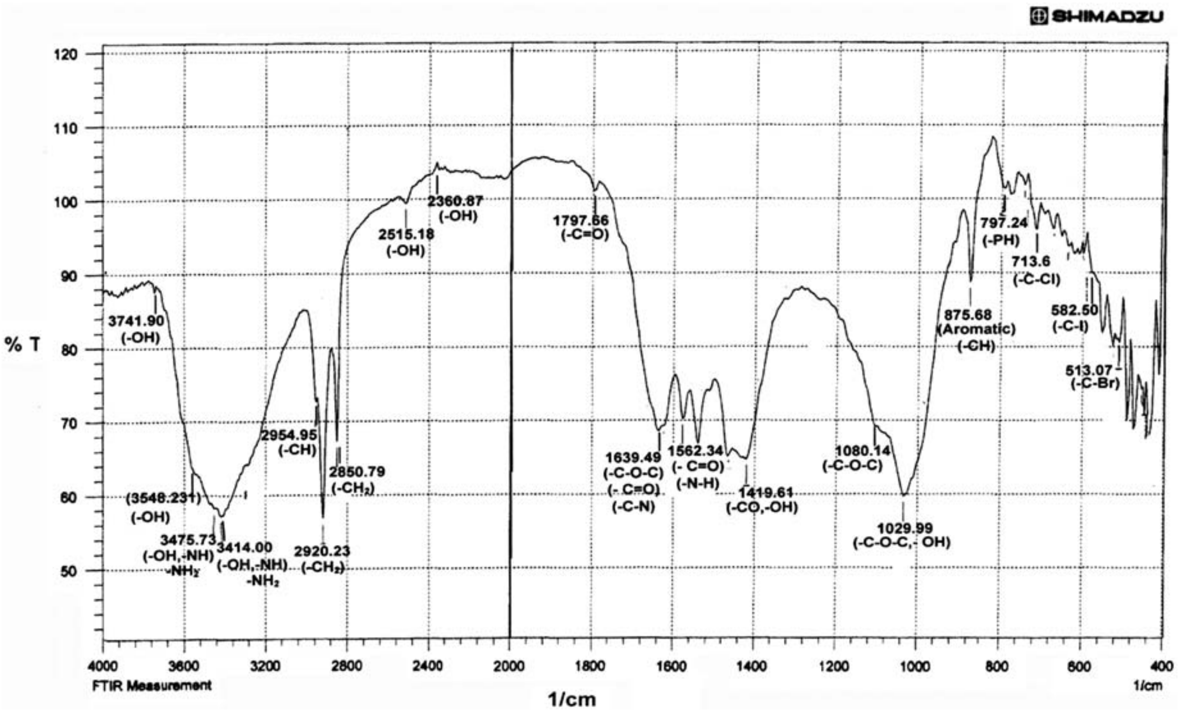

Fig. 1. FT-IR spectrum of DAGS.

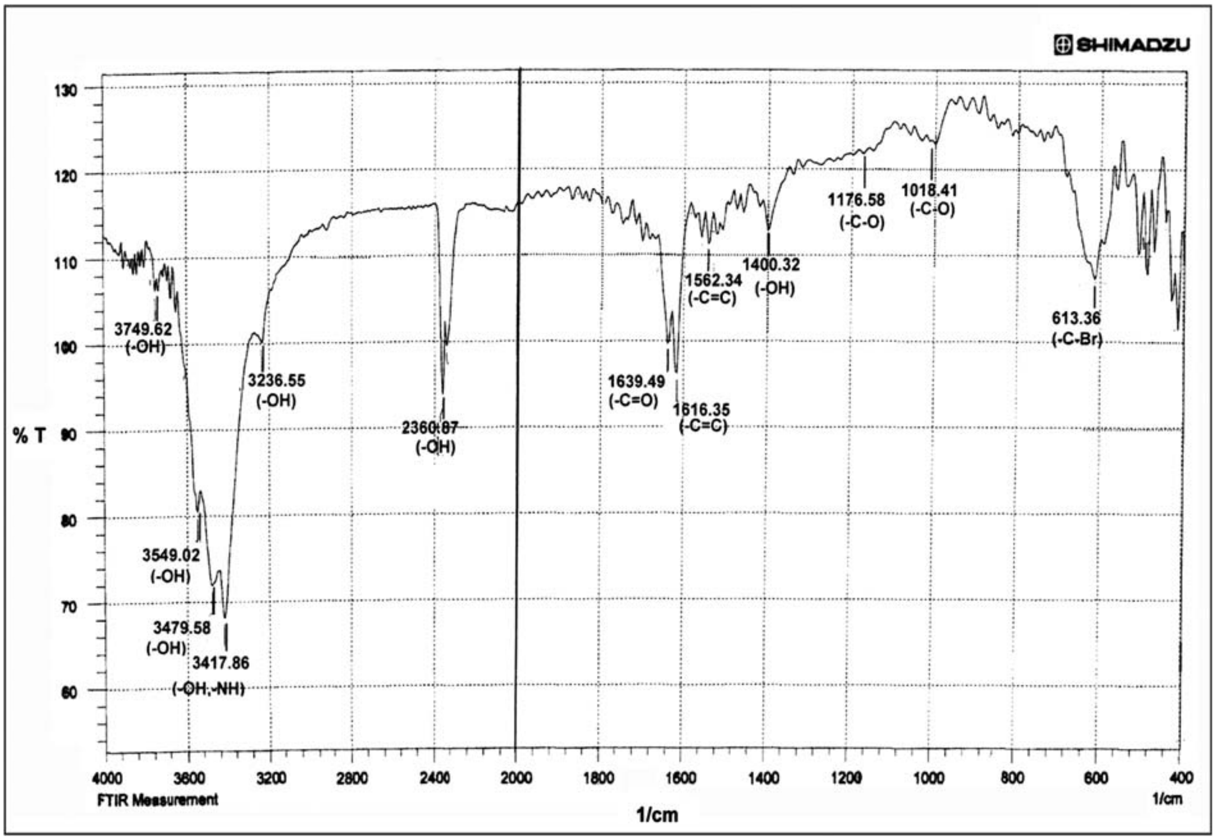

Fig. 2. FT-IR spectrum of GAC.

and 4, respectively. However, onto DAGS, the biosorption isotherms are shown in Figs. 5 and 6, respectively. The parameters for each model were estimated by nonlinear regression using STATISTICA version 6 and EXCEL 2007 software. All parameters with correlation coefficient are summarized in Table 4.

From the figures and tables for single-component systems for phenol and lead adsorption/biosorption onto GAC and DAGS, and from FT-IR figures, the following conclusions can be drawn:

For GAC

- The equilibrium isotherm for each solute is of favorable type since $R_s < 1$ ($R_s = 0.3243$, 0.1821 for Ph and Pb^{2+}, respectively). From Figs. 3 and 5, the adsorption isotherm is of favorable type and relatively high adsorbent loading as obtained at low concentrations of solute in water according to Perry and Chilton [29]. Also, the adsorption isotherm is of type (I), where monolayer of adsorbate is adsorbed onto the surface of GAC according to [IUPAC] classification of adsorption isotherm [30].
- For phenol, Langmuir and combination of Langmuir–Freundlich models gave the best fit of the experimental data with high correlation coefficients (0.9976), while the experimental data for lead were described successfully with Langmuir model with correlation coefficient (0.9935). The difference in q_m values between two models may refer to combined between two of difference assumption models of Langmuir and Freundlich. Ahmed, 2006, using Langmuir and combination of Langmuir–Freundlich models, evaluated the adsorption of phenol, furfural and parachlorophenol onto GAC. The q_m values were 0.3199 and 1.576 kg/kg [31].
- Using Langmuir model, it was found that, the maximum amount of adsorbate adsorbed per mass of activated carbon (q_m) for Ph is greater than that for Pb^{2+} ($q_{m,Ph} = 83.28803$ mg/g; $q_{m,Pb^{2+}} = 65.2850$ mg/g). At the same time, the adsorption percentage efficiency for phenol is greater than for lead ($E_{ad.Ph} = 96.222\%$; $E_{ad.Pb^{2+}} = 95.456\%$). This can be explained by:

  (a) Phenol has less solubility (86,000 mg/l) in water in comparison with lead nitrate (520,000 mg/l) and consequently with lead.
  (b) Molecular cross-sectional area (molecular volume) for phenol is greater than lead (21.40 Å^2 for lead; 30.49 Å^2 for phenol).

The adsorption capacity decreases with increasing solubility and increases with increasing molecular volume [31]. Abdul-Hameed, 2009, studied the

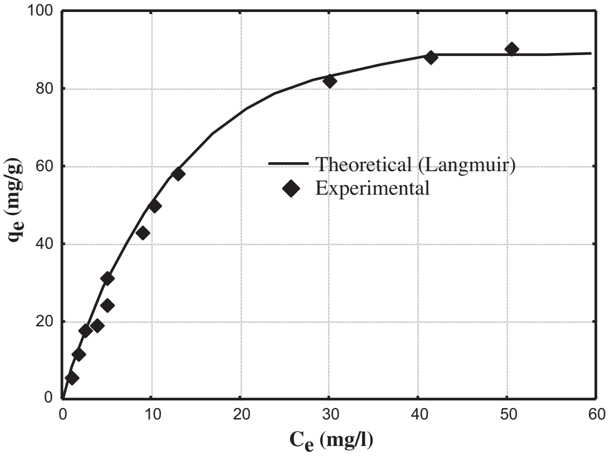

Fig. 3. Adsorption isotherm for Ph onto GAC.

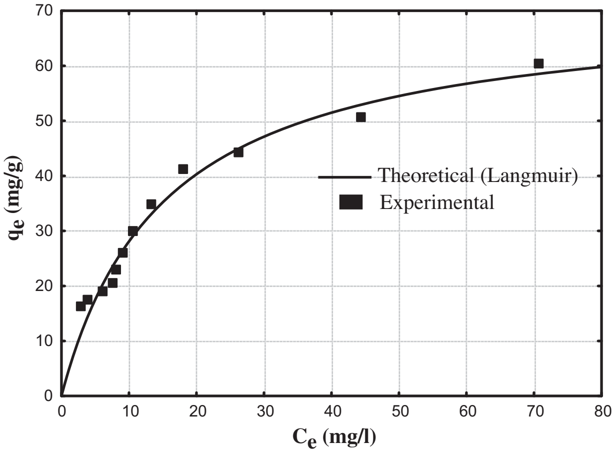

Fig. 4. Adsorption isotherm for Pb^{2+} onto GAC.

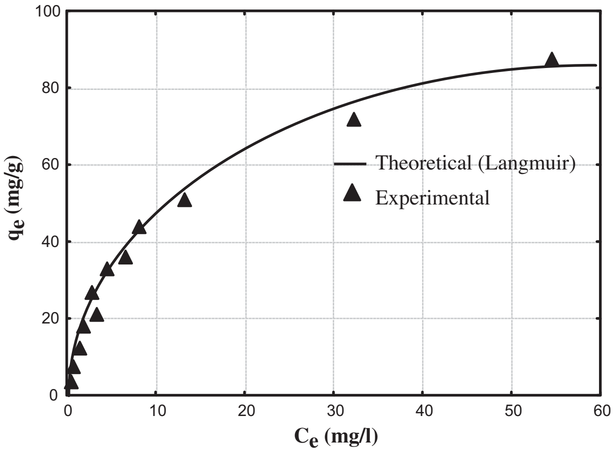

Fig. 5. Biosorption isotherm for Ph onto DAGS.

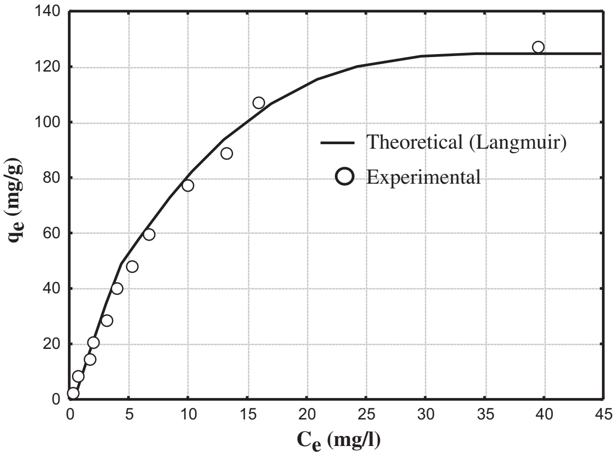

Fig. 6. Biosorption isotherm for Pb^{2+} onto DAGS.

adsorption capacity of lead (II), mercury (II) and cadmium (II) onto GAC. Since lead nitrate salts has less solubility (1,570 mg/l) in water in comparison with mercury chloride salts (2,800 mg/l) and cadmium nitrate salts (7,200 mg/l), it will expect to have a highest adsorption rate. Thus, maximum adsorption capacity (q_m) follow the sequence as: Pb^{2+}>Hg^{2+}>Cd^{2+} [32].

For DAGS:

- The equilibrium isotherm for each single component is of favorable type ($0 < R_s < 1$), and its relatively high loading onto DAGS was obtained.
- The Langmuir and combination of Langmuir–Freundlich models gave the best fit for the experimental data for phenol and lead onto DAGS ($R^2 = 0.9921$ and 0.9956, respectively).
- On contrast of GAC, the maximum biosorbed amount (q_m) onto DAGS for Pb^{2+} is greater than that for Ph. $q_{m,Pb^{2+}} = 125.4523$ mg/g; $q_{m,Ph} =$ 90.5421 mg/g. At the same time, the biosorption percentage efficiency for lead is greater than for phenol ($E_{bio.Pb^{2+}} = 98.570$; $E_{bio.Ph} = 97.879$). This behavior can be explained as:
- Most of functional groups are negative. The affinity between lead cation (Pb^{2+}) and these groups is more than for negative phenol.
- Cation exchange capacity (CEC) represents the total amount of lead cation that can be replaced by positive ions (K^+,Na^+,Ca^{2+} and Mg^{2+}) on anaerobic sludge. CEC for DAGS used in this study was 51.153 meq/100 g. Thawornchaisit and Pakulanon, 2006, used dried sewage sludge of about 38.2 meq/100 g for biosorption of phenol with adsorption capacity (q_m) of 17.3 mg/g [33].

Aksu and Akpnar, 2000, investigated the equilibrium uptake of phenol and nickel(II) ions onto dried aerobic activated sludge in a batch system. The maximum biosorption capacity (q_m) was 180.9 and

Table 4
Parameters of single solute isotherm for Ph and Pb^{2+} onto GAC and DAGS

Model	Parameters	GAC		DAGS	
		Ph	Pb^{2+}	Ph	Pb^{2+}
Freundlich model	K_F (mg/g)(l/mg)$^{1/n_F}$	7.346	3.7865	6.9782	11.2331
	n_F	1.9451	2.7891	1.8543	1.9765
	R^2	0.9891	0.9750	0.9763	0.9821
Langmuir model	q_m (mg/g)	83.28803	65.2850	90.5421	125.4523
	b (l/mg)	0.0602	0.1258	0.0650	0.0926
	R^2	0.9976	0.9935	0.9921	0.9956
	R_s	0.3243	0.1821	0.3452	0.1776
	$E_{ad./bio.}$ (%)	96.222	95.456	97.879	98.570
Redlich–Peterson model	A_R (l/mg)	9.4361	4.8889	40.4532	13.7865
	B_R (l/mg)^{m_R}	1.5674	0.0647	1.9876	0.3427
	m_R	0.6545	1.2471	7.3425	1.7689
	R^2	0.9867	0.9723	0.9643	0.99321
Combination of Langnuir–Freundlich model	q_m (mg/g)	73.7623	45.2343	85.4671	96.8383
	b (l/mg)$^{1/n}$	0.0764	0.2435	0.0453	0.1457
	n_F	1.457	0.8764	1.6789	1.9790
	R^2	0.9976	0.9905	0.9933	0.9936

300.7 mg/g for phenol and nickel, respectively. As a result, nickel adsorbed more strongly than phenol [13].

4.2.2. Adsorption isotherms constants for binary component systems

The adsorption/biosorption isotherms for binary component systems of Ph and Pb^{2+} onto GAC and DAGS are shown in Figs. 7 and 8, respectively, whereas Table 5 represents the parameters of each used model and their correlation coefficient (R^2).

For phenol and lead adsorption onto GAC, the behavior of the equilibrium isotherms for all the binary systems are of a favorable type (Type I according to IUPAC). The extended Langmuir and Redlich–Peterson models seem to give the best fitting for the experimental data ($R^2 = 0.9964$) for phenol adsorption. While for lead adsorption, the extended Langmuir model gives highest value of ($R^2 = 0.9950$). There is a weak competition in binary systems in the adsorption capacity of phenol ($\Delta q_{m,Ph} = 12.0470$ mg/g), whereas the uptake of lead is very much reduced by the presence of phenol solute due to high affinity between phenol and GAC ($\Delta q_{m,Pb^{2+}} = 44.7418$ mg/g) as cleared from Fig. 7. It is clearly observed that the adsorption of lead (II) was also significantly inhibited by coexisting phenol with a similar trend. The prediction of multi-component equilibrium data has always been complicated due to the interactive and competitive effects involved. The behavior of each species in a multi-component system depends strongly on the physical and chemical properties of both sorbent–sorbate. In addition, the number and kind of species present and the pH of solution also affects the equilibrium constants [34].

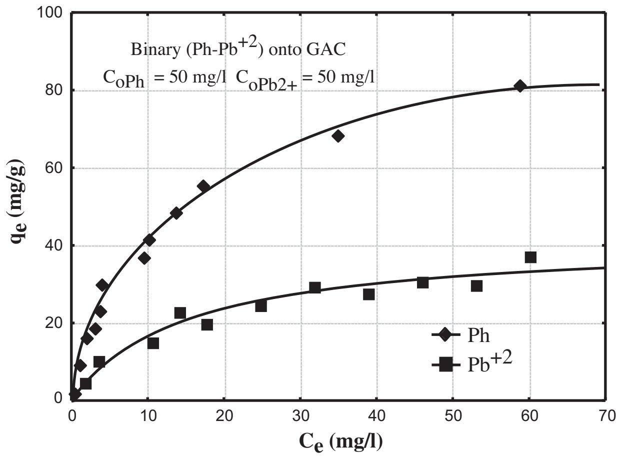

Fig. 7. Adsorption isotherm for (Ph-Pb^{2+}) onto GAC.

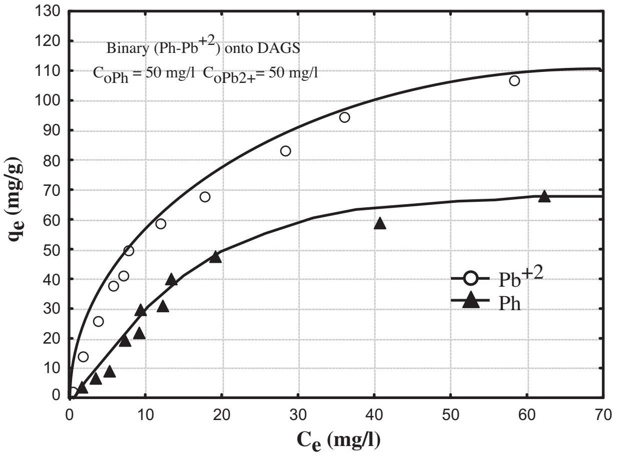

Fig. 8. Biosorption isotherm for (Ph-Pb^{2+}) onto DAGS.

For biosorption onto DAGS, the behavior of the equilibrium isotherms for all the binary systems is of a favorable type. For phenol, the extended Langmuir model gives highest value of ($R^2 = 0.9923$). For lead the extended Langmuir and Redlich–Peterson are the most fitting models ($R^2 = 0.9945$). Aksu and Akpınar, (2000) applied extended Langmuir and extended Freundlich and Redlich–Peterson models to describe the competitive adsorption of phenol and nickel onto dried activated sludge. They found that, the experimental data fitted very well to the Redlich–Peterson model [3]. And again on contract of GAC, there is a weak competition in binary systems in the biosorption capacity of lead onto DAGS, respectively ($\Delta q_{m,Pb^{2+}} = 23.5791$ mg/g), whereas the uptake of phenol is highly reduced by the presence of lead solute due to higher affinity between lead and biosorption sites ($\Delta q_{m,Ph=}59.7578$ mg/g) as shown from Fig. 8.

Ridha, 2011 studied the biosorption of heavy metals using expanded granular sludge reactor. Four models were used to represent the biosorption capacity of Pb^{2+}, Cr^{3+} and Cd^{2+} and from which the best fitted model to experimental data was found to be the extended Langmuir and combination of Langmuir–Freundlich models of 0.958 and 0.997, respectively [34].

In conclusion, it was clear that DAGS was more efficient in biosorption of phenol and lead than GAC. The following reasons can be responsible for this behavior:

(a) Functional groups play the major role in DAGS biosorption capacity. Number of functional groups of DAGS is greater than those of GAC as cleared from Figs. 1 and 2.

Table 5
Parameters of a binary solute isotherm for Ph and Pb^{2+} onto GAC and DAGS

Model	Parameters	GAC		DAGD	
		Ph	Pb^{2+}	Ph	Pb^{2+}
Extended Langmuir Model	q_m (mg/g)	71.2333	20.5432	30.7843	101.8732
	b (l/mg)	0.0202	0.4326	0.0677	0.1243
	R^2	0.9964	0.9950	0.9923	0.9945
	R_s	0.3761	0.1542	0.2432	0.4325
	$E_{ad./bio.}$ (%)	94.3421	92.8711	93.3242	96.3210
Combination of Langnuir–Freundlich Model	q_m (mg/g)	65.5429	10.5642	10.6743	21.8653
	b $(l/mg)^{1/n}$	0.2186	5.0321	5.6531	4.9762
	n_F	8.5642	2.9753	1.5986	0.1298
	R^2	0.9621	0.9541	0.9432	0.7979
Extended Freundlich Model	K_F $(mg/g)(l/mg)^{1/n_F}$	30.6521	18.8732	14.8965	66.0430
	n_F	0.0752	0.2354	0.2654	0.8975
	b	0.9432	0.2543	0.6543	0.7853
	R^2	0.9964	0.9543	0.9398	0.9945
Redlich–Peterson Model	K_R (l/mg)	10.5421	3.2141	6.9872	8.5423
	b_R $(l/mg)^{m_R}$	1.6542	0.7862	0.0126	0.1543
	m_R	0.8762	0.6522	0.4433	0.1004
	R^2	0.9964	0.9832	0.9904	0.9945

(b) CEC for DAGS is 51.153 meq/100 gm while for GAC, the CEC equal to zero.

Aksu and Yener, (2001), studied the potential use of dried activated sludge and fly ash as a substitute for GAC for removing mono-chlorinated phenol. The sorption of *o*- and *p*-chlorophenol was expressed by the Freundlich, Langmuir and Redlich–Peterson adsorption models. They concluded that dried activated sludge and fly ash may be used as low-cost, natural and abundant sources for the removal of the studied adsorbents [35].

5. Conclusions

In industry, effluents rarely contain a single component; hence, adsorption systems design must be based on multi-component effluents, making multi-component equilibrium data a necessity. The adsorption/biosorption of phenol, lead(II) and phenol–lead (II) mixtures on the GAC and DAGS have been investigated in this study, and the data have been analyzed by Freundlich, Langmuir, combination of Langmuir–Freundlich and Redlich–Peterson isotherms.

The main features of adsorption/biosorption for phenol and lead (II) by GAC and DAGS in individual solutions are as follows: the adsorption/biosorption is favorable; phenol is adsorbed better than lead (II) onto GAC, while lead (II) is biosorbed more strongly than phenol onto DAGS; and of the four models examined, the Langmuir and combination of Langmuir–Freundlich models are found the most suitable for describing the adsorption/biosorption equilibrium of either phenol and lead (II) onto both adsorbents.

The applicability's of the multi-component extended Langmuir, combination of Langmuir–Freundlich, extended Freundlich and Redlich–Peterson models to the adsorption/biosorption of phenol and lead (II) ions from the binary mixtures by GAC and DAGS was also checked. It was seen that the biosorption equilibrium data fitted well to all the multi-component adsorption models in the studied concentration with little difference in correlation coefficient.

The model parameters obtained in this work can be used to estimate reactor volume and required adsorbent/biosorbent quantity for desired separation, purification degree, etc. from mass balance in a batch mono component or binary system with satisfactory agreement with experimental results. Moreover, using these data multi-stage continuous systems can be also designed and stage number can be found for desired purification.

Finally, cheaply available DAS can be used as an efficient biosorbent material for the removal of single phenol, single lead (II) and binary phenol–lead (II) mixtures from wastewaters compared to expensive GAC. The adsorption/biosorption equilibrium of these systems can be defined mathematically with proposed adsorption models. Although the mathematical models were developed for one- and two component systems, the models may be applicable to other multi-component systems, which can represent real wastewater systems.

Nomenclature

Å — Angstrom, 1×10^{-10} m
A_R — Redlich–Peterson model parameter, l/mg
AAS — atomic absorption spectrophotometer
B_R — Redlich–Peterson model parameter, $(\mathrm{l/mg})^{m}{}_{R}$
b — Langmuir adsorption constant related to the affinity to binding sites, l/mg
b_{RK} — Redlich–Peterson model parameter derived from the corresponding individual isotherm equations, $(\mathrm{l/mg})^{m_R}$
bi — individual Langmuir adsorption constant of each component, l/mg
C_o — equilibrium concentration, mg/l
C_e — equilibrium concentration, mg/l
$E_{ad./bio}$ — adsorption/biosorption efficiency, %
GC — gas chromatography
HNO_3 — nitric acid
I — component number $(1, 2, \ldots)$
IUPAC — International Union of Pure and Applied Chemistry
K_F — Freundlich adsorption constant, related to adsorption intensity, $(\mathrm{mg/g})(\mathrm{mg/l})^{1/n_F}$
K_{Fi} — individual Freundlich adsorption constant of each component, $(\mathrm{mg/g})(\mathrm{mg/l})^{1/n_F}$
K_{Ri} — individual Redlich–Peterson adsorption constant of each component, (l/mg)
m_{Ri} — Redlich–Peterson model parameter
n_F — Freundlich adsorption constant, related to the affinity to binding sites
n_{Fi} — individual Freundlich adsorption constant of each component
NaOH — sodium hydroxide
q_{eq} — adsorbed phenol/lead quantity per gram of GAC/DAGS at equilibrium, mg/g
q_m — Langmuir adsorption constant of the pollutants shows the maximum amount of pollutants bound to the GAC/DAGS, mg/g
q_{ei} — amount of adsorbate adsorbed per mass of adsorbent of component i, mg/g
q_{mi} — individual Langmuir adsorption constant of each component, mg/g
R^2 — correlation coefficient, %
V_L — volume of solution, L
W — mass of GAC/DAGS, gm

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