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# Competitive biosorption of phenol and lead from synthetic wastewater onto live and dead microorganisms

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**ABSTRACT**

The comparison between the living and dead microorganisms for removing phenol and lead from aqueous solution was examined in a batch system. The working sorption pH, temperature, mixing speed and contact time were fixed at 4, 30°C, 250 rpm and 24 h respectively. Biosorption isotherms were developed for both the single and binary component systems and expressed by four models. Model parameters were estimated by the non-linear regression method using STATISTICA version-6 and EXCEEL-2007 software. The maximum loading capacity ($q_m$) of the phenol was 30.2018 and 70.0183 mg $g^{-1}$ and for lead was 36.7888 and 89.8783 mg $g^{-1}$ onto live and dead microorganisms in single system respectively. However, in binary system the loading capacity decreased because of competition between compounds to binding sites of biosorbents. Desorption efficiency from living microorganisms was 85.974% and 80.096% under 0.1 M of $Na_2CO_3$ and HCl, while it was 95.352% and 96.632% from dead microorganisms for phenol and lead respectively.

*Keywords:* Biosorption; Live microorganisms; Dead microorganisms; Phenol; Lead; Biosorption isotherms

## 1. Introduction

Phenolics are present in different concentrations in wastewaters of industries such as coal conversion, coke preparation, synthetic rubber, pesticide, insecticide, petroleum refineries, pulp and paper, plastic, textile, dye, polymeric resin, pharmaceuticals, wood, etc. Phenol and phenolic compounds are among the most common organic pollutants of wastewaters that require careful treatment before being discharged into the receiving body of waters. It should be noted that the contamination of drinking water by phenolics at even a concentration of 1 mg $l^{-1}$ could bring about significant taste and odor problems making it unfit for use [1]. Toxic metal compounds are frequently used in industrial processes and are widely distributed in the environment. Lead is one of the major toxic heavy metals pollutants, which entered the water streams through various industrial operations [2]. Lead is used as industrial raw material in the manufacture of storage batteries, pigments, leaded glass, fuels, photographic materials, solder and steel products. Lead poisoning in humans causes severe damage to kidney, nervous system, reproductive system, liver and brain [3].

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A number of treatment methods for removing heavy metals and organics from domestic and industrial wastewater include chemical precipitation, ion exchange, filtration, membrane separation and adsorption. Most heavy metal salts are soluble in water and, as a consequence, cannot be separated by ordinary physical separation methods [1]. Conventional methods for removing metals/organics from aqueous solutions include: chemical precipitation, chemical oxidation or reduction, ion exchange, filtration, reverse osmosis, membrane technologies, and evaporation recovery. These processes may be ineffective or extremely expensive, especially when the metals in solution are in the range of (1–100 mg $l^{-1}$) [1,2].

Biosorption, based on living or dead microorganisms or plants, offers the reduction of toxic metal levels to environmentally acceptable limits in a cost-effective and environmentally friendly manner. The big advantages of biosorption are the low operating cost, minimization of the volume of chemical and/or biological sludge to be disposed of, and high efficiency in detoxifying very dilute effluents [3–6]. 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 microorganisms overgrown in such wastewater systems can be separated and utilized for 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 microorganisms 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 microorganisms cell wall, including carboxyl, 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 at 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. The 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. Sorbate*

A standard solution of phenol and lead (II) with concentration of (1000 mg $l^{-1}$) was prepared as follows: A (1 g) of phenol crystals was dissolved in (1 l) of distilled water and the specific concentration was measured by using gas chromatograph (GC). For lead, A (1.5985 g) of $Pb(NO_3)_2$ salt was dissolved in (1 l) of distilled water and the specific concentration was measured by using atomic absorption spectrophotometer (AAS).

### *2.2. Biosorbent*

The microorganisms used in the study were isolated 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 are about (7500 $m^3$). The density of the anaerobic sludge was measured by weighting a known volume and its found to be 1350 kg $m^{-3}$. The sludge was collected from about 40 cm depth of drying bed surface where anaerobic conditions are predominate. The observation of methane gas bubbles during collection of sludge proved this fact. To identify species of microorganisms present in anaerobic sludge, the sludge was serially diluted with distilled water. Aliquots (0.1 ml) were spread on nutrient agar and cultivated in incubator (memmert, ICP 500, Germany) at 30°C for 3–7 d. The microorganisms found in the sludge were heterogeneous and consist mainly from facilitative anaerobic bacteria, yeast, fungi and protozoa according to the biochemical tests and by using an intelligent system (Api 32 system, SHIMADZU, Japan) to diagnosis different species of bacteria in short time using a strake consist of 32 chamber. The steps in the preparation of dead microorganisms were as follows:

- Drying of anaerobic sludge at dry climate condition (Temperature 30 ± 5°C and Relative humidity of 45%) for 2 d.
- Formation of flocks of dead microorganisms.
- Grinding the flocks by used agate mortar.
- Sieving the resulting biosorbent with two sieves of 20/30 mesh number respectively.

- The microorganisms 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, dead microorganisms 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 live and dead microorganisms were conducted at the laboratories of the Ministry of Industry and Minerals (Ibn Sina State Company), Ministry of Oil (Petroleum Development and Research Center), Al-Mustansiriya University (Collage of engineering, Environmental Department) and are listed in Table 1. Plates 1–4 show the stages in preparation of dead microorganisms.

### 2.3. FT-IR analysis of dead microorganisms

The functional groups of microorganisms were detected by FT-IR analysis. The proportion of dead microorganisms/KBr was 1/100. The background was 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 were measured by pH meter (ORION 3 STAR, Thermo, US) and its found to be 5.45 and 4.40 respectively. The biosorption of metals and organics decrease at low pH values because of competition for binding sites between cations and protons, while at pH higher than 5.5, solubility of metal complexes decreases sufficiently allowing precipitation, which may complicate the sorption process and do not bind to the biosorption sites on the surface of the live and dead microorganisms. Therefore the optimum pH was found around 4 [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 ml) of each solution was placed in bottles of (250 ml) in volume, containing (0.05, 0.1, 0.15, …, 0.6 g) of dead microorganisms. For live microorganisms, an equivalent volumes to weights were used from known the anaerobic sludge density 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 were 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 [15]:

Table 1
Properties of live and dead microorganisms

| Property | Dead microorganisms | | |
|---|---|---|---|
| Physical properties | | | |
| Actual density, kg $cm^{-3}$ | 1741.6 | | |
| Apparent density, kg $cm^{-3}$ | 609.9 | | |
| BET surface area, $m^2$ $g^{-1}$ | 94.53 | | |
| Particle porosity | 0.65 | | |
| Bed porosity | 0.72 | | |
| Average particle diameter, mm | 0.775 | | |
| Chemical properties | | | |
| pH | 7.5 | | |
| Ash content, % | 12 | | |
| CEC, meq/100 g | 51.153 | | |
| Biological properties | Live microorganisms | | |
| Species of bacteria | CFU $ml^{-1}$ | Gram-positive | Gram-negative |
| *Pseudomonas aeruginosa* | $3.5 \times 10^6$ | – | – |
| *Escherichia coli* | $4.3 \times 10^6$ | – | – |
| *Bacillus subtilis* | $2.4 \times 10^4$ | + | – |
| *Proteus mirabilis* | $5.0 \times 10^5$ | – | – |
| *Entrobacter cloacae* | $3.0 \times 10^5$ | – | – |
| *Salmonella* sp. | $20 \times 10^6$ | – | – |
| *Shigella dysenteria* | $25 \times 10^5$ | – | – |
| *Staphylococcus xylosus* | $1.36 \times 10^5$ | + | – |
| *Aeromonas caviae* | $2.22 \times 10^4$ | – | – |
| *Klebsiella pneumonia* | $4.3 \times 10^4$ | – | – |
| Species of yeast | | – | – |
| Candida albicans | 17,200 | – | – |
| Species of protozoa | – | – | – |
| Entamo eby | – | – | – |
| Guardig lambilig | – | – | – |
| Ova of worm | – | | |
| Species of Fungi | – | – | – |
| Penicillium chrysogenum | – | – | – |

Plate 1. Anaerobic sludge during drying.

Plate 2. Flocks of drying anaerobic sludge.

Plate 3. A sample of prepared dead microorganisms.

$$q_e = \frac{V_L\left(C_o - C_e\right)}{W} \quad (1)$$

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

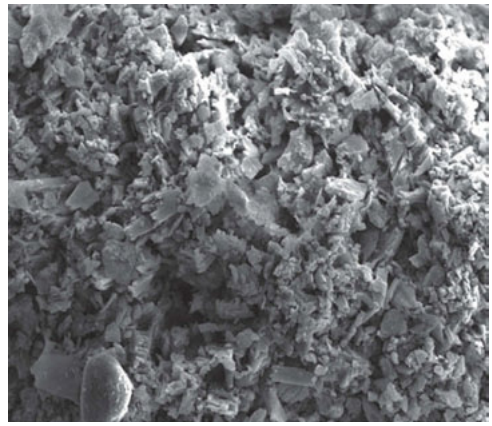

Plate 4. SEM image of dead microorganisms shows the amorphous structures.

$$E_{bio.} = \frac{\left(C_o - C_e\right)}{C_o} \times 100 \quad (2)$$

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

## 3. Adsorption isotherm models

Biosorption is usually described through isotherm, which is the equilibrium relationship between the sorbate concentration in the fluid phase and the sorbate concentration in the biosorbent particles at a given temperature. It is a plot of the amount of sorbate per unit weight of biosorbent ($q_e$) against the equilibrium concentration of the adsorbate remaining in solution ($C_e$) [16].

### *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*

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]:

$$q_e = k_F C_e^{1/n_F} \quad (3)$$

#### *3.1.2. Langmuir model*

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

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (4)$$

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:

$$R_s = \frac{1}{1 + b C_o} \quad (5)$$

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

#### 3.1.3. Reddlich–Peterson model

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

$$q_e = \frac{A_R C_e}{1 + B_R C_e^{m_R}} \quad (6)$$

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

#### 3.1.4. Combination of Langmuir–Freundlich model

This model is 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 vice-versa. The Sips model can be expressed as [21]:

$$q_e = \frac{b q_m C_e^{1/n_F}}{1 + b C_e^{1/n_F}} \quad (7)$$

### 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:

Table 2
Values of separation factor and type of isotherm

| Values of *R*s | Type of isotherm |
|---|---|
| *R*s > 1 | Unfavorable |
| *R*s = 0 | Linear |
| 0 < *R*s < 1 | Favorable |
| *R*s < 0 | Irreversible |

#### 3.2.1. Extended Langmuir model

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

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

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

#### 3.2.2. Combinationof Langmuir–Freundlich model

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

$$q_{e,i} = \frac{q_{m,i} b_i C_{e,i}^{1/n_{Fi}}}{1 + \sum_{i=1}^{N} b_i C_{e,i}^{1/n_{Fi}}} \quad (9)$$

#### 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]:

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

#### 3.2.4. Redlich–Peterson model

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

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

## 4. Phenol and lead desorption

Desorption experiments were performed in order to demonstrate the ability of exhausted live and dead microorganisms for regeneration and reuse. The desorption

Table 3
Eluants used in desorption of Ph and $Pb^{+2}$ from live and dead microorganisms

| Acid eluants | | Alkaline elunts | | Mineral salt eluant | Other eluant |
|---|---|---|---|---|---|
| HCl | $H_2SO_4$ | NaOH | $Na_2CO_3$ | EDTA | DDW |
| pH | pH | pH | pH | pH | pH |
| 1.956 | 2.180 | 12.798 | 11.282 | 5.241 | 7 |

procedure was the same as that previously described for biosorption experiments. Six eluants have been examined (EDTA, $Na_2CO_3$, NaOH, $H_2SO_4$, HCl and DDW) in the present study as listed in Table 3. The Ph and $Pb^{+2}$-loaded live and dead microorganisms was conducted with 50 ml of 0.1 M eluant for 24 h to allow Ph/$Pb^{+2}$ to be released from the biosorbents.

Thereafter, the desorbed Ph/$Pb^{+2}$ was analyzed and the eluting efficiencies of the desorbents $E_d$ are expressed as follows:

$$E_d(\%) = \frac{m_{d.}}{m_{bio.}} \frac{C_{d.} \times V_e}{C_{bio.} \times V_L} = \frac{C_{d.} \times V_e}{(C_o - C_e) \times V_L} \quad (12)$$

## 5. Results and discussion

### 5.1. FTIR analysis of microorganisms

The FT-IR analysis of microorganisms is shown in Fig. 1. According to FT-IR microorganisms figure, the band between 3741 and 3414 $cm^{-1}$ indicating the presence of OH, NH and $NH_2$ groups. A 2954.95 $cm^{-1}$ asymmetric vibration of CH, 2920 $cm^{-1}$ symmetric vibration of CH and 2850 $cm^{-1}$ symmetric vibration of CH. 2515.18, 2360.87 and 1797.66 $cm^{-1}$ vibration of carboxylic acids. 1639.49 and 1562.34 $cm^{-1}$ stretching vibration of C=O and NH peptidic bond of proteins. A 1419.61 $cm^{-1}$ of phenolic OH and CO stretching. The 1080.14 $cm^{-1}$ band is vibration of C–O–C polysaccrides. A 1029 $cm^{-1}$ band is vibration of C–O–C and OH groups. The <1000 $cm^{-1}$ is finger print zone which are phosphate and alkyl halides groups [26].

Results of FT-IR spectra show that microorganisms has different functional groups responsible for biosorption process. The anaerobic sludge biosorbent is known as a rich organic mass and composes of microorganisms (bacteria, yeast, fungi and protozoa) as has been identified. The biochemical composition of these organic mass are protein, lipid extra cellular polysaccharides, nucleic acids, cell wall compositions and other cellular compounds of the microorganisms. FTIR result showed that microorganisms biosorbent has 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].

### 5.2. Biosorption isotherms

#### 5.2.1. Biosorption isotherms constants for single component systems

The biosorption isotherms for single component system of Ph and $Pb^{+2}$ onto live and dead microorganisms

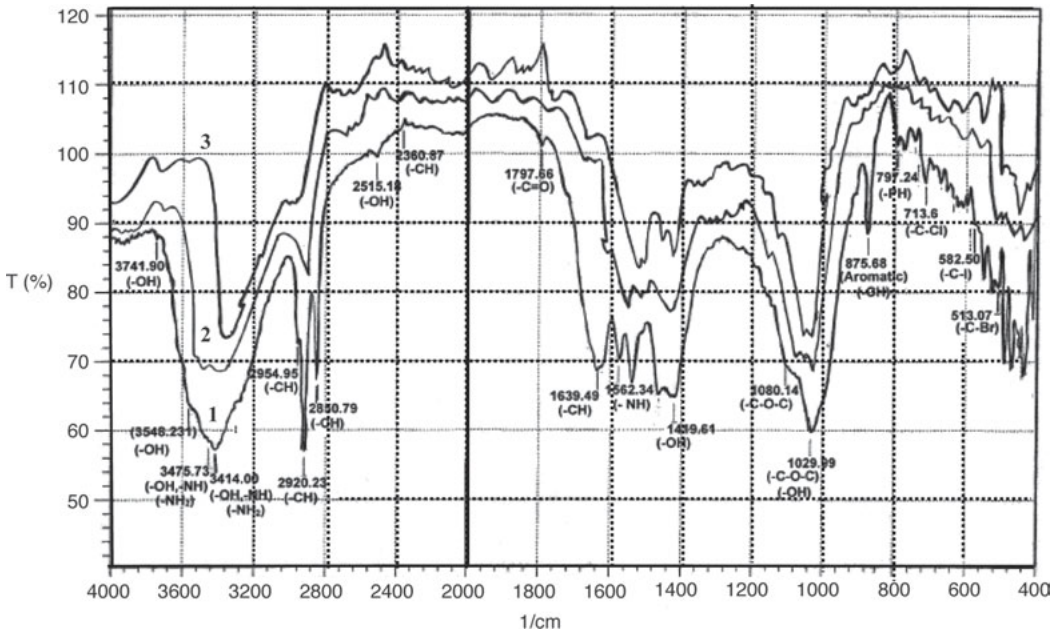


Fig.1. FT-IR spectra of dead microorganisms (1) before phenol and lead biosorption (2) after phenol biosorption (3) after lead biosorption.

are shown in Figs. 2 and 3. The parameters for each model were estimated by non liner 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, and from FTIR figure and tables for phenol and lead biosorption onto live and dead microorganisms, the following conclusions can be drawn: The equilibrium isotherm for each single component is of favorable type ($0 < R_s < 1$), and its relatively high loading onto live and dead microorganisms were obtained. The Langmuir and Reddlich–Peterson models gave the best fit for the experimental data for a phenol onto live microorganisms. While onto dead, the Langmuir and combination of Langmuir–Freundlich gave the highest value of

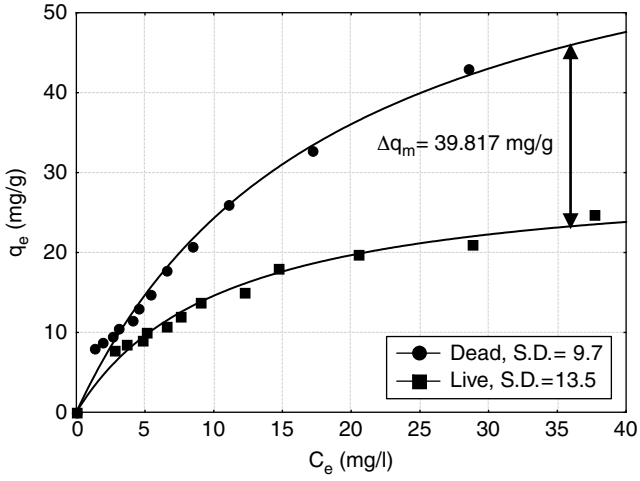


Fig. 2. Biosorption isotherm of phenol onto dead and live microorganisms in single system.

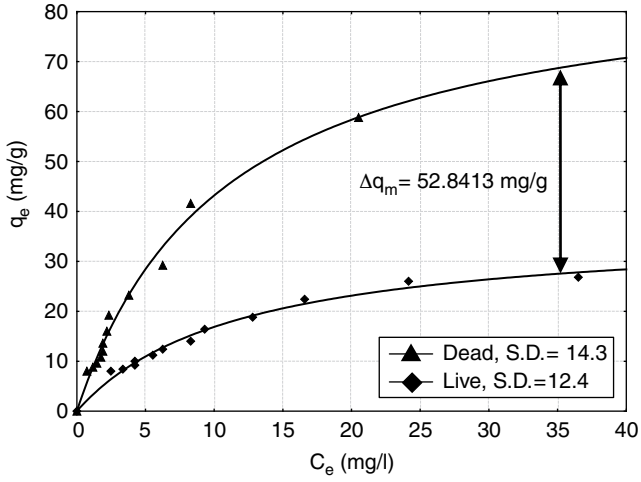


Fig. 3. Biosorption isotherm of lead onto dead and live microorganisms in single system.

Table 4
Parameters of single solute isotherm for Ph and $Pb^{+2}$ onto live and dead microorganisms

| Model | Parameters | Live | | Dead | |
|---|---|---|---|---|---|
| | | Ph | $Pb^{+2}$ | Ph | $Pb^{+2}$ |
| Freundlich model | $K_F$ (mg $g^{-1}$)(l $mg^{-1})^{1/n}{}_F$ | 4.9068 | 5.2368 | 5.7184 | 7.0332 |
| | $n_F$ | 2.2316 | 2.0830 | 1.6483 | 2.3448 |
| | $R^2$ | 0.9946 | 0.9868 | 0.9956 | 0.9750 |
| Langmuir model | $q_m$ (mg $g^{-1}$) | 30.2018 | 36.7888 | 70.0183 | 89.8783 |
| | $b$ (l $mg^{-1}$) | 0.0934 | 0.0847 | 0.0531 | 0.0926 |
| | $R^2$ | 0.9962 | 0.9944 | 0.9964 | 0.9936 |
| | $R_s$ | 0.1764 | 0.1910 | 0.2736 | 0.1776 |
| | $E_{bio.}$ (%) | 94.460 | 95.180 | 97.440 | 98.460 |
| Reddlich–Peterson model | $A_R$ (l $mg^{-1}$) | 31.9738 | 3.1183 | 31.9738 | 8.6582 |
| | $B_R$ (l $mg^{-1})^{m}{}_R$ | 1.3667 | 0.0848 | 1.3667 | 0.1164 |
| | $m_R$ | 5.0575 | 0.9999 | 5.0575 | 0.9428 |
| | $R^2$ | 0.9958 | 0.9942 | 0.9962 | 0.99350 |
| Combination of Langnuir–Freundlich model | $q_m$ (mg $g^{-1}$) | 50.4829 | 39.9486 | 236.1165 | 96.8383 |
| | $b$ (l $mg^{-1})^{1/n}$ | 0.0842 | 0.0873 | 0.0219 | 0.0889 |
| | $n_F$ | 1.5099 | 1.0919 | 1.4386 | 1.0527 |
| | $R^2$ | 0.9960 | 0.9944 | 0.9964 | 0.9936 |

($R^2$ = 0.9962). With respect to lead onto live and dead microorganisms the Langmuir and combination of Langmuir- Frendlich models gives the best fit; ($R^2$ = 0.9944, 0.9936) respectively. Aksu and Yener [28] investigated the adsorption phenomena of phenol and *o*-chlorophenol onto dried activated sludge (dead microorganisms) using Langmuir and Freundlich models. They found that, the adsorption equilibrium data fitted very well with to both the models in the studied concentration of 100 mg $l^{-1}$ for both pollutants [28]. The maximum biosorbed amount ($q_m$) for $Pb^{+2}$ is greater than that for Ph onto both live and dead microorganisms. $q_{m,Pb}^{+2}$ = 89.8783 and 36.7888 mg $g^{-1}$ and $q_{m,Ph}$ = 70.0183 and 30.2018 mg $g^{-1}$ onto dead and live microorganisms respectively. At the same time, the adsorption percentage efficiency for lead is greater than for phenol. This behavior can be explained as:

(a) Most of functional groups are negative. The affinity between lead cation ($Pb^{+2}$) and these groups are more than for negative phenol [29].
(b) 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 live and dead microorganisms [30].

The difference in maximum bisorption uptake ($\Delta q_m$ = 39.817 and 52.8413 mg $g^{-1}$) for phenol and lead onto live and dead microorganisms respectively. This is because, these pollutants (Ph and $Pb^{+2}$) are toxicants to live microorganisms. They may kill a part and consequently reduced their activity, therefore dead microorganisms was found be more efficient in biosorption capacity.

*5.2.2. Biosorption isotherms constants for binary component systems*

The biosorption isotherms for binary component systems of Ph and $Pb^{2+}$ onto live and dead microorganisms are shown in Figs. 4–7 respectively, whereas Table 5 represents the parameters of each used model and their correlation coefficient ($R^2$).

From the above figures and table, It is clear that: the extended Langmuir and Reddlich–Peterson models seems to give the best fitting ($R^2$ = 0.9987) for the experimental data for phenol biosorption onto live microorganisms, while onto dead microorganisms, the extended Langmuir model give highest value of ($R^2$ = 0.9973). For lead biosorbed onto live microorganisms, the extended Langmuir and combination of Langmuir–Freundlich are the best fit models. However onto dead microorganisms, the Extended Langmuir and Reddlich–Peterson are the most fitting models. Aksu and Akpınar [13] applied extended Langmuir, extended Freundlich and Redlich–Peterson models to describe the competitive adsorption

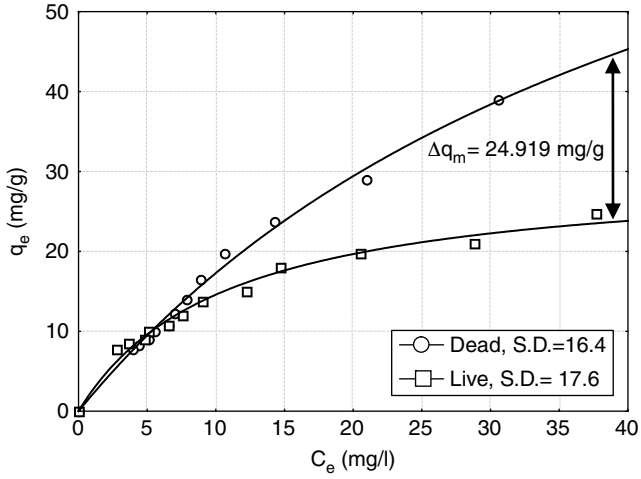


Fig. 4. Biosorption isotherm of phenol onto dead and live microorganisms in binary system.

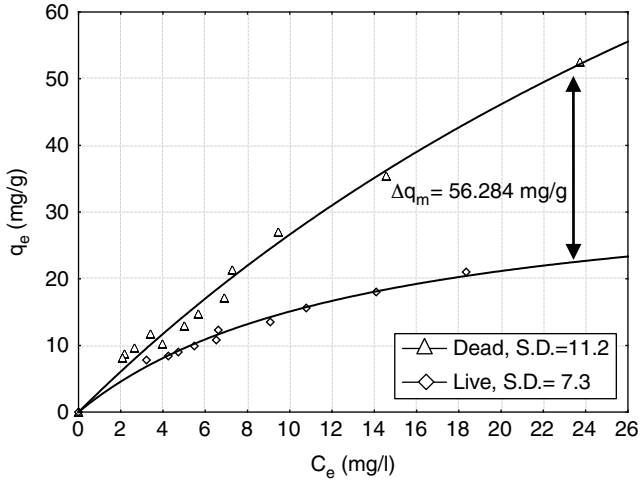


Fig. 5. Biosorption isotherm of lead onto dead and live microorganisms in binary systems.

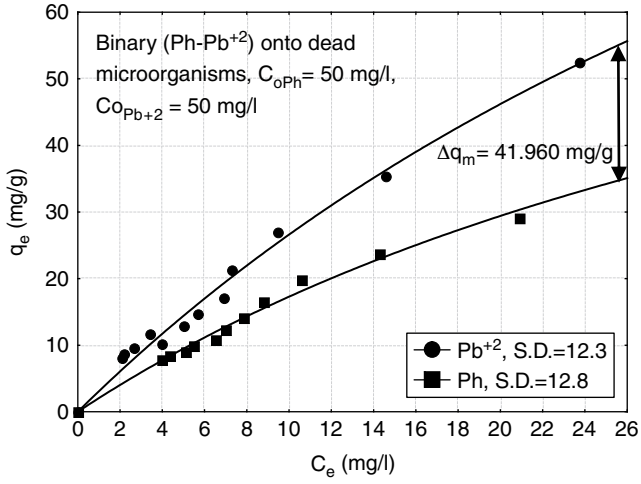


Fig. 6. Biosorption isotherm of (Ph-$Pb^{+2}$) onto dead microorganisms in binary system.

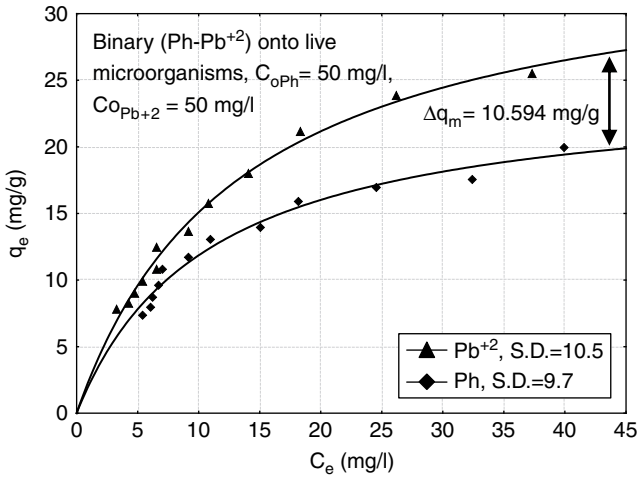


Fig. 7. Biosorption isotherm of (Ph-$Pb^{+2}$) onto live microorganisms in binary system.

of phenol and nickel onto dried activated sludge. They found that, the experimental data fitted very well to the Redlich–Peterson model [13].

The behavior of the equilibrium isotherms for all the binary systems are of a favorable type. The $q_m$ values and the biosorption efficiency for the binary systems are less than those in single systems due to competition between the solutes. There is a weak competition in binary systems in the biosorption capacity of lead, whereas the uptake of phenol is very much reduced by the presence of lead solute due to higher affinity between lead and biosorption sites.

### 5.3. Desorption and regeneration studies

The desorption efficiencies of desorbing eluants under batch experimental conditions for live and dead microorganisms are shown in Table 6 and Figs. 8–11. The average equilibrium concentration ($C_e$) was found to be 2.77, 1.285, 2.41 and 0.865 mg $l^{-1}$ for phenol and lead onto live and dead microorganisms respectively.

It is clear from the Figs. 10 and 11 and Table 6 that the eluation tendency as a percentage recovery of phenol followed the sequence as:

$Na_2CO_3$ > NaOH > EDTA > $H_2SO_4$ > HCL > DDW

This observed trend may be due to formation of ions. Phenoxide ions have more energy than phenol itself due to no charge separation in the canonical structures as well as having negative charge on the more electronegative element, oxygen. Thus the ion is more stable in water. Therefore, it is expected that the adsorbed phenol should be eluated more easily with alkaline eluants than with acidic and DDW eluants. Acidic eluants can protonate the oxygen of phenol but the ion formed is less

Table 5
Parameters of a binary solute isotherm for Ph and $Pb^{+2}$ onto live and dead microorganisms

| Model | Parameters | Live | | Dead | |
|---|---|---|---|---|---|
| | | Ph | $Pb^{+2}$ | Ph | $Pb^{+2}$ |
| Extended Langmuir model | $q_m$ (mg $g^{-1}$) | 16.5571 | 27.1508 | 41.4758 | 83.4349 |
| | $b$ (l $mg^{-1}$) | 0.1457 | 0.0790 | 0.0529 | 0.0830 |
| | $R^2$ | 0.9987 | 0.9971 | 0.9973 | 0.9962 |
| | $R_s$ | 0.1207 | 0.2020 | 0.2743 | 0.9142 |
| | $E_{ad./bio.}$ (%) | 89.064 | 93.488 | 92.020 | 95.780 |
| Combination of Langnuir–Freundlich model | $q_m$ (mg $g^{-1}$) | 0.03416 | 35.6098 | $2.8709\times 10^{16}$ | 12.8560 |
| | $b$ (l $mg^{-1})^{1/n}$ | 95.6526 | 14.0359 | 4.8381 | 4.3793 |
| | $n_F$ | $9.7332 \times 10^4$ | 1.0039 | 1.4916 | 0.0833 |
| | $R^2$ | 0.9703 | 0.9971 | 0.9877 | 0.7979 |
| Reddlich–Peterson model | $K_R$ (l $mg^{-1}$) | 13.3332 | 11.2354 | 3.1773 | 2.4367 |
| | $b_R$ (l $mg^{-1})^{m}{}_R$ | 0.1086 | 13.7829 | 0.0126 | 11.4763 |
| | $m_R$ | 1.0124 | 0.7116 | 0.4433 | 0.1004 |
| | $R^2$ | 0.9987 | 0.9944 | 0.9904 | 0.9962 |
| Extended Freundlich model | $K_F$ (mg $g^{-1}$)(l $mg^{-1})^{1/n}{}_F$ | 0.07175 | 66.0430 | 12.1540 | 66.0430 |
| | $n_F$ | 0.1683 | 0.7754 | 0.1369 | 0.7754 |
| | $b$ | 4.0344 | 0.1160 | 4.0344 | 0.1160 |
| | $R^2$ | 0.9895 | 0.9921 | 0.9895 | 0.9921 |

Table 6
Desorption efficiency of the different eluants

| Desorption of $Pb^{+2}$ from dead microorganisms $V_e$ = 50 ml $C_{bio.}$ = 49.135 mg/l | | Desorption of $Pb^{+2}$ from live microorganisms $V_e$ = 50 ml $C_{bio.}$ = 47.590 mg/l | | Desorption of Ph from dead microorganisms $V_e$ = 50 ml $C_{bio.}$ = 48.715 mg/l | | Desorption of Ph from live microorganisms $V_e$ = 50 ml $C_{bio.}$ = 47.230 mg/l | | Eluant (0.1 M) |
|---|---|---|---|---|---|---|---|---|
| $E_{d.}$(%) | $C_{d.}$(mg/l) | $E_{d.}$(%) | $C_{d.}$(mg/l) | $E_{d.}$(%) | $C_{d.}$(mg/l) | $E_{d.}$(%) | $C_{d.}$(mg/l) | |
| 96.632 | 94.960 | 84.405 | 80.146 | 6.980 | 6.801 | 2.362 | 2.231 | HCl |
| 75.561 | 74.254 | 63.376 | 60.321 | 8.570 | 8.350 | 5.634 | 5.322 | $H_2SO_4$ |
| 20.240 | 19.890 | 8.812 | 8.387 | 90.251 | 87.932 | 74.354 | 70.235 | NaOH |
| 85.869 | 84.383 | 79.588 | 70.752 | 95.352 | 92.901 | 85.974 | 81.211 | $Na_2CO_3$ |
| 94.382 | 92.749 | 80.096 | 76.235 | 90.002 | 87.689 | 72.233 | 68.324 | EDTA |
| 10.641 | 10.458 | 3.839 | 3.652 | 5.640 | 5.495 | 1.282 | 1.211 | DDW |

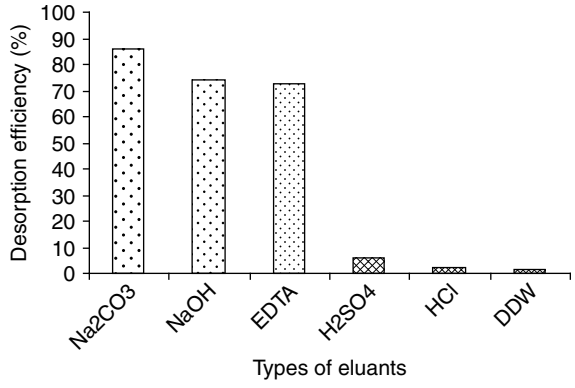


Fig. 8. Desorption efficiency of Ph from live microorganisms.

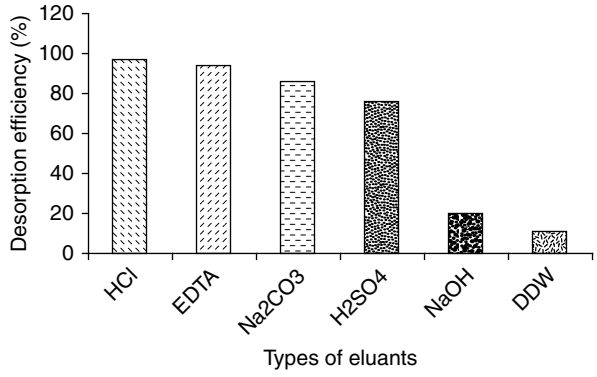


Fig. 10. Desorption efficiency of $Pb^{+2}$ from live microorganisms.

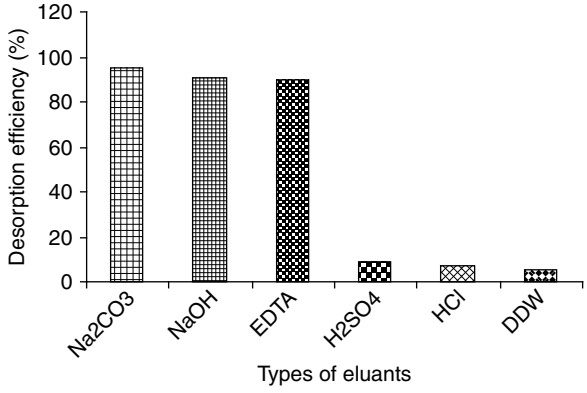


Fig. 9. Desorption efficiency of Ph from dead microorganisms.

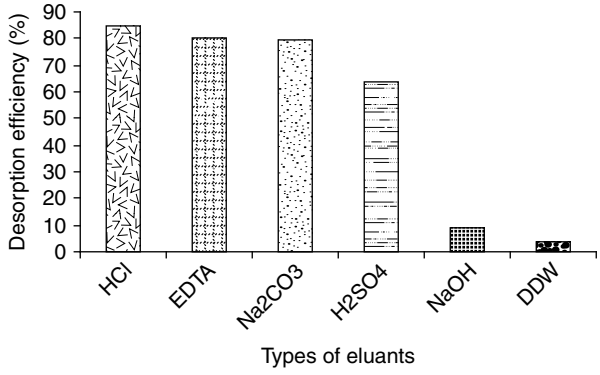


Fig. 11. Desorption efficiency of $Pb^{+2}$ from dead microorganisms.

stable in due to charge separation in the canonical structures and positive charge on the electronegative element (oxygen). A similar conclusion was given by Qadeer and Akhtar [31] in desorption of phenol from activated carbon. The eluation of adsorbed phenol was carried out by DW, NaOH and HCl with the following efficiency [31]:

0.5M NaOH (99%) > 0.1M HCl (12%) > DW (6 %)

However, for lead the process is reverse and followed the following sequence:

HCl > EDTA > $Na_2CO_3$ > $H_2SO_4$ > NaOH > DDW

The desorping efficiency of phenol and lead by $Na_2CO_3$ and HCl from dead microorganisms are more significantly higher than that form live microorganisms.

Alpat et al. [32] evaluate the efficiency of desorbing elutants of 0.1 M of HCl, $HNO_3$, $NaNO_3$, EDTA solutions and deionized water in desorption process of $Ni^{+2}$ (similar metal ion to $Pb^{+2}$) from *Circinella* sp. (type of fungi) biosorbent with the following consequence [32]:

HCl (100%) = EDTA > HNO3 (93%) > NaNO3 (16%) > DW (1.550%).

## 6. Conclusions

Cheaply available anaerobic sludge can be used as an efficient biosorbent material source for both live and dead heterogeneous microorganism for removal of single phenol, single lead (II) and binary phenol–lead (II) mixtures from wastewaters. The biosorption equilibrium of these systems can be defined mathematically with proposed biosorption 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. This study demonstrated that the binding capacity and desorbing efficiency of dead microorganisms are significantly higher than that of live microorganisms at the same tested conditions.

## Symbol

$A_R$ — Reddlich–Peterson model parameter, l $mg^{-1}$
AAS — Atomic Absorption Spectrophotometer
$B_R$ — Reddlich–Peterson model parameter, $(l\ mg^{-1})^{m}{}_{R}$
$B$ — Langmuir adsorption constant related to the affinity to binding sites, l $mg^{-1}$
$b_{RK}$ — Redlich–Peterson model parameter derived from the corresponding individual isotherm equations $(l\ mg^{-1})^{m}{}_{R}$
$b_i$ — Individual Langmuir adsorption constant of each component, l $mg^{-1}$
$C_o$ — Equilibrium concentration, mg $l^{-1}$
$C_e$ — Equilibrium concentration, mg $l^{-1}$
CEC — Cation Exchange Capacity, meq 100 $g^{-1}$
$C_{d.}$ — Desorbed concentration, mg $l^{-1}$
$C_{bio.}$ — Biosorbed concentration, mg $l^{-1}$
DDW — Deionized Distilled Water
$E_{bio}$ — Adsorption/biosorption efficiency, %
EDTA — Ethylene Diamine Tetra acetic Acid
GC — Gas Chromatography
$HNO_3$ — Nitric acid
$H_2SO_4$ — Sulphoric acid
HCl — Hydrochloric acid
i — Component number (1,2, …)
$K_F$ — Freundlich adsorption constant, related to adsorption intensity, $(mg\ g^{-1})(mg\ l^{-1})^{1/nF}$
$K_{Fi}$ — Individual Freundlich adsorption constant of each component, $(mg\ g^{-1})(mg\ l^{-1})^{1/nF}$
$K_{Ri}$ — Individual Redlich–Peterson adsorption constant of each component, $(l\ mg^{-1})$
$m_{Ri}$ — Reddlich–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
$Na_2CO_3$ — Sodium carbonate
Ph — Phenol
$Pb^{+2}$ — Lead
$q_{eq}$ — Biosorbed phenol/lead quantity per gram of biosorbent at equilibrium, mg $g^{-1}$
$q_m$ — Langmuir adsorption constant of the pollutants shows the maximum amount of pollutants bound to the live/dead microorganisms, or maximum uptake capacity mg $g^{-1}$
$q_{ei}$ — Amount of adsorbate adsorbed per mass of adsorbent of component i, mg $g^{-1}$
$q_{mi}$ — Individual Langmuir adsorption constant of each component, mg $g^{-1}$
$R^2$ — Correlation coefficient, %
S.D. — Standard Deviation
$V_L$ — Volume of solution, l
$V_e$ — Volume of eluant, l
$W$ — Mass of biosorbent, g

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