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Biosorption of Naphthalene from Refinery Simulated Waste-Water on Blank Alginate Beads and Immobilized Dead Algal Cells

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Abstract: The potential use of blank alginate beads and immobilized dead algal cells for the removal of naphthalene from aqueous solutions was investigated in this study. The effects of contact time, solution pH, and naphthalene concentration on the sorption of naphthalene on blank alginate beads or immobilized dead algal cells were studied. The effect of the presence of other pollutants on the sorption of naphthalene on immobilized dead algal cells was also studied.

Batch adsorption experiments showed that the removal of naphthalene on both sorbents was pH dependent and significant removal of naphthalene was obtained at pH 4. Dynamic sorption experiments revealed that the biosorption of naphthalene on either sorbent was rapid where the equilibrium uptake occurred within 10 minutes, and the biosorption of naphthalene on either sorbent followed the pseudo-second order kinetics. Analysis of the equilibrium sorption data showed that naphthalene sorption on either sorbent could be fitted to the Langmuir, Freundlich, and Dubinin-Radushkevich (D–R) isotherm equations. Competitive biosorption experiments showed that biosorption of naphthalene on immobilized dead algal cells was adversely affected by the presence of either heavy metals such as copper and nickel, and chelating agents such as citric acid.

Keywords: Biosorption; Immobilized dead algal cells; Isotherms; Naphthalene

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INTRODUCTION

Refineries and surface petroleum operations are potential major contributors to ground water and surface water contamination. Some refineries use deep-injection wells to dispose of wastewater generated inside the plants, and some of these wastes end up in aquifers and groundwater. Wastewater in refineries may be highly contaminated given the number of sources it can come into contact with during the refinery process (such as equipment leaks and spills and the desalting of crude oil). This contaminated water may be process wastewaters from desalting, water from cooling towers, stormwater, distillation, or cracking. It may contain oil residuals and many other hazardous compounds. This water is recycled through many stages during the refining process and goes through several treatment processes, including a wastewater treatment plant, before being released into surface waters (1).

Naphthalene is a poly aromatic hydrocarbon (PAH) that has many industrial uses and is a major component encountered by the coal and tar-based industries. It has been detected in soil, oil contaminated sediments, and both industrial and urban wastewater. Naphthalene has also occasionally been isolated as contaminant at waste sites and was classified as a priority pollutant by the U.S. Environmental Protection Agency (2). To protect aquatic life, the permissible concentrations of naphthalene are 2.3 and 0.6 mg/l on acute and chronic toxicity, respectively. Naphthalene is moderately toxic by subcutaneous route, and poisoning of naphthalene may occur by ingestion of large doses, inhalation, or skin absorption (3). Biological degradation (2, 4), adsorption (5,6) and chemical oxidation (7) are the most widely used methods of removing naphthalene from wastewater.

Biosorption, which involves the use of biomass or natural substances as adsorbents, has proved to be an attractive alternative to traditional physicochemical means for removing pollutants, e.g., toxic heavy metal, from wastewaters. Living or dead algal cells are being increasingly considered as biosorbents to remove heavy metals from aqueous solutions (8–15). However, using dead cells eliminates the possibility of metal toxicity limitations, the need for growth media and repeated use of cells will be easier. These biosorbents are usually used in powder form, which creates practical problems when used in continuous processes since separation of this powder after contact with water will be difficult. Cell immobilization, which involves localization or confining the cells on suitable natural or synthetic materials support, introduces an attractive technique to fix and retain the cells inside the treatment unit (13). The main advantages of this technique include: improved biomass performance and biosorption capacity, increased mechanical strength, and the

ease of biomass separation from pollutant bearing solutions (13). Alginate biopolymer has been used extensively in cell immobilization studies. Its advantages include ease of preparation, biocompatibility and capability to retain cells by entrapment in its matrix fine pores.

In this study, the sorption of naphthalene on either blank alginate beads or immobilized algal cells is investigated. The effects of different parameters, such as solution pH, shaking time, and naphthalene concentration on the sorption capacity will be studied. The Langmuir, Freundlich, and Dubinin–Radushkevich isotherm models will be used to fit the sorption of naphthalene on the either sorbent. Dynamics studies of the sorption process will be investigated using Weber and Morris equation. The competitive adsorption of naphthalene with other pollutants on the algal cells will also be investigated.

EXPERIMENTAL

Chemicals

A stock solution of 30 ppm naphthalene was prepared with 1.0 g of powdered naphthalene (Merck) in a 2-liter conical flask that was filled with deionized water. The stock solution was mixed and stirred for 24 h to achieve the maximum solubility of naphthalene in water at room temperature. 0.1 N of hydrochloric acid (HCl) and sodium hydroxide (NaOH) were used to adjust the initial pH of the solution.

Preparation of Biosorbent

Immobilized algal cells were prepared by entrapping powdered green alga *Chlorella vulgaris* cells (Watershed, USA) in an alginate matrix produced by ionic polymerization in calcium chloride solution, according to the following procedures (13): the powdered algal cells were suspended in a 2% sodium alginate (BDH, UK) solution kept at a temperature of 60°C. The mixture was then dropped into a 2% calcium chloride (BDH, UK) solution using a peristaltic pump. The drops of Na-alginate solution gelled into 3.5 ± 0.1 mm diameter beads upon contact with calcium chloride solution. The beads were washed well and then rinsed in deionized water and stored at 4°C.

Determination of Functional Groups

The functional acidic groups on the prepared algal cells were determined using Boehm's titration method (11): 1.0 g of powdered algal cells was

Table 1. The functional groups on the Algal cells

Functional group	Meq H^+/g algae
Carboxyl	0.02
Lactones and Lactols	0.01
Phenols	0.035

dispersed in 50 ml of deionized water. The suspension was mixed with 0.1 N solutions of sodium bicarbonate, sodium carbonate, and sodium hydroxide, and then shaken for 48 h at room temperature. After this time, the sample was left for 6 h so that particles could settle. The sample was then filtered and 10 ml of filtrate were titrated with 0.1 N volumetric HCl standard using methyl red as the indicator. According to Boehm's titration method, sodium bicarbonate can neutralize carboxyl groups, sodium carbonate can neutralize carboxyl, lactones and lactols groups, and sodium hydroxide can neutralize carboxyl, lactones, lactols, and phenols groups. Table 1 lists the different functional groups available on algal cells.

Equilibrium Adsorption Isotherm

Batch sorption experiments were conducted in 100 ml bottles by mixing 50 ml of naphthalene solution with the desired concentration and amount of sorbent. Different naphthalene initial concentrations were used (5–30 ppm). The mixtures in these bottles were agitated for a predetermined time in a shaker at 25°C. The naphthalene solution was then separated from the sorbent and the concentration of naphthalene was determined using UV spectrophotometer at wavelength of 273 nm for naphthalene. The naphthalene uptake, which represents the amount sorbate sorbed per unit mass of sorbent, was calculated using the following mass balance relationship:

$$\mathrm{Qe} = \frac{(\mathrm{Co} - \mathrm{Ce})\mathrm{V}}{\mathrm{W}} \tag{1}$$

Where Q_e is the uptake (mg/g) at equilibrium, C_o the initial concentration sorbate (mg/ml), C_e the concentration at equilibrium (mg/ml), V the initial volume of solutions, and W is the mass of sorbent (g).

Adsorption Dynamics

The dynamic studies were carried out by conducting batch biosorption experiments with 24 ppm of naphthalene at pH 4.0. Samples were taken at different time periods and analyzed for naphthalene concentrations.

Competitive Biosorption

The competitive biosorption naphthalene with nickel, copper, sodium chloride, and citric acid has been investigated. The studies involved experiments with constant naphthalene concentration and varying other metals and chelating agents concentrations (50–250 ppm).

All the experiments have been conducted at 25°C using the same procedures used in the single adsorption experiments, and were carried out in triplicate.

RESULTS AND DISCUSSION

Effect of pH on Naphthalene Biosorption

The uptake of naphthalene by immobilized dead algal cells is profoundly affected by the pH of the sorption system. This is mainly due to the biosorption mechanisms that reflect the nature of the physico-chemical interactions between the sorbate and the cell adsorptive sites. The solution chemistry of different types of sorbates may also play an important role as the pH of the sorption system changes (12–14). The solubility of naphthalene is affected by pH as is the ionization state of biomass functional groups (carboxyl, phenol, lactones) of the immobilized algal cells. The effect of pH on the sorption uptake of naphthalene on immobilized algal cells is shown in Figs. 1 and 2. These figures reveal that the maximum naphthalene uptake was observed at pH 4.0. This is due to the fact that at pH below 4.0, the overall surface charge on the cells becomes positive (11–14) with exponentially increasing concentration of protons in the solution which compete for carboxyl and carbonyl sites, reducing thus the uptake of other cationic species at low pH values. The naphthalene uptake increase at higher pH is due to the nature of the specific interaction between naphthalene and active sites of algal cells; the aromatic solutes adsorb onto algal cell by electrostatic interactions and by weak attraction (Van der Waals forces) between naphthalene aromatic rings and carbon-oxygen complexes in the algal biomass.

Effect of Contact Time and Dynamics of Naphthalene Biosorption

The effect of contact time on the biosorption of naphthalene on immobilized dead algal cell and blank alginate beads was investigated by determining the uptake of naphthalene at different time intervals (3–120 min) using 0.3 g of algal cells. Figure 3 depicts the variation of naphthalene uptake versus time. In the first 10 minutes, the uptake of naphthalene

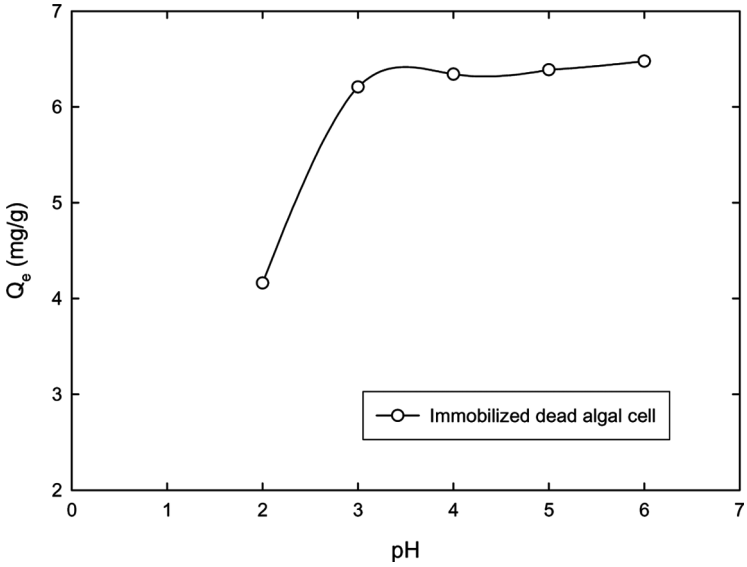

Figure 1. The naphthalene uptake versus pH (initial naphthalene concentration = 24 ppm, mass of algal cells = 0.15 g).

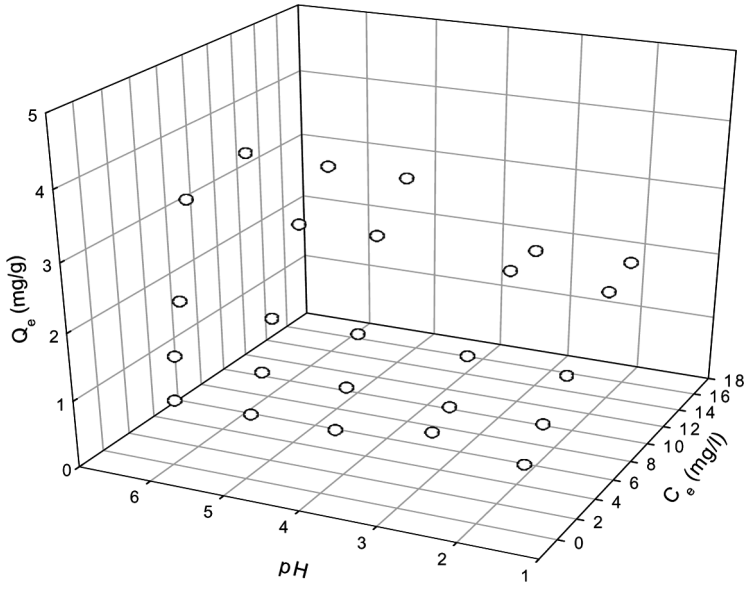

Figure 2. Effect of pH on naphthalene removal (mass of algal cells = 0.3 g).

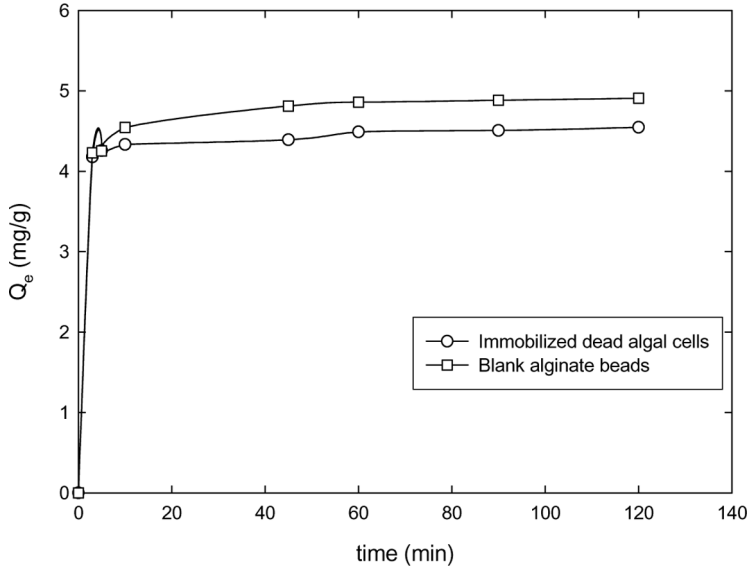

Figure 3. The naphthalene uptake versus time (initial naphthalene concentration = 24 ppm, pH = 4.0, mass of algal cells = 0.3).

increased rapidly and linearly with increasing time, about 90% of the naphthalene was removed in this time. However, to ensure adequate equilibrium time, the experiments were run for 120 min.

The dynamic behavior of the given experimental sorption system corresponds to the pseudo-second order kinetics as suggested by Ho and Mckay (16,17). It is based on the sorption capacity of the sorbent and is given by:

$$\frac{dQ_t}{dt} = k_{2,ads}(Q_e - Q_t)^2 \tag{2}$$

An integrated pseudo-second order rate law can be obtained from equation (2) for the boundary conditions $t = 0$ to $t = t$ and $Q_t = 0$ to $Q_t = Q_t$, and is given by:

$$\frac{1}{(Q_e - Q_t)} = \frac{1}{Q_e} + kt \tag{3}$$

Equation (3) can be rearranged to obtain a linear form:

$$\frac{t}{Q_t} = \frac{t}{Q_e} + \frac{1}{Q_e^2 k} \tag{4}$$

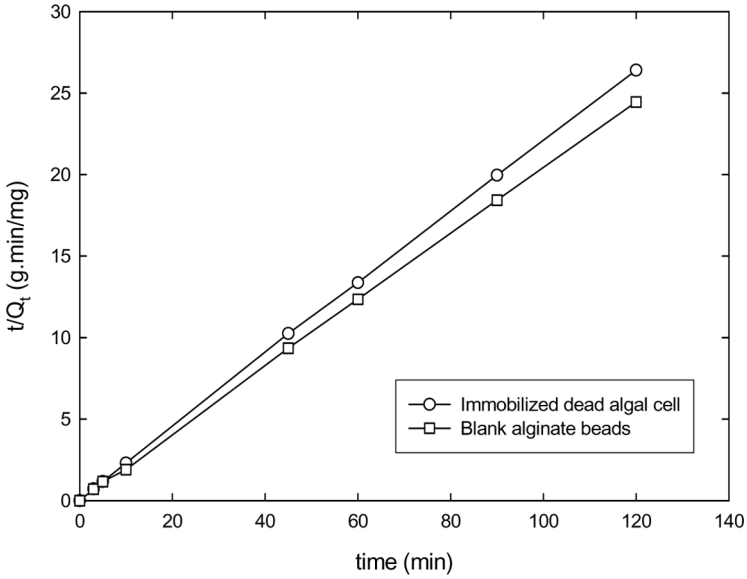

Figure 4. Kinetics of biosorption of naphthalene: pseudo-second order kinetics (mass of algal cell = 0.3 g, initial naphthalene concentration = 24 ppm, T = 25°C, pH = 4.0).

where Q_e is the amount of sorbate sorbed at equilibrium (mg g^{-1}); t is the reaction time (min); Q_t is the amount of sorbate sorbed at time t (mg g^{-1}); k is the equilibrium rate constant of pseudo-second order sorption (g mg^{-1} min^{-1}). Based on Equation (4), the plot of t/Q_t versus t should result in a straight line with slope $1/Q_e$ and intercept $1/kQ_e^2$. Figure 4 demonstrates the sorption dynamics for 24 ppm naphthalene solutions, the results are summarized in Table 2. The relationships between t/Q_t versus t for naphthalene were linear with R^2 value for the pseudo-second order for naphthalene of 0.99. These results proved that the biosorption dynamics for naphthalene is pseudo-second order (Eq. (4)).

The contribution of intraparticle diffusion mechanism can be tested applying the Weber and Morris equation (18):

$$Q_t = k_d \; t^{0.5} \tag{5}$$

where k_d is the rate constant of intraparticle diffusion. According to the Weber and Morris equation for intraparticle diffusion mechanism, the plot of Q_t vs. $t^{0.5}$ should be linear. Figure 5 is the plot of Q_t versus $t^{0.5}$ that confirms the validity of the linear relationship. The results can be represented by such a linear relationship but they do not pass through

Table 2. Kinetic parameters for the biosorption of naphthalene on immobilized dead algal cells and blank alginate beads

	Pseudo-second order kinetics parameters		
Biosorbent	$k_{2,ads}$ (g/mg · min)	Q_e (mg/g)	R^2
Immobilized dead algal cells	0.46	4.54	0.99
Blank alginate beads	0.23	4.92	0.99

the origin. This indicates that intraparticle diffusion is involved in the sorption process but it is not the only rate-limiting mechanism and that some other mechanisms are involved.

Biosorption Isotherm

The relationship between the equilibrium concentration of naphthalene and the biosorption capacity of immobilized dead algal cells is displayed in Fig. 6. This figure reveals that the uptake significantly increased with the equilibrium naphthalene concentration. The maximum sorption capacity of the immobilized dead algal cells for naphthalene was 3.97 mg/g at pH 4.0. The equilibrium concentration provides an important driving force to overcome all naphthalene mass transfer resistances between the aqueous

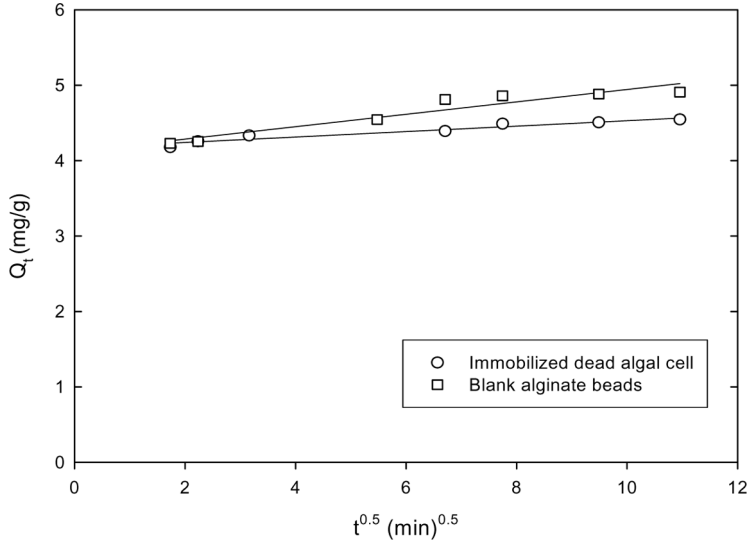

Figure 5. Application of the Weber–Morris equation for the sorption of naphthalene.

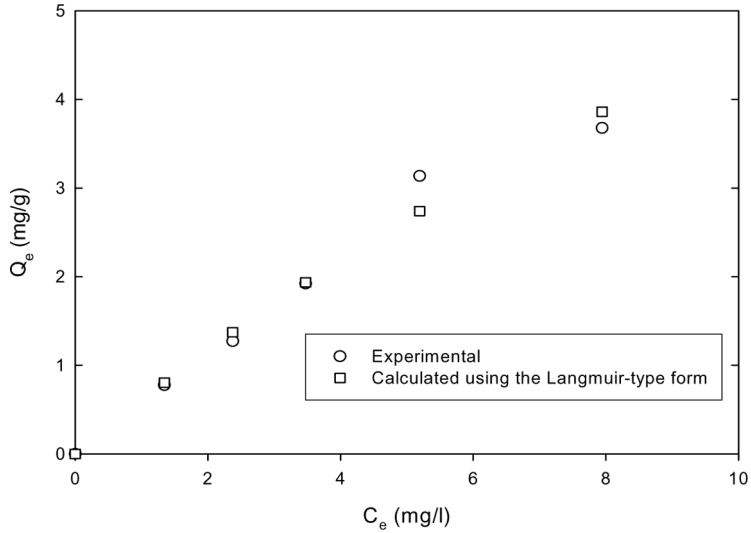

Figure 6. Experimental isotherms of naphthalene sorbed on immobilized algal cells (pH = 4.0, mass of algal cell = 0.3 g).

and solid phases. Hence a higher equilibrium concentration of naphthalene enhances the sorption process (13). The high sorption capacity of the immobilized dead algal cells was due to the highly active functional groups such as carboxyl. Different sorbent materials with a wide range of adsorption capacities for naphthalene compounds have been studied. Table 3 shows a comparison between the adsorption capacity of these sorbents and the results of this study.

Different isotherm models were used in this study to describe the sorption isotherm relationship for the given experimental system with naphthalene.

Table 3. Adsorption capacities for naphthalene using different sorbents

Adsorbent	Adsorption capacity (mmol/g)	Reference
Kaolinite	1.28	Lee and Kim, 2002
Halloysite	1.73	Lee and Kim, 2002
Zeolite	0.17	Chang et al., 2004
Immobilized dead algal cells Chlorella vulgaris	0.041	This study

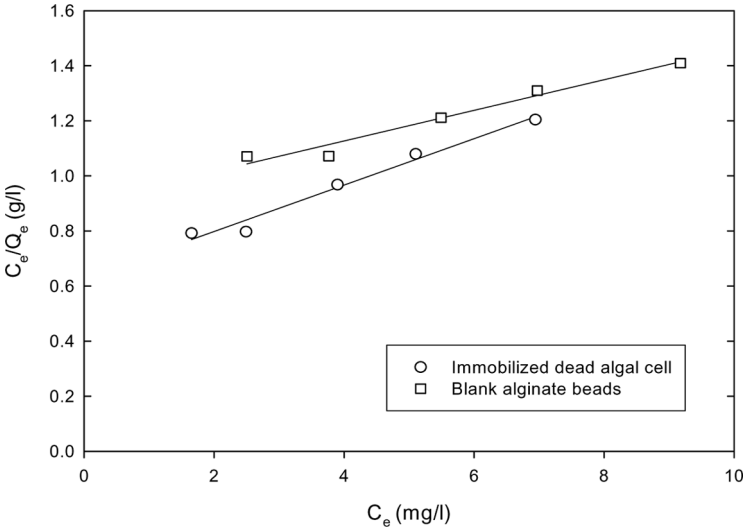

Figure 7. Langmuir isotherms of naphthalene sorbed on different sorbents (mass of algal cells = 0.3 g, pH = 4.0).

The Langmuir isotherm is one of the most commonly used models:

$$Q = Q_{\max} \frac{bC_e}{1 + bC_e} \tag{6}$$

where $Q_{\max}$ is the maximum sorbate uptake under the given conditions, b is a coefficient related to the affinity between the sorbent and sorbate. The sorption data were analyzed according to the linear form of Langmuir isotherm and the linear plots are shown in Fig. 7 for naphthalene. The corresponding values of the model parameters are listed in Table 4. The Langmuir isotherm provides an excellent fit for naphthalene since the correlation coefficient R^2 was 0.96 for blank alginate beads and 0.97 for immobilized dead algal celsl. It should be noticed that saturation was not attained in the case of naphthalene due to solubility limitations; the maximum initial concentration of naphthalene used was 30 ppm.

Composite Fractional Error Function (CFEF) was used as a non-linear error function to determine the Langmuir parameters and is given by (19)

$$\text{CFEF} = \min \sum_{i=1}^{P} \left[\frac{(Q_{e,\exp} - Q_{e,\text{cal}})^2}{Q_{e,\exp}} \right]_I \tag{7}$$

The Langmuir isotherm constants were consistent and close to those established by linear regression. The values of the non-linear objective

Table 4. Adsorption of linear isotherms parameters for the sorption of naphthalene by blank alginate beads and immobilized algal cells

Model	Parameter	Blank alginate beads	Immobilized algal cells
Freundlich	K $(l/mg)^{1/n}$ (mg/g)	1.19	2.2
	n	1.29	1.67
	R^2	0.99	0.98
Langmuir	Q_m (mg/g)	17.98	11.87
	b (l/mg)	0.061	0.13
	R^2	0.97	0.96
D–R	Q_D(mmol/g)	2.37	2.33
	B_D $(l/J^2 \cdot mol^2)$	$6.1 * 10^{-9}$	$6.0 * 10^{-9}$
	E (kJ/mole)	9.12	9.05
	R^2	0.99	0.96

functions are shown in Table 4. The effect of pH on naphthalene biosorption by immobilized dead algal cells can be modeled using the Langmuir-type model (12):

$$Q_e = \frac{Q_c(pH)\beta C_e}{1 + \beta C_e} \tag{8}$$

This model incorporates the effect of pH on biosorption via the monolayer sorption capacity. The results shown in Fig. 2 suggest that the dependency of monolayer sorption capacity on pH can be simulated using the exponential form:

$$Q_c = A_1 e^{A_2 pH} \tag{9}$$

The isotherm experimental data at different equilibrium pH values were fitted by CFEF non-linear regression to evaluate the adjustable parameters of equations (8) and (9), and the results obtained were: $A_1 = 0.15\,mg/g$, $A_2 = 0.84$, $\beta = 0.037 l/mg$. These parameters were used to calculate the uptake of naphthalene by immobilized dead algal cells at pH 4.0 as shown in Fig. 6 which indicates that the proposed model could fit the experimental data well.

The Freundlich equation is one of the earliest empirical equations used to describe sorption equilibrium data. It does not indicate a finite uptake capacity of the sorbent and can thus be reasonably applied in the low to intermediate concentrations ranges. The Freundlich isotherm model is given by the equation

$$Q_e = KC_e^{1/n} \tag{10}$$

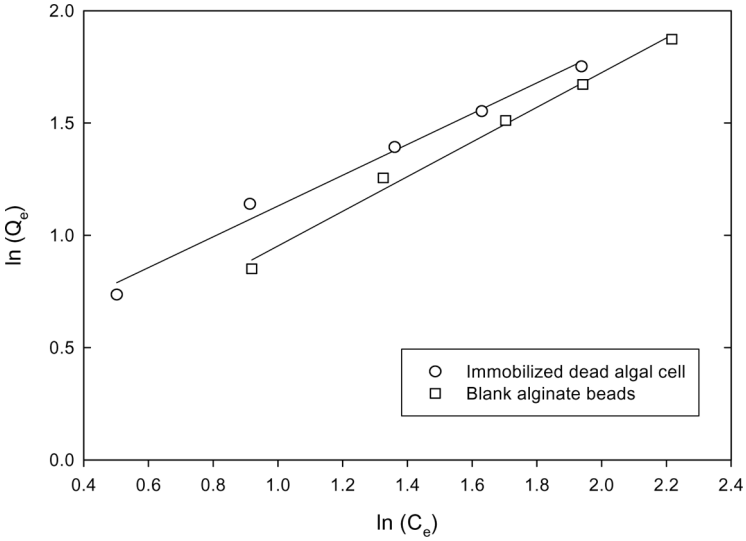

Figure 8. Freundlich isotherms of naphthalene sorbed on different sorbents (mass of algal cell = 0.3 g, pH = 4.0).

where K and n are the Freundlich constants which represent sorption capacity and sorption intensity, respectively. Their values are listed in Table 4. The linearized Freundlich isotherm plots for the sorption of naphthalene onto both blank alginate beads and immobilized dead algal cells are presented in Fig. 8. The fit of the Freundlich equation to the experimental data was good since R^2 for naphthalene was 0.98 for immobilized dead algal cells and 0.99 for blank alginate beads. As noted in Table 4, the values of n were greater than unity, indicating that naphthalene exhibited increased adsorption on immobilized dead algal cells at higher concentrations (20). The Freundlich isotherm constants were also determined by non-linear regression Composite Fractional Error Function (CFEF) as shown in Table 5. The results demonstrate that the values of K and n obtained by non linear regression are remarkably consistent and quite similar to the linear transform values from Table 4.

Another less commonly used model that could be used to describe sorption of naphthalene on immobilized dead algal cells is the Dubinin-Radushkevich (D-R) isotherm relationship. This isotherm is generally expressed as follows (21):

$$Q_e = Q_D e^{\left(-B_D[RT\ln\left(1+\frac{1}{C_e}\right)]^2\right)} \tag{11}$$

The constant, B_D, is related to the mean free energy of sorption per mole of the sorbate as it is transferred to the surface of the solid from infinite

Table 5. Adsorption of non-linear isotherms parameters for the sorption naphthalene by blank alginate beads and immobilized algal cells

Model	Blank alginate beads	Immobilized algal cells
Freundlich: K $(l/mg)^{1/n}$ (mg/g)	1.31	3.21
Freundlich n	1.29	1.09
CFEF	0.19	0.15
Langmuir Q_m (mg/g)	13.87	15.75
Langmuir b (l/mg)	0.10	0.074
CFEF	0.1	0.05

distance in the solution and this energy can be computed using the following relationship (21–23):

$$E = \frac{1}{\sqrt{2B_D}} \tag{12}$$

The experimental data of this study were fitted to these equations and the result is shown in Fig. 9, and the parameters of the model are listed in Table 4. The magnitude of E is useful for estimating the type of adsorption process. Values of E for naphthalene were determined to be 9.05 kJ/mole

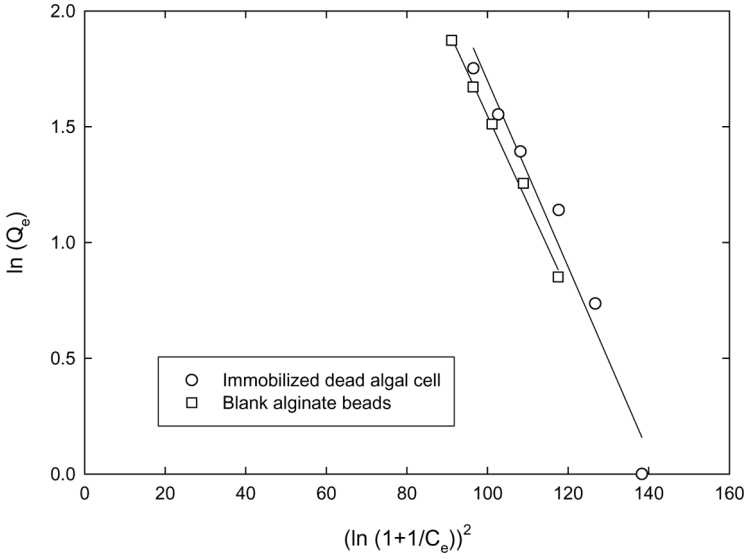

Figure 9. Dubinin–Radushkevich equation isotherm of phenol sorbed on different sorbents (mass of algal cells = 0.024 g, pH = 11.0).

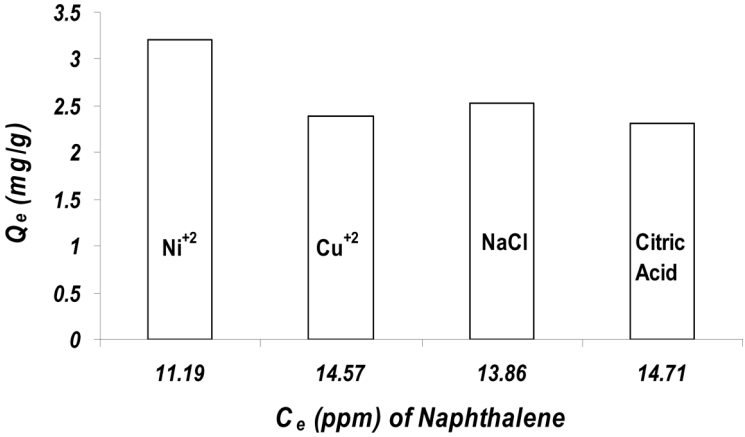

Figure 10. Effect of impurities on naphthalene uptake on immobilized dead algal cells (mass of algal cell = 0.3 g, initial naphthalene concentration = 24 ppm, T = 25°C, pH = 4.0).

for immobilized dead algal cells and 9.12 kJ for blank alginate beads. The range for E values in ion-exchange mechanisms is 8–16 kJ/mole. Thus, ion-exchange appears to have made a major contribution in the adsorption of naphthalene onto immobilized dead algal cells and blank alginate beads.

Competitive of Sorption of Naphthalene with Other Pollutants

The effect of the presence of Cu^{+2}, Ni^{+2}, sodium chloride, and citric acid on naphthalene biosorption on immobilized algal cells is shown in Fig. 10. Figure 10 shows that the uptake of naphthalene seems to decrease significantly with the addition of metals such as nickel and cupper ions, salts, e.g., NaCl, and chelating agent (citric acid). This decrease in the uptake is attributed to the competition of these compounds with naphthalene for the adsorption sites on the surface and that some sites might be occupied by the other component. As a consequence, the first component has a smaller ''parking space'' and its uptake is decreased (24), similar results were obtained by Nollet et al. (25) for the removal of organic materials by fly ash where the interference of ions lead to decrease in the uptake.

CONCLUSIONS

This study proved the technical feasibility of using immobilized algal cells and blank alginate beads to remove naphthalene from simulated refinery wastewater. The batch adsorption experimental results showed that

solution pH played an important role in the sorption capacity of either sorbent. The dynamics studies indicated that the sorption process followed the pseudo-second order kinetics. Equilibrium data of the sorption of naphthalene on either sorbent were fitted to three adsorption isotherm models: Langmuir, Freundlich, and D–R isotherm models; the Freundlich isotherm gave the best fit of the data. The results also revealed that the sorption mechanism of naphthalene on either sorbent involves ion exchange and intraparticle diffusion mechanisms. The presence of metal ions, and chelating agents was found to suppress the biosorption of naphthalene on immobilized dead algal.

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