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Adsorption of zinc from aqueous solution using marine green algae—*Ulva fasciata* sp.

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Abstract

The removal of zinc from aqueous solution by adsorption on *Ulva fasciata* sp. was studied as a function of contact time, pH of the solution, metal ion concentration, adsorbent concentration and adsorbent size. Batch experiments results showed that the adsorptive capacity of *U. fasciata* sp. was 13.5 mg/g of adsorbent. The Langmuir and Freundlich models were used to describe the adsorption equilibrium of zinc on *U. fasciata* sp. and the adsorption followed the Langmuir isotherm. The Langmuir and Freundlich constants for adsorption of zinc on *U. fasciata* sp. were determined. The pseudo first and second order rate expressions were used to correlate the experimental data. The kinetic constants were determined for both the models and the second order rate expression was found to be more suitable.

Keywords: *Ulva fasciata* sp.; Adsorption; Zinc; Equilibrium studies; Kinetic studies

1. Introduction

Metals like Cd, Hg, Pb, Cr, Ni, Cu, Zn, and Co are, at elevated concentrations, detrimental to human health and ecosystem stability, and threshold values have been set for these metals for waste water discharged into natural recipients and for drinking water. WHO and EU recommend in their guidelines for drinking water quality a threshold limit for zinc and WHO finds it unacceptable with more than 3 mg/l zinc in drinking water [1,2]. Runoff water from industries, roads and cities may contain high concentrations of heavy metals. In order to fulfil the threshold criteria and to reduce pollution, contaminated waters need to be cleaned. Common cleaning methods comprise chemical precipitation, ion exchange, electrolysis, membrane filtration, and sorption to metal oxides, clays and organic sorbents. These methods differ with respect to cost, complexity and efficiency [3–6].

Biosorbents are an alternative to conventional methods. The term ‘biosorbent’ includes the usage of dead biomass (such as fibre, peat, and wool) as well as living plants and bacteria as sorbents [3]. Biosorbents represent cheap filter materials often with high affinity and capacity, and they are already available in most places. There are some limitations pertaining to the usage of living organisms as sorbents, e.g., they cannot function at low pH level, or at toxic levels of metal ions, while plant fibres on the contrary are chemically and physically more robust. Biosorption is not restricted to one sorption mechanism only, but comprises several mechanisms such as ion exchange, chelation, precipitation, sorption by physical forces, and ion entrapment in inter- and intrafibrillar capillaries and spaces of the structural lignin and polysaccharide networks [3,7]. Some types of biosorbents are broad range with no specific priority of metal ion bonding, while others can be specific for certain types of metal ions [7].

Plant fibres consist mainly of lignin, cellulose, hemicellulose, and some pectin and extractives (mainly fat, fatty acids, fatty alcohols, phenols, terpenes, steroids, resin acids, rosin and waxes). Metal ions sorb mainly to carboxylic (primarily present in pectin and hemicellulose but also extractives and lignin), phenolic (lignin and extractives) and to some extent hydroxylic (cellulose, hemicellulose, lignin, extractives, and pectin) and carbonyl groups (lignin) [8–10]. Strong bonding of metal ions by the hydroxylic, carboxylic and phenolic groups often involves complexation and ion exchange [3,7].

In many laboratory tests of metal ion sorption to plant fibres, ground fibres have been used [8,11–16]. However, it is possible to form a filter by whole, unground fibres using a simple non-

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woven matforming technology. These mats just need a mesh cassette to be kept in place, and are easily handled and disposed off after use [17].

Most studies of metal ions sorption to plant fibres are based on experiments with metal concentrations in the mg/l range [8,11–16], which frequently exceeds the level of contamination in natural waters.

The objectives of the present investigation were to quantify the adsorption of zinc to unmodified *Ulva fasciata* sp. at relative low concentrations with particular focus on adsorption kinetics, the pH dependence of adsorption, adsorption strength and capacity. Zinc was chosen because it represents rather different types of metal ions with different binding affinities and mechanisms.

2. Materials and methods

2.1. Preparation of adsorbent

The green colored marine algae *U. fasciata* sp. used in the present study was collected from the coastal belt of Visakhapatnam, Andhra Pradesh, India. The collected algae was washed with deionized water several times to remove impurities. The washing process was continued till the wash water contains no dirt. The washed algae was then completely dried in sunlight for 10 days. The resulting product was directly used as adsorbent. The dried algae was then cut into small pieces and was powdered using domestic mixer. In the present study the powdered materials in the range of 75–212 μm particle size were then directly used as adsorbents without any pretreatment.

2.2. Chemical and metal solution

The stock solution of zinc was prepared by dissolving the sulphate salt in distilled water. The test solutions containing single zinc ions were prepared by diluting 1 g/l stock metal ion solution. The initial metal ion concentration ranged from 20 to 100 mg/l. The pH of each solution was adjusted to the required value with HCl or NaOH before mixing the adsorbent.

2.3. Analysis of zinc

The concentration of initial and final zinc in the adsorption experiments was determined by using atomic absorption spectrophotometer (GBC Avanta Ver 1.32, Australia) at a wavelength of 213.9 nm, slit width 0.2 nm and lamp current 5.0 mA.

The results are given as a unit of adsorbed and unadsorbed metal concentrations per gram of adsorbent in solution at equilibrium and calculated by

$$q_e = \frac{(C_o - C_{eq})V}{X} \tag{1}$$

where X is the adsorbent concentration (g/l), q_e the adsorbed metal ion quantity per gram of adsorbent at equilibrium (mg/g), C_0 the initial metal concentration (mg/l), C_{eq} the metal concentration at equilibrium (mg/l) and V is the working solution volume (ml).

2.4. Metal adsorption experiments

Adsorption experiments were conducted at 30 °C in batch with 0.1 g of the *U. fasciata* sp. in a 30 ml of working solution volume. The flasks were then agitated at 180 rpm.

Experiments for determining the kinetics of the process were performed at 20–100 mg/l initial metal concentrations for zinc. Samples were taken at desired intervals and the adsorbent was removed by filtration using Whatman filter paper. The heavy metal concentration in the resulting supernatant was determined. The impact of the solution pH on the metal biosorption was investigated in the same way except that the initial pH of the solutions was adjusted from 2.0 to 10.0 with the addition of either 0.1 M NaOH or 0.1 M HCl.

2.5. Adsorption equilibrium

Equilibrium studies were carried out by agitating 30 ml of zinc solutions of initial concentrations varying from 20 to 100 mg/l with 0.1–0.5 g of algae at room temperature for 20 min at a constant stirring speed at a pH of 5.

During the adsorption, a rapid equilibrium is established between adsorbed metal ions on the adsorbent (q_e) and unadsorbed metal ions in solution (C_{eq}). This equilibrium can be represented by the Langmuir [18] or Freundlich [19] adsorption isotherms, which are widely used to analyse data for water and wastewater treatment applications. The Langmuir equation which is valid for monolayer adsorption on to a surface a finite number of identical sites and is given by

$$q_e = \frac{Q_{max} b C_{eq}}{1 + b C_{eq}} \tag{2}$$

where Q_{max} is the maximum amount of the metal ion per unit weight of algae to form a complete monolayer on the surface bound at high C_{eq} (mg/g), and b is a constant related to the affinity of the binding sites (l/mg) Q_{max} represents a practical limiting adsorption capacity when the surface is fully covered with metal ions and assists in the comparison of adsorption performance, particularly in cases where the sorbent did not reach its full saturation in experiments. Q_{max} and b can be determined from the linear plot of C_{eq}/q_e versus C_{eq} [18–20].

The empirical Freundlich equation based on adsorption on a heterogeneous surface is given by

$$q_e = K_F C_{eq}^n \tag{3}$$

where K_F and n are Freundlich constants characteristic of the system. K_F and n are indicators of adsorption capacity and adsorption intensity, respectively. Eq. (3) can be linearized in logarithmic form and Freundlich constants can be determined. The Freundlich isotherm is also more widely used but provides no information on the monolayer adsorption capacity, in contrast to the Langmuir model [20–24].

3. Results and discussion

3.1. The effect of pH

Earlier studies on heavy metal adsorption have shown that pH was the single most important parameter affecting the adsorption process [25,26]. In all cases, metal adsorption by the *U. fasciata* sp. increases with increasing pH reaching to a maximum and then showed a rapid decline in adsorption. The equilibrium metal uptake of the *U. fasciata* sp. from 20 to 100 mg/l zinc solution at various pH values is shown in Fig. 1. The pH dependence of metal uptake could be related to the functional groups of the biomass and also to solution chemistry. At pH values less than 6, metals are in their free ionic form and as such the sharp increase in metal uptake. This leads to the hypothesis that the cell wall functional groups and their associated ionic state are responsible for the extent of adsorption.

Biosorbent materials primarily contain weak acidic and basic functional groups. It follows from the theory of acid-base equilibria that, in the pH range 2.5–5, the binding of heavy metal cations is determined primarily by the state of dissociation of the weak acidic groups. Carboxyl groups (–COOH) are the important groups for metal uptake by biological materials [27,28]. At pH 5, there are lower numbers of competing hydrogen ions and more ligands are exposed with negative charges, resulting in greater zinc sorption. But for pH values from 6 to 10, lower adsorption capacity was observed for zinc, this might be due to the precipitation and lower polarity of zinc ions at higher pH values. In this study, these zinc cations at around 5 would be expected to interact more strongly with the negatively charged binding sites in the adsorbent. As a result, the optimum pH for zinc adsorption was found as 5 and the other adsorption experiments were performed at this pH value. The effect of pH on the adsorption of zinc has been investigated by various investigators using a variety of different adsorbent types [29,30,31], and the optimum adsorption capacity of zinc at pH 5 has been reported.

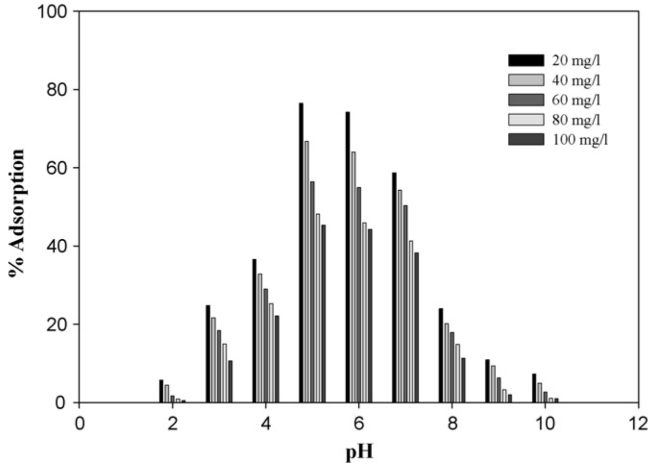

Fig. 1. Effect of pH on the adsorption of zinc onto *Ulva fasciata* sp. (weight of the adsorbent: 0.1 g/30 ml, volume of the zinc solution: 30 ml).

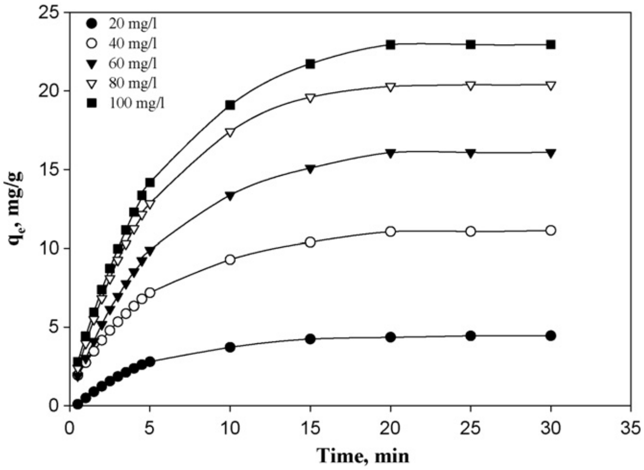

Fig. 2. Adsorption kinetics for zinc onto *U. fasciata* sp. (weight of the adsorbent: 0.1 g/30 ml, volume of the zinc solution: 30 ml, pH 5).

3.2. The effect of contact time

Fig. 2 shows the effect of contact time on the adsorption of zinc by adsorbent from aqueous solution. The rate of zinc adsorption by the *U. fasciata* sp. was very rapid, reaching maximum adsorption capacity within 20 min of contact time and the adsorption does not change significantly with further increase in contact time. Microbial metal uptake by nonliving cells, which is metabolism-independent passive binding process to cell walls (adsorption), and to other external surfaces, and is generally considered as a rapid process, taking place within a few minutes [32]. The rapid metal sorption is also highly desirable for successful deployment of the biosorbents for practical applications [33].

3.3. Effect of adsorbent concentration

The effect of variation of adsorbent concentration on zinc uptake and zinc % removal is shown in Fig. 3. Fig. 3 shows that while the percentage removal of zinc increases with the increase in adsorbent concentration, zinc uptake increases by increasing adsorbent concentration. The increase in adsorbent

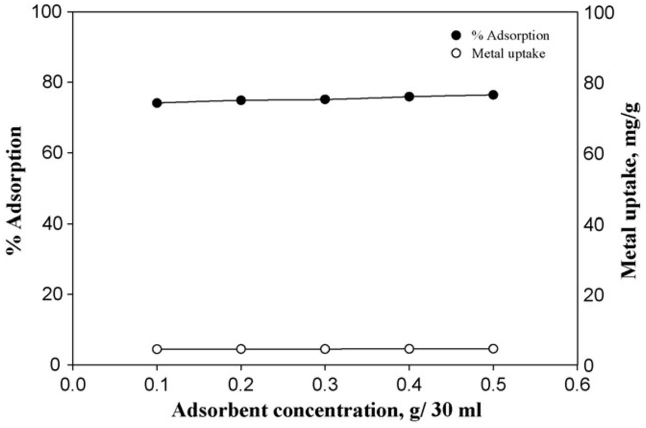

Fig. 3. Effect of adsorbent concentration on zinc adsorption on *U. fasciata* sp. (initial zinc ion concentration = 20 mg/l, adsorbent size = 75 μm, pH 5.0).

concentration from 0.1 to 0.5 g resulted in an increase from 74.1 to 76.42% in adsorption of zinc. This is because of the availability of more binding sites for complexation of zinc ions. The increase in metal uptake by increasing adsorbent concentration is attributed to many reasons, such as availability of solute, electrostatic interactions, interference between binding sites, and reduced mixing at high biomass densities. Thus, the adsorption sites remain unsaturated during the sorption process due to a lower adsorptive capacity utilization of the sorbent, which decreases the adsorption efficiency. Some of these reasons contributed also in limiting the maximum percentage removal, thus, 100% removal was not attained. This suggests that a more economical design for the removal of heavy metal ions can be carried out using small batches of sorbent rather than in a single batch [34].

3.4. *Effect of adsorbent size*

The effect of different adsorbent particle sizes (75–212 μm) on percentage removal of zinc was investigated.

Fig. 4 reveals that the adsorption of zinc on *U. fasciata* sp. decreases from 74.1 to 58.5% with the increased particle size from 75 to 212 μm at an initial concentration of 20 mg/l. It is well known that decreasing the particle size of the adsorbent increases the surface area, which in turn increases in adsorption capacity.

3.5. *Adsorption kinetics*

The prediction of adsorption rate gives important information for designing batch adsorption systems. Information on the kinetics of solute uptake is required for selecting optimum operating conditions for full-scale batch process. Fig. 2 shows the plot between amount adsorbed, q_e (mg/g) versus time, t (min) for different initial solute concentrations. From the figure it was observed that q_e value increased with increase in initial zinc concentration. But, however, the adsorption rate within the first 5 min was observed to be very high and thereafter the reaction proceeds at a slower rate till equilibrium and finally a steady state was obtained after equilibrium. The saturation time was found to be 20 min based on the initial metal concentration. The kinetics of the adsorption data was analysed using two kinetic models, pseudo-first order and pseudo-second order kinetic model. These models correlate solute uptake, which are important in predicting the reactor volume. These models are explained as follows.

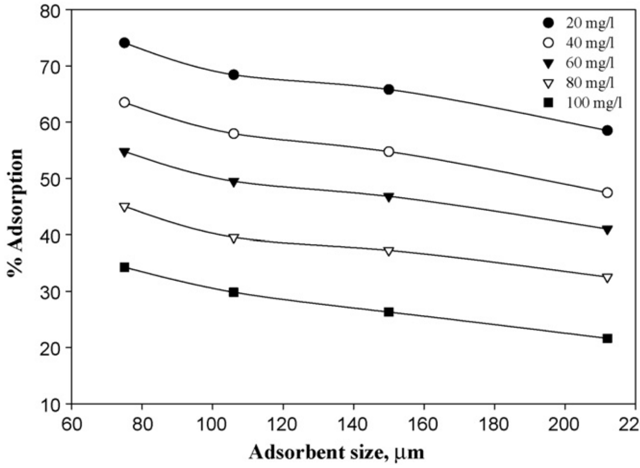

Fig. 4. Effect of adsorbent size on the sorption of zinc onto *U. fasciata* sp. (weight of the adsorbent: 0.1 g/30 ml, volume of the zinc solution: 30 ml, pH 5).

3.5.1. *Pseudo-first order model*

The possibility of adsorption data following Lagergren pseudo-first order kinetics is given by:

$$\frac{\mathrm{d}q}{\mathrm{d}t} = K_I(q_e - q) \tag{4}$$

Integrating Eq. (4) with respect to integration conditions $q=0$ to $q=q$ at $t=0$ to $t=t$, the kinetic rate expression becomes:

$$\log(q_e - q) = \log q_e - \frac{K_I}{2.303}t \tag{5}$$

The pseudo first order rate constant K_I can be obtained from the slope of plot between $\log(q_e - q)$ versus time, t (not shown). The calculated K_I values and their corresponding linear regression correlation coefficient values are shown in Table 1. The linear regression correlation coefficient values R_I^2 found in the range of 0.919–0.9795, which shows that this model can be applied to predict the adsorption kinetic model.

3.5.2. *Pseudo-second order model*

A pseudo-second order model proposed by Ho and McKay [35] can be used to explain the adsorption kinetics. This model is based on the assumption the adsorption follows second order chemisorption. The pseudo-second order model can be expressed as:

$$\frac{\mathrm{d}q}{\mathrm{d}t} = K_{II}(q_e - q)^2 \tag{6}$$

Separating the variables in Eq. (6) gives:

$$\frac{\mathrm{d}q}{(q_e - q)^2} = K_{II}\mathrm{d}t \tag{7}$$

Integrating Eq. (7) for the boundary conditions $q=0$ to $q=q$ at $t=0$ to $t=t$, Eq. (7) simplifies to:

$$\frac{t}{q_t} = \frac{1}{K_{II}q_e^2} + \frac{1}{q_e}t \tag{8}$$

where t is the contact time (min), q_e (mg/g) and q_t (mg/g) are the amount of the solute adsorbed at equilibrium and at any time, t. A plot between t/q_t versus (Fig. 5) gives the value of the constant K_{II} (g/mg min) and also q_e (mg/g) can be calculated.

The pseudo-second order rate constant K_II, the calculated q_e value and the corresponding linear regression correlation coefficient values R_II^2 are given in Table 1. At all initial zinc concentrations, the linear regression correlation coefficient R_II^2 values were higher and ranged from 0.9980 to 0.9988. The higher R_II^2 values confirm that the adsorption data are well represented by pseudo-second order kinetics and supports the assumption behind the model that the adsorption is due to chemisorption.

Table 1
Kinetic constants for zinc onto *Ulva fasciata* sp.

Initial concentration (mg/l)	Pseudo-second order			Pseudo-first order		
	Rate constant K_{I} (g/mg min)	Amount of zinc adsorbed on adsorbent, q_{e} (mg/g)	Correlation coefficient, R_I^2	Rate constant, K_{II} (g/mg min)	Amount of zinc adsorbed on adsorbent, q_{e} (mg/g)	Correlation coefficient, R_{II}^2
20	0.2552	2.1587	0.9448	0.0129	7.9618	0.9985
40	0.2391	2.6429	0.919	0.0168	12.195	0.9980
60	0.1861	2.7259	0.9795	0.0094	14.793	0.9984
80	0.1771	2.8725	0.9744	0.0075	16.4474	0.9981
100	0.1688	3.2082	0.9765	0.0038	22.936	0.9988

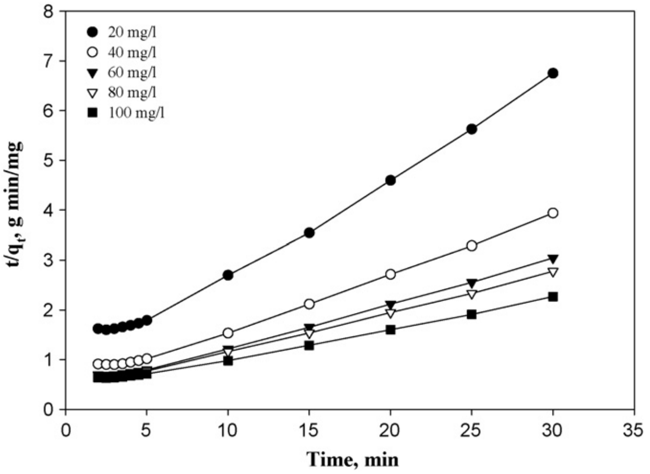

Fig. 5. Pseudo-second order kinetics for zinc onto *U. fasciata* sp. (weight of the adsorbent: 0.1 g/30 ml, volume of the zinc solution: 30 ml, pH 5).

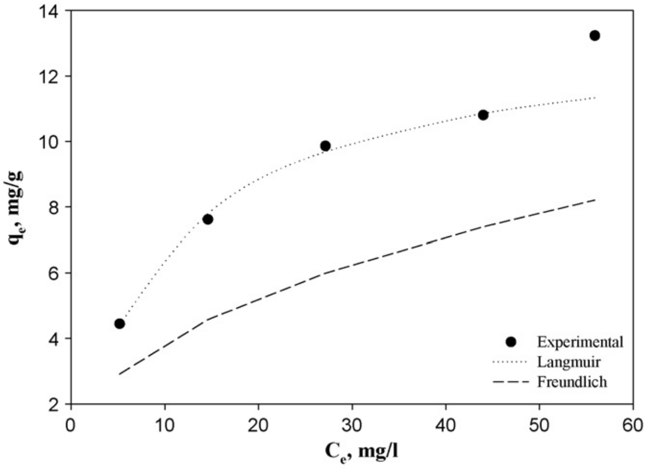

Fig. 6. Equilibrium curves for zinc onto *U. fasciata* sp.

3.6. Adsorption equilibrium

The adsorption equilibrium defines the distribution of a solute phase between the liquid phases and solid phases after the adsorption reaction reached equilibrium condition. In the present study, equilibrium studies were carried out at room temperature 30 °C. The equilibrium data were analysed using two of the most commonly used isotherm equations, Langmuir and Freundlich isotherm models.

The equilibrium data were very well represented by the Langmuir equilibrium model (Fig. 6). The calculated isotherm constants at room temperature 30 °C were given in Table 2. The best-fit equilibrium model was determined based on the linear regression correlation coefficient R^2. From the table it was observed that the adsorption data were very well represented by Langmuir isotherm with an average higher correlation coefficient of 0.9989. The higher R^2 value for Langmuir isotherm confirms the approximation of equilibrium data to Henrys law at lower initial concentration. From Table 2, the Langmuir adsorption capacity $Q_{\max}$ (mg/g) is 13.5 and the equilibrium constant b (l/mg) is 0.0936. The Freundlich constant K_{F} indicates the sorption capacity of the sorbent and the value of K_{F} is 1.4209 mg/g. Furthermore, the value of '*n*' at equilibrium is 0.4359. It is noted that the value of '*n*' is smaller than 1, reflecting the unfavorable adsorption.

Table 2
Equilibrium constants for zinc onto *U. fasciata* sp.

Freundlich isotherm	
K_{F} (mg/g)	1.4209
n (g/l)	0.4359
R^2	0.9828
Langmuir isotherm	
b (l/mg)	0.0936
$Q_{\max}$ (mg/g)	13.5
R^2	0.9989

4. Conclusion

The biomass of the marine algae *U. fasciata* sp. demonstrated a good capacity of zinc biosorption, highlighting its potential for effluent treatment processes. The kinetics of zinc adsorption by inactive biomass of the marine algae *U. fasciata* sp. was fast, reaching 80% of the total adsorption capacity in five minutes. The adsorption process is a function of the adsorbent concentration, pH, metal ion concentration and adsorbent size.

U. fasciata sp. posses adsorption capacity of 13.5 mg/g, confirming that the algae under these conditions can be effectively used as adsorbent. The experimental data gave good fit with Langmuir isotherm and the adsorption coefficients agreed well with the conditions of favorable adsorption. Kinetic studies indicated that the adsorption tends to follow pseudo-second order kinetics for the range of concentrations studied for the entire adsorption period.

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