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A Comparative Study of the Biosorption of Iron(III)–Cyanide Complex Anions to *Rhizopus arrhizus and Chlorella vulgaris*

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ABSTRACT

In this study a comparative biosorption of iron(III)–cyanide complex anions from aqueous solutions to *Rhizopus arrhizus* and *Chlorella vulgaris* was investigated. The iron(III)–cyanide complex ion-binding capacities of the biosorbents were shown as a function of initial pH, initial iron(III)–cyanide complex ion, and biosorbent concentrations. The results indicated that a significant reduction of iron(III)–cyanide complex ions was achieved at pH 13, a highly alkaline condition for both the biosorbents. The maximum loading capacities of the biosorbents were found to be 612.2 mg/g for *R. arrhizus* at 1996.2 mg/L initial iron(III)–cyanide complex ion concentration and 387.0 mg/g for *C. vulgaris* at 845.4 mg/L initial iron(III)–cyanide complex ion concentration at this pH. The Freundlich, Langmuir, and Redlich–Peterson adsorption models were fitted to the equilibrium data at pH 3, 7, and 13. The equilibrium data of the biosorbents could be best fitted by all the adsorption models over the entire concentration range at pH 13.

Key Words. Iron(III)–cyanide complex anions; *Rhizopus arrhizus*; *Chlorella vulgaris*; Biosorption; Batch stirred reactor

INTRODUCTION

Cyanide is commonly found as a contaminant in wastewaters from various industries that include metal plating, steel tempering, mining, photography,

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pharmaceuticals, coal coking, ore leaching, and plastics. In addition to cyanide, these wastes may contain other contaminants, including heavy metals. Waste effluents from steel tempering, coal coking, and mining industries, for example, contain significant quantities of nickel, copper, zinc, and iron. Since cyanide is highly reactive, it will readily bind metals as a strong ligand to form complexes of variable stability and toxicity. Examples include the well-known hexacyano complexes of iron [both iron(II)– and iron(III)–cyanide complex ions] and the tetracyano complexes of divalent nickel, copper, and zinc. Chemical and biological methods mentioned in the literature can be used for removing heavy metal cyanide complex ions from wastewater. Traditionally, biological treatment, activated carbon adsorption, solvent extraction, and chemical oxidation with ozone and ultraviolet radiation are the most widely used methods for removing metal cyanide complex ions including iron–cyanide complexes which are anionic and very stable complexes from wastewaters. Current chemical treatment methods are not always well adapted and efficient with regard to technological, cost, and disposal considerations. Biological treatments are feasible alternatives to chemical methods because a wide range of microorganisms are known to metabolize such chemicals (1–8).

These types of compounds are expected to constitute a significant fraction of cyanide-related wastes, but their sorption by microorganisms (biosorption) has not generally been investigated. Biosorption has been generally used for the treatment of heavy metal pollutants in wastewaters and can also be used for the treatment of wastewaters containing metal–cyanide complex ions. Since little is known about the biosorption of metal–cyanide complex ions to biomasses, the adsorptive properties of microorganisms for metal–cyanide complex ions must also be investigated.

Adsorption is also a well-known equilibrium separation process for wastewater treatment. Equilibrium studies on adsorption give information about the capacity of the adsorbent or the amount required to remove a unit mass of pollutant under the system conditions. The most widely used isotherm equation for modeling equilibrium is the Langmuir equation which is valid for monolayer sorption onto a surface with a finite number of identical sites and is given by

$$q_{eq} = \frac{Q^0 b C_{eq}}{1 + bC_{eq}} \tag{1}$$

where C_{eq} and q_{eq} are residual (equilibrium) pollutant concentration left in solution after binding (mg/L) and the amount of pollutant bound to the adsorbent (mg/g), respectively. Q^0 is the maximum amount of the pollutant per unit weight of adsorbent used 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^0 and b can be determined from the linear plot of C_{eq}/q_{eq} vs C_{eq} (9–11, 16).

The Freundlich model is more widely used but provides no information on the monolayer adsorption capacity, in contrast to the Langmuir model. The empirical Freundlich equation based on sorption on a heterogenous surface is given by

$$q_{eq} = K_F C_{eq}^{1/n} \tag{2}$$

where K_F and n are the Freundlich constants characteristic of the system. K_F and n are indicators of adsorption capacity and adsorption intensity, respectively. Equation (2) can be linearized in logarithmic form, and the Freundlich constants can be determined. The higher the value of n, the lower the slope expressed by $1/n$, and thus the lower the affinity (9–11).

The three-parameter Redlich–Peterson equation was proposed to improve the fit by the Langmuir or Freundlich equation and is given by

$$q_{eq} = \frac{K_{RP} C_{eq}}{1 + a_{RP} C_{eq}^{\beta}} \tag{3}$$

where K_{RP}, a_{RP}, and β are the Redlich–Peterson parameters. β lies between 0 and 1. For $\beta = 1$, Eq. (3) converts to the Langmuir form. Equation (3) may be converted into a linear form

$$\ln\left[K_{RP}\frac{C_{eq}}{q_{eq}} - 1\right] = \ln a_{RP} + \beta \ln C_{eq} \tag{4}$$

The two parameters in the Langmuir and Freundlich equations can be graphically determined, but plotting the left-hand side of Eq. (4) against $\ln C_{eq}$ to obtain the Redlich–Peterson constants is not applicable because of the three unknowns, K_{RP}, a_{RP}, and β, so the three parameters in the Redlich–Peterson equation are obtained by using a least-squares fitting procedure to minimize the deviation between calculated and measured data (9–14).

Relatively little work appears to have been done on the ability of biomass to adsorb metal–cyanide complex anions. The scope of this study is the application of the biosorption method, used succesfully in recent years for the removal of heavy metal ions and organics, to the treatment of heavy metal–cyanide complex ions (9–11, 16). In the study the uptake capacity and yield of biosorption of iron(III)–cyanide complex ions by *Rhizopus arrhizus*, a filamentous fungus, and *Chlorella vulgaris*, a green algae, were investigated as a function of initial pH, initial iron(III)–cyanide complex ion, and biosorbent concentrations in a batch system. Equilibrium modeling has been carried

out using Langmuir, Freundlich, and Redlich–Peterson isotherm equations, and constants have been calculated under optimum conditions by the nonlinear regression method.

EXPERIMENTAL

Microorganisms and Growth Conditions

Rhizopus arrhizus, a filamentous fungus obtained from the US Department of Agriculture Culture Collection, and *Chlorella vulgaris*, a green algae obtained from Sammlung von Algen Kulturen Pflanzen Physiologisches Institut, Universitat Göttingen, Germany, were used in this study. *R. arrhizus* was grown at 25°C in agitated liquid media containing malt extract (17 g/L) and soya peptone (5.4 g/L). The pH of growth medium was adjusted to 5.4–5.6 with dilute H_2SO_4. *C. vulgaris* was grown at the same temperature at pH 6.8 in agitated and aerated liquid media containing glucose (5.0 g/L), yeast extract (1.0 g/L), and triptone (1.0 g/L).

Preparation of the Microorganisms for Biosorption

After the growth period, *R. arrhizus* was washed twice with distilled water, inactivated using 1% formaldehyde, and then dried at 110°C for 24 hours. After a 4–5 days inoculation period, *C. vulgaris* cells were also centrifuged and washed twice with distilled water and dried at 60°C for 24 hours. For the biosorption studies, a weighed amount of dried biomass was suspended in 100 mL of double-distilled water and homogenized in a homogenizer (Janke and Kunkel, IKA-Labortechnick, Ultra Turrax T25) at 8000 rpm for 20 minutes and then stored in a refrigerator at +4°C.

The average particle size of each microorganism in the suspension was measured by using an optical microscope, and the density of each microorganism in the suspension was determined with a pycnometer.

Chemicals

The test solutions containing iron(III)–cyanide complex ions were prepared by diluting the 1.0-g/L iron(III)–cyanide complex ion stock solution to the desired concentrations. The stock solution was prepared by dissolving 1.551 g potassium ferricyanide ($K_3Fe[CN]_6$) of analytical reagent grade, obtained from Fisher, in 1 L of double-distilled water. The ranges of concentration of iron(III)–cyanide complex ions prepared from the stock solution varied between 50 and 2000 mg/L. Before mixing with the fungal suspansion, the pH of each test solution was adjusted to the required value with dilute H_2SO_4 and dilute NaOH.

Biosorption Studies

The factors effecting uptake capacities of biosorbents were examined in Erlenmayer flasks. A microorganism suspension of 15 mL was contacted with 135 mL of solution containing a known concentration of iron(III)–cyanide complex ion in an Erlenmayer flask at the desired temperature and pH. All the final solutions contained a fixed mass of biosorbent (0.5–2.0 g/L).

The flasks were agitated on a shaker at a 125-rpm constant shaking rate for 24 hours to ensure equilibrium was reached. Samples of 5 mL were taken before mixing the biosorbent solution and iron(III)–cyanide complex ion-bearing solution at 5 minute intervals at the beginning of adsorption and at 15–30 minute intervals after reaching equilibrium, centrifuged at 5000 rpm for 3 minutes, and then the supernatant liquid was used to analyze for iron(III)–cyanide complex ions.

The studies were performed at a constant temperature of 25°C to be representative of environmentally relevant conditions.

Analysis of Iron(III)–Cyanide Complex Ions

The concentration of residual iron(III)–cyanide complex ions in the biosorption medium was determined iodometrically. In this method, iron(III)–cyanide complex ions were oxidized to iron(II)–cyanide complex ions by potassium iodide in the acidic medium, and iodine was formed. The amount of iodine [or indirectly the amount of iron(III)–cyanide complex ions] was determined by titration with sodium thiosulfate solution (17).

RESULTS AND DISCUSSION

The kinetic and equilibrium results were given as the units of adsorbed iron(III)–cyanide complex ion quantity per gram of biosorbent at any time (q, mg/g), initial adsorption rate (r_{ad}, mg/g/min) calculated by derivating the q (mg/g) versus t (min) plot at $t = 0$, and adsorbed iron(III)–cyanide complex ion quantity per gram of biosorbent at equilibrium (q_{eq}, mg/g) and unadsorbed iron(III)–cyanide complex ion concentration in solution at equilibrium (C_{eq}, mg/L). The adsorption yield [Ad (%)] was defined as the ratio of adsorbed concentration of iron(III)–cyanide complex ions at equilibrium (or at the end of biosorption when the equilibrium was not observed) to the initial iron(III)–cyanide complex ion concentration and calculated from

$$Ad\,(\%) = \frac{qX}{C_0}\,100 \tag{5}$$

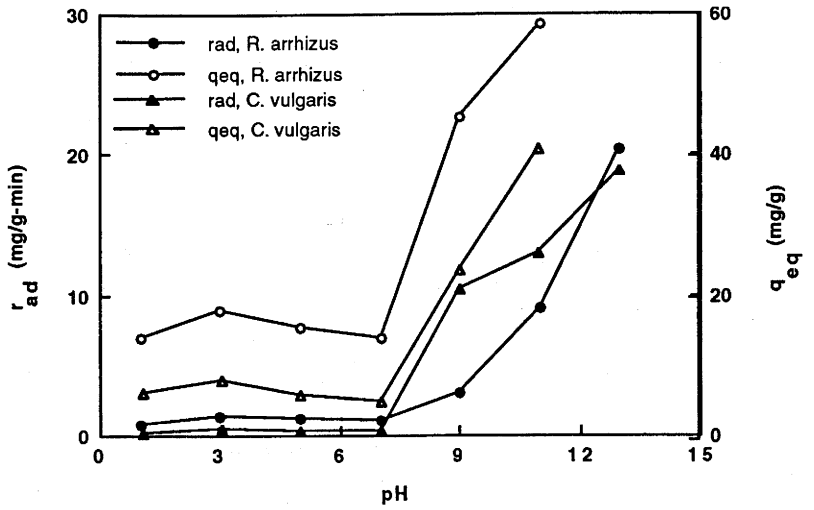

FIG. 1 The effect of initial pH on the initial adsorption rate and equilibrium uptake of iron(III)–cyanide complex ions by *R. arrhizus* and *C. vulgaris* (C_0 = 100 mg/L; X = 1.0 g/L; temperature = 25°C; agitation rate = 125 rpm).

Effect of Initial pH

The most critical parameter in the treatment of iron(III)–cyanide complex ions by the biosorbents that affects the initial sorption rate and capacity is the pH of the sorption medium. The variation of adsorption rate and equilibrium uptake with initial pH is given in Fig. 1. From Fig. 1 the sharpest increase in iron(III)–cyanide complex ion removal occurs between pH 10 and 13 for both microorganisms.

The cell walls of *R. arrhizus* and *C. vulgaris* essentially consist of various organic compounds such as chitin, acidic polysaccharides, lipids, amino acids, and other cellular components of the microorganisms which maintain an extensive complexing capacity for iron(III)–cyanide complex ions due to the pH. They can absorb components through their outer membranes which contain proteins and lipids. Figure 1 shows that as the pH was lowered, however, the overall surface charge on the cells became positive, and this led to electrostatic attractions between negatively charged iron(III)–cyanide complex ions and positively charged binding sites, hence the rapid rise in binding efficiency at pH 1.0–3.0. As the pH increased, however, the overall surface charge on the cells became negative and biosorption decreased. An explanation that appears more reasonable is that the increase in biosorption observed at increasing pH values may be caused by alterations in the sorbent surface and the interaction of

iron(III)–cyanide complex ions with the cells with primarily electrostatic forces or by complex formation or electron sharing in nature or in membrane transport. At high pH values a competitive adsorption between iron(III)–cyanide complex ions and OH^- ions onto active sites of microbial cells occurs, and this can be proposed as an alternative adsorption mechanism (9, 11, 18). In fact, the behavior and mechanism(s) of biosorption of a biomass are not well understood.

Effect of Initial Iron(III)–Cyanide Complex Ion Concentration

The effect of the initial iron(III)–cyanide complex ion concentration on the initial adsorption rate and the capacity of each biomass was investigated at initial pH values of 3.0, 7.0, and 13.0. The initial adsorption rate and the equilibrium sorption capacity of each biomass increased with an increase of the initial iron(III)–cyanide complex ion concentration up to 2000 mg/L for *R. arrhizus* and up to 1000 mg/L for *C. vulgaris* at all the pH values studied, as shown in Table 1. The highest equilibrium uptakes were observed at pH 13 for

TABLE 1
Comparison of the Initial Adsorption Rates, Equilibrium Adsorbed Quantities, and Adsorption Yields of Iron (III)–Cyanide Complex Ions Obtained at Different Initial Iron(III)–cyanide Complex Ion Concentrations at Initial pH Values of 3.0, 7.0, and 13.0 for Each Biosorbent (X = 1.0 g/L, temperature = 25°C, agitation rate = 125 rpm)

pH 3				pH 7				pH 13			
C_0 (mg/L)	r_{ad} (mg/gmin)	q_{eq} (mg/g)	Ad (%)	C_0 (mg/L)	r_{ad} (mg/gmin)	q_{eq} (mg/g)	Ad (%)	C_0 (mg/L)	r_{ad} (mg/gmin)	q_{eq} (mg/g)	Ad (%)
					R. arrhizus						
55.4	0.32	9.0	16.2	56.3	0.28	8.0	14.2	62.0	9.86	—	100.0
119.6	0.83	17.3	14.5	133.1	1.03	15.0	11.3	108.9	19.45	—	100.0
217.0	2.35	28.0	12.9	213.9	1.55	18.5	8.6	264.0	54.43	—	100.0
325.5	3.60	36.0	11.1	365.2	2.08	26.3	7.2	321.8	65.72	—	100.0
737.9	3.72	55.4	7.5	614.2	3.15	32.0	5.2	437.3	78.73	368.0	84.2
171.9	3.64	60.0	4.7	1352.0	3.20	36.0	2.7	643.3	123.40	433.3	67.3
1993.5	3.72	64.2	3.2	2089.7	3.24	37.4	1.8	985.9	150.89	570.5	57.9
								1216.8	153.45	589.0	48.4
								1996.2	154.00	612.2	30.7
					C. vulgaris						
49.7	0.43	7.8	15.7	39.7	0.32	4.2	10.6	42.0	15.32	—	100.0
109.3	0.58	9.9	9.1	84.4	0.45	5.1	6.0	89.1	18.41	—	100.0
139.1	0.72	11.0	7.9	139.1	0.54	6.9	5.0	125.9	32.25	—	100.0
506.6	1.15	19.7	3.9	228.1	0.55	7.3	3.2	230.7	37.49	219.7	95.2
765.0	1.40	21.8	2.8	508.6	0.58	11.9	2.3	419.4	48.35	316.4	75.4
932.5	1.45	22.4	2.4	754.5	0.56	13.0	1.7	681.5	56.08	322.8	47.4
				1054.0	0.54	14.2	1.3	845.4	58.44	387.0	45.8

both microorganisms. Equilibrium was not observed up to 437.3 and 230.7 mg/L initial iron(III)–cyanide complex ion concentrations for *R. arrhizus* and *C. vulgaris*, respectively; all the iron(III)–cyanide complex ions in the adsorption medium were removed because of the higher adsorption capacities of the microorganisms at this pH value. When the initial iron(III)–cyanide complex ion concentration was increased from 62.0 to 1996.2 mg/L for *R. arrhizus* and from 42.0 to 845.4 mg/L for *C. vulgaris*, the loading capacities of biosorbents increased from 62.0 to 612.2 mg/g for *R. arrhizus* and from 42.0 to 387.0 mg/g for *C. vulgaris* at pH 13. The increase of loading capacities of the biosorbents with the increase of iron(III)–cyanide complex ion concentration may be due to the higher probability of collisions between the ions and biosorbents. The adsorption yields obtained from experimental data at different initial iron(III)–cyanide complex ion concentrations and pH values are also presented in Table 1 for both kinds of biomass. From Table 1, increasing the iron(III)–cyanide complex ion concentration generally caused a decrease in the adsorption yield at all the pH values studied. A lower initial iron(III)–cyanide complex ion concentration also favored a higher sorption yield. It is interesting to note that for iron(III)–cyanide complex ion biosorption by *R. arrhizus*, the rates and equilibrium uptakes and adsorption yields were higher than those of *C. vulgaris*. This difference in biosorption rates and yields cannot be explained by the difference in specific surface areas of inactive *R. arrhizus* and *C. vulgaris* because *R. arrhizus* has a smaller specific surface area. (Average cell sizes and densities of *R. arrhizus* and *C. vulgaris* were measured as 27.2 and 5.0 μm, and 1.048 and 1.026 g/mL, respectively. Assuming spherical particles, the surface area per unit weight of dried cells can be calculated from the $6/\rho_p d_p$ formula. The specific surface areas of *R. arrhizus* and *C. vulgaris* were determined to be 0.21 and 1.17 m^2/g, respectively.) Conceptually, it can be suggested that both surface area and the type of surface play an important role in the microbial sorption of iron(III)–cyanide complex ions from water. The present available information does not allow the observed differences in priority iron(III)–cyanide complex ion biosorption rates by different biomass types to be explained.

Effect of Biosorbent Concentration

The effect of biosorbent concentration on the initial adsorption rate and equilibrium uptake of iron(III)–cyanide complex ions is shown in Fig. 2 for each biosorbent at approximately 600 mg/L of initial iron(III)–cyanide complex ion concentration and at pH 13. It is observed that initial removal rates increase when larger quantities of biosorbents are used. Increasing the amount of biosorbent added also decreases the equilibrium uptake based on the calcu-

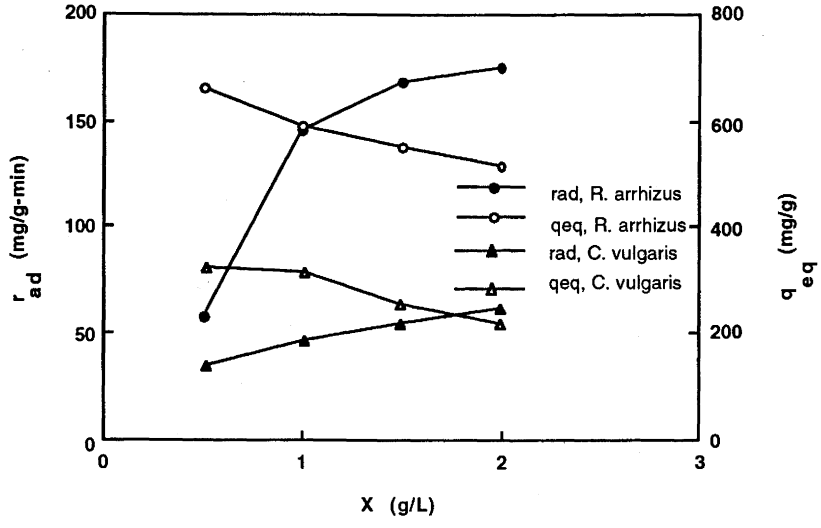

FIG. 2 The effect of biosorbent concentration on the initial adsorption rate and equilibrium uptake of iron(III)–cyanide complex ions *R. arrhizus* and *C. vulgaris* (C_0 = 500 mg/L; pH 13.0; temperature = 25°C; agitation rate = 125 rpm).

lation of equilibrium capacity [q_{eq} = iron(III)–cyanide complex ion removed/g biosorbent] for each biosorbent (9, 16).

Comparison of the Biosorption Characteristics of Iron(III)–Cyanide Complex Ions to *R. arrhizus* and *C. vulgaris*

The physical, chemical, and biological nature of the biosorbents could possibly have strong effects on both adsorption rate and biosorption capacity. Figure 3 shows the adsorption kinetics of iron(III)–cyanide complex ion removal by each biosorbent by plotting the iron(III)–cyanide complex ion uptake capacity, q, versus the time for each for approximately 100 and 600 mg/L of initial iron(III)–cyanide complex ion concentrations at pH 13. The results clearly show that the initial sorption of iron(III)–cyanide complex ions occurs very rapidly for both kinds of biomass for both initial iron(III)–cyanide complex ion concentrations. Equilibrium was not observed at 100 mg/L of initial iron(III)–cyanide complex ion concentration; all the iron(III)–cyanide complex ions were bound onto each biosorbent in a few minutes. Biosorption reached equilibrium in 10–15 minutes for a 600 mg/L initial iron(III)–cyanide

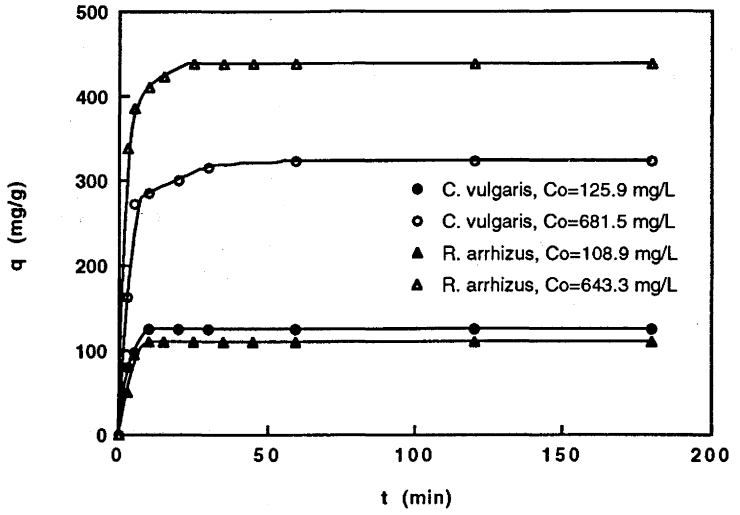

FIG. 3 The biosorption curves of iron(III)–cyanide complex ions at each initial iron(III)–cyanide complex ion concentration of approximately 100 and 600 mg/L at pH 13 (X = 1.0 g/L; temperature = 25°C; agitation rate = 125 rpm).

complex ion concentration for both kinds of biomass. The biosorption capacity of *C. vulgaris* appeared to be lower than that of *R. arrhizus* at this concentration value.

Freundlich, Langmuir, and Redlich–Peterson Adsorption Isotherms

Analysis of the adsorption isotherms for iron(III)–cyanide complex ions is important for developing an equation that can represent the results for use in design purposes. Out of several isotherm equations, three have been applied to this study; the Freundlich, Langmuir, and Redlich–Peterson isotherms. To determine the isotherms, initial pollutant concentrations were varied while the sorbent weight in each sample was kept constant. The Freundlich, Langmuir, and Redlich–Peterson isotherms obtained at 25°C for each biosorbent and at three different pH values are shown in Figs. 4, 5, and 6. The Freundlich, Langmuir, and Redlich–Peterson adsorption constants evaluated from the Freundlich, Langmuir, and Redlich–Peterson adsorption models at different initial pH values with the normalized deviations are also given in Table 2.

From Table 2, the magnitude of K_F and n, the Freundlich constants, shows an easy uptake of iron(III)–cyanide complex ions from wastewater with high adsorptive capacities of the biosorbents, especially at pH 13. Table 2 also

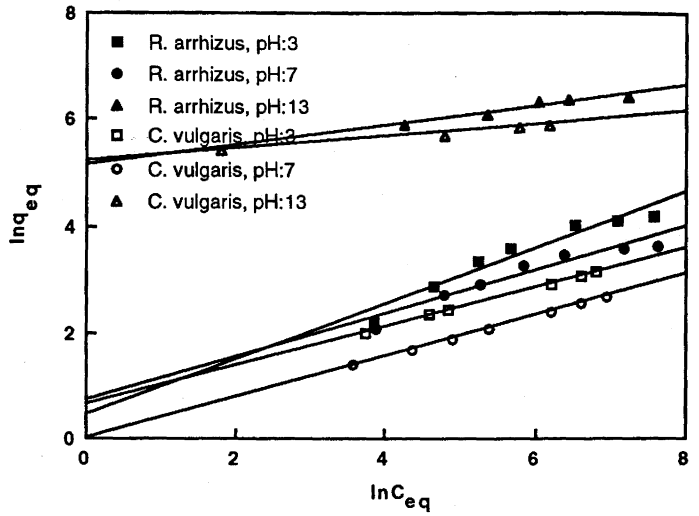

FIG. 4 The linearized Freundlich adsorption isotherms of iron(III)–cyanide complex ions obtained at different pH values for each biosorbent.

TABLE 2
Comparison of the Freundlich, Langmuir, and Redlich–Peterson Adsorption Constants with the Normalized Deviations Obtained at Initial pH Values of 3.0, 7.0, and 13.0 for Each Biosorbent at 25°C

	Freundlich model			Langmuir model			Redlich–Peterson Model			
pH	K_F	n	Δq_{eq}	Q^0	b	Δq_{eq}	a_{RP}	K_{RP}	β	Δq_{eq}
					R. arrhizus					
3.0	3.43	2.5	19.1	79.7	0.003	3.7	0.003	0.24	1.00	3.7
7.0	3.63	3.2	15.3	41.7	0.005	2.9	0.005	0.20	1.00	2.9
13.0	181.80	5.7	5.8	619.4	0.530	5.4	0.050	17.62	0.92	4.5
					C. vulgaris					
3.0	1.95	2.8	3.6	23.3	0.008	7.3	0.28	0.81	0.69	4.2
7.0	1.01	2.6	5.4	16.4	0.005	9.9	1.79	1.97	0.63	5.6
13.0	164.20	7.6	5.6	359.3	0.140	6.0	0.71	14.80	0.90	4.6

shows that n is greater than unity, indicating that iron(III)–cyanide complex ions are favorably adsorbed by *R. arrhizus* and *C. vulgaris* at all the pH values studied. The magnitude of K_F also indicates the high adsorption capacities of the biosorbents at pH 13.0.

Values of Q^0 and b for different pH values have been calculated from the plots in Fig. 5, and the results are also tabulated in Table 2. The maximum capacity Q^0 determined from the Langmuir isotherm defines the total capacity of each biosorbent for iron(III)–cyanide complex ions. Table 2 also shows that the adsorption capacities of the microorganisms are highest at pH 13. The magnitude of Q^0 was significantly higher for the iron(III)–cyanide complex ion–*R. arrhizus* system in comparison to the uptake of iron(III)–cyanide complex ions on *C. vulgaris*. A large value of b at pH 13, related to binding energy, also implied strong bonding of iron(III)–cyanide complex ions to *R. arrhizus*.

Plots of $\ln[K_{RP}C_{eq}/q_{eq} - 1]$ against in C_{eq} are linear over the entire range of iron(III)–cyanide complex ion concentrations for both biosorbents, as shown in Fig. 6. The Redlich–Peterson parameters found at different pH values are also tabulated in Table 2. It can be seen that at pH 3.0 and 7.0 the values of β are equal to 1.0, and β tends to unity for pH 13; that is, the isotherms are approaching the Langmuir form for *R. arrhizus*. The values of β show that

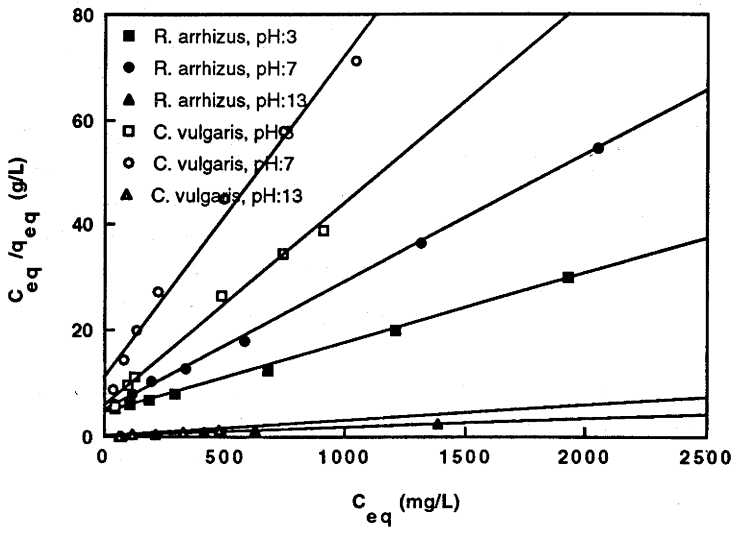

FIG. 5 The linearized Langmuir adsorption isotherms of iron(III)–cyanide complex ions obtained at different pH values for each biosorbent.

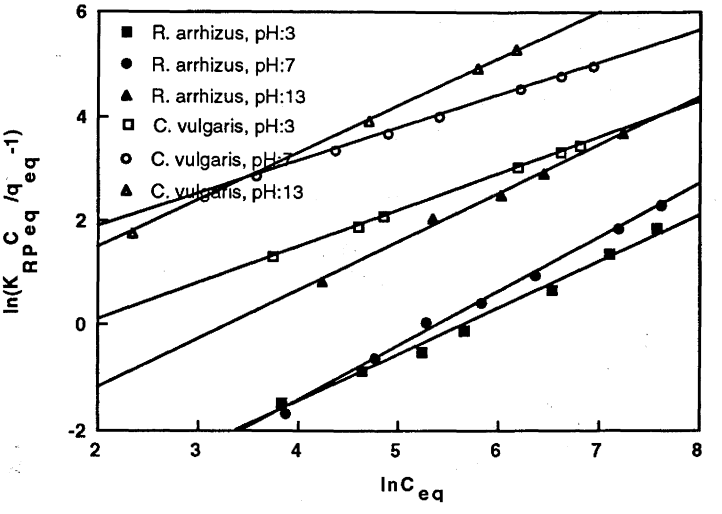

FIG. 6 The linearized Redlich–Peterson adsorption isotherms of iron(III)–cyanide complex ions obtained at different pH values for each biosorbent.

iron(III)–cyanide complex ion biosorption by *C. vulgaris* is not similar to the Langmuir type.

In order to compare the validity of the isotherm equations more definitely, a normalized deviation, Δq_{eq}, is calculated as follows:

$$\Delta q_{eq}\,(\%) = \frac{\sum_{i=1}^{N} \left| \frac{q_{eq,i,exp} - q_{eq,i,calc}}{q_{eq,i,exp}} \right|}{N} \times 100 \qquad (6)$$

where the subcripts "exp" and "calc" show the experimental and calculated values, and N is the number of measurements.

As shown in Table 2, Δq_{eq} values obtained for the Freundlich equation are rather large at pH 3.0 and 7.0 for *R. arrhizus* (Δq_{eq} = 19.1 and 15.3%). The Langmuir and Redlich–Peterson fits are better than the Freundlich fit at the same pH values (Δq_{eq} = 3.7 and 2.9%) for this biosorbent. The normalized deviations found in all the adsorption models were very low at pH 13.0. It is concluded that the Langmuir and Redlich–Peterson models provide a more realistic description of the biosorption process by *R. arrhizus* at lower pH values, and the equilibrium data fit very well to all the isotherm models at pH 13.0.

From Table 2, Δq_{eq} values obtained for the Langmuir model are slightly large for all pH values for *C. vulgaris* (Δq_{eq} = 7.3, 9.9, and 6.0% at pH 3, 7,

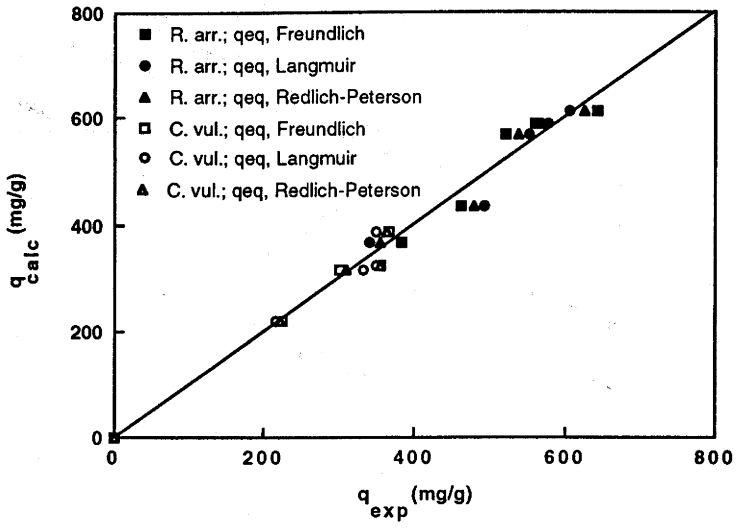

FIG. 7 The comparison of the experimental q_{eq} values with the calculated q_{eq} values obtained from the Freundlich, Langmuir, and Redlich–Peterson adsorption models for each biosorbent at pH 13.0.

and 13, respectively). The Freundlich and Redlich–Peterson fits are better than the Langmuir fit at the same pH values for this biosorbent. The normalized deviations found in all the adsorption models are also very low at pH 13.0. It is concluded that the Freundlich and Redlich–Peterson models provide a more realistic description of the biosorption process by *C. vulgaris* for all pH values.

The theoretical equilibrium uptake data obtained from the Freundlich, Langmuir, and Redlich–Peterson adsorption models are also compared with the experimental results at pH 13.0 in Fig. 7 for both biosorbents. The figure also shows that the adsorption equilibrium uptake data of the biosorbents fits very well to all the models in the concentration ranges studied for iron(III)–cyanide complex ions at pH 13.0.

CONCLUSION

In this study the capabilities of dried *R. arrhizus* and *C. vulgaris* for removing iron(III)–cyanide complex ions from aqueous solutions were examined, including equilibrium and dynamic studies. Experiments were performed as a function of pH, initial iron(III)–cyanide complex ion concentration, and the amount of biosorbent. In conventional biological treat-

ment systems where insufficient contact time is available for biodegradation to occur, biosorption results in the removal of toxic compounds from aqueous waste streams and in the accumulation of hazardous pollutants in microbial sludge in a short time. The experimental results showed that although the sorption capacity of *R. arrhizus* is higher than that of *C. vulgaris* both microorganisms have a considerable potential for the rapid uptake of iron(III)–cyanide complex ions from wastewaters over a wide range of pH and iron(III)–cyanide complex ion concentrations of 1000–2000 mg/L.

The Freundlich, Langmuir, and Redlich–Peterson adsorption models were used for the mathematical description of the biosorption of iron(III)–cyanide complex ions to dried *R. arrhizus* and *C. vulgaris*. The isotherm constants were evaluated by computer to compare the biosorptive capacities of the dried microorganisms for iron(III)–cyanide complex ions. It was seen that the adsorption equilibrium data fitted very well to all the models at pH 13.0 for both microorganisms.

It may be concluded that dried *R. arrhizus* and *C. vulgaris* may be used successfully for the removal of iron(III)–cyanide complex ions due to the pH of wastewater. (They may also be effective for removing other harmful or undesirable species present in effluents such as heavy metal ions.) Higher adsorption capacities for the selective removal of iron(III)–cyanide complex ions with *R. arrhizus* and *C. vulgaris* could be carried out in a batch reactor by adjusting the pH of wastewater and diluting wastewater to lower pollutant concentration levels. Biosorptions by *R. arrhizus* and *C. vulgaris* can be proposed as alternatives to more costly methods (biological treatment, activated carbon adsorption, solvent extraction, chemical oxidation) for the removal of iron(III)–cyanide complex ions from waste streams.

NOTATION

a_{RP}	parameter in the Redlich–Peterson equation
Ad	adsorption yield (%)
b	Langmuir adsorption constant of iron(III)–cyanide complex ions
C_{eq}	unadsorbed iron(III)–cyanide complex ion concentration at equilibrium (mg/L)
C_0	initial iron(III)–cyanide complex ion concentration (mg/L)
K_F	Freundlich adsorption constant of iron(III)–cyanide complex ions
K_{RP}	parameter in the Redlich–Peterson equation
n	Freundlich adsorption constant of iron(III)–cyanide complex ions
q	amount of iron(III)–cyanide complex ions adsorbed per unit weight of biosorbent at any time (mg/g)
q_{eq}	amount of iron(III)–cyanide complex ions adsorbed per unit weight of biosorbent at equilibrium (mg/g)

Q^0 Langmuir adsorption constant of iron(III)–cyanide complex ions
r_{ad} initial adsorption rate of iron(III)–cyanide complex ions (mg/g/min)
X biosorbent concentration (g/L)
β constant in Redlich–Peterson equation
Δq_{eq} normalized deviation defined in Eq. (6)

REFERENCES

1. Kirk-Othmer. *Encyclopedia of Chemical Technology, Vol. 12*, 3rd ed., Wiley, New York, NY, 1982, pp. 25–33.
2. B. N. Aronstein, A. Maka, and V. J. Srivastava, *Appl. Microbiol. Biotechnol., 41*, 700 (1994).
3. R. O. Bucsh, D. J. Spottiswood, and G. W. Lower, *J. Water Pollut. Control Fed., 52*(12), 2925 (1988).
4. J. Silva-Avalos, M. G. Richmond, O. Nagappan, and D. Kunz, *Appl. Environ. Microbiol., 56*, 3664 (1990).
5. A. E. Short, S. F. Haselmann, and M. J. Semmens, *J. Environ. Sci. Health A, 32*(1), 215 (1997).
6. M. M. M. Gonçalves, A. F. Pinto, and M. Granato, *Environ. Technol., 19*, 133 (1998).
7. W. Zaban and R. Helwick, *Plat. Surf. Finish., 67*, 56 (1980).
8. A. E. J. Pettet and G. C. Ware, *Chem. Ind.*, p. 1232 (1955).
9. Z. Aksu, "Biosorption of Heavy Metals by Microalgae in Batch and Continuous Systems," in *Algae for Wastewater Treatment*, (Y.-S. Wong and N. F. Y. Tam, Eds.), Springer-Verlag and Landes Bioscience, Germany, 1998, Chap. 3, pp. 37–53.
10. Y. Sağ, Ü. Açikel, Z. Aksu, and T. Kutsal, *Process Biochem., 33*, 273 (1998).
11. Z. Aksu and J. Yener, *Ibid., 33*, 649 (1998).
12. G. McKay and J. F. Porter, *J. Chem. Tech. Biotechnol., 69*, 309 (1997).
13. R.-S. Juang, R.-L. Tseng, F.-C. Wu, and S.-H. Lee, *Ibid., 70*, 391 (1997).
14. M. M. Nassar and Y. H. Magdy *Chem. Eng. J., 66*, 223 (1997).
15. O. J. Redlich and D. L. Peterson, *J. Phys. Chem., 63*, 1024 (1959).
16. F. Veglio, F. Beolchini, and A. Gasbarro, *Process Biochem., 32*, 99 (1997).
17. A. I. Vogel, *A Textbook of Quantitative Inorganic Analysis, Theory and Practice*, 9th ed., Lowe and Brydone Printers, London, 1948.
18. C. Huang, C. P. Huang, and A. L. Morehart, *Water Res., 25*, 1365 (1991).

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