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J. Tijero[a]; M. J. Martin[a]; F. J. Mirada[a]
[a] DEPARTMENT OF CHEMICAL ENGINEERING, UNIVERSITY OF MADRID, MADRID, SPAIN

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NOTE

The Influence of Sludge Age on Copper (2+) and Chromium (3+) Uptake by Activated Sludge

J. TIJERO, M. J. MARTIN, and F. J. MIRADA*

DEPARTMENT OF CHEMICAL ENGINEERING
UNIVERSITY OF MADRID
28040 MADRID, SPAIN

Abstract

This paper reports the results obtained on Cu^{2+} and Cr^{3+} uptake by activated sludge of 7 and 12 d sludge age. Removal efficiencies of these heavy metals decrease when their initial concentrations increase. For the Cu^{2+}, sludges of lower age adsorb 12% less over the range of the metal concentration added. The Cr^{3+} adsorption was a function of both sludge age and initial concentration. For an initial concentration of 32 mg/L, both sludges gave identical removals. The stability of bound, metal-activated sludge increases when the sludge age increases for Cu^{2+}. The opposite effect has been noted with Cr^{3+}.

INTRODUCTION

The retention of metals by activated sludge during wastewater treatment is a very important process both for the effect it has on microorganisms and because its contribution in reducing this type of contamination.

During biological treatment, insoluble metal species (precipitates) are largely removed by a combination of floculation and settling processes (*1–12*). However, the removal of soluble metal species depends on their affinity for any settleable organic matter within the system (*3–13*).

*To whom correspondence should be addressed.

The organic composition of activated sludge provides bound sites for metals. That binding is carried out by different mechanisms, depending on the metal type.

The behavior of the majority of metals which are removed to a significant extent is related to one of the principal parameters that control the composition of organic matter: The sludge age.

It has been demonstrated (*6–15*) that an increase of sludge age produces a rise of fluvic fraction, mainly responsible for metal removal because of its large number of functional groups. At the same time, an increase of carboxy groups occurs on the polymeric surface of the active biomass (*18*).

Many different factors have been shown to affect the removal of metals in the activated sludge process. Factors related to environmental physicochemical conditions include such operating parameters as pH, ionic strength, concentration of complexing inorganic and organic ligands, and other variables; the biological factor of sludge age, which controls extracellular polymer concentration (type and concentration of ligands); and a factor related to the ion:metal valency and ionic radius have a decisive influence on the interaction capacity (*3*, *18*).

However, there is models that allow prediction of the fate of heavy metals in the activated sludge process. The ones proposed by Nelson (*19*), Sarzanini (*20*), and Rudd, Sterrit, and Lester (*21–23*) stand out for their formulation and predictive character. All of them start from the equilibrium reactions for complex formation and with a series of simplifications that allow conditional complexation parameters, whose values are indicative of the affinity level of ions to the biological sludge, to be obtained. The use of these parameters is limited to conditions identical or very similar to those for which they were determined.

EXPERIMENTAL

This work studies the uptake of Cu^{2+} and Cr^{3+} by activated 7 and 12 day old sludges. The corresponding adsorption isotherms and complexation parameters were also determinated.

Experiments were carried out at 20°C in a discontinuous stirred tank reactor. The samples were taken at regular time intervals until the equilibrium state was reached. 0.5 g/L of activated sludge was used in each experiment. The concentration of metal was in the 2.0–35.0 mg/L range. Heavy metals were incorporated as $CuSO_4$ and $Cr(NO_3)_3 \cdot 9H_2O$ in the required quantity in each experiment. In order to avoid precipitation of the corresponding hydroxides, the pH value was kept at 5. Adjustment of the pH value was made with the acid corresponding to the anion of the salt used in the addition of a metal ion or, otherwise, with NaOH.

Heavy metal analyses were performed on the total volume and on the filtered sample. In the first case the samples were digested with nitric and sulfuric acids (*24*) before metal determination. A IL-357 atomic absorption spectrophotometer was used for all analyses. The difference between the determinations was the metal quantity held by the activated sludge.

The adsorption models tested were the ones proposed by Langmuir, Freundlich, and Prausnitz. The complexation parameters were calculated by means of the models proposed for Nelson, Sarzanini, and Rudd, Sterrit, and Lester. Finally, the activity coefficient (γ), needed to apply the Sarzanini model, was determined by the Debye-Hückel limit law.

RESULTS AND DISCUSSION

Figure 1 shows the results relative to the removal level of metal in terms of the initial concentration for both types of sludges tested (7 and 12 days sludge age).

The degree of removal for Cu^{2+} decreases when the initial metal concentration increases with both sludge ages. For a 7-day sludge age the removal level was 12% below that obtained for a 12-day sludge age in all the concentration ranges tested. However, the highest metal removal level for Cr^{3+} was reached at low metal concentration and a 7-day sludge age. For high metal concentrations, the degree of adsorption does not depend on the sludge age.

This behavior can be explained by considering the role played by ion size in the principal mechanism by which ion removal is carried out: adsorption on the polymeric matrix of the biological sludge.

In this way, Cu^{2+} with an ionic radius of 0.80 Å can form complexes based on carboxy and hydroxy metal binding whereas Cr^{3+}, with a ionic radius of 0.69 Å, is more sterically disabled for the formation of the first binding type because of difficulty in reaching the binding distance. The behavioral differences of both ions in relation to the sludge age is due to an increase of carboxy groups on the polymeric surface when the sludge age is increased.

Figures 2 and 3 collect the experimental results obtained in order to determine the adsorption isotherms. Each figure shows the metal uptake by the activate sludge n (g/kg) in terms of the free metal C_e (mg/L).

They show a characteristic L-shape. The L-curve is indicative of a reduction in the number of available binding sites as the free metal concentration increases, so that the proportion of total metal bound at

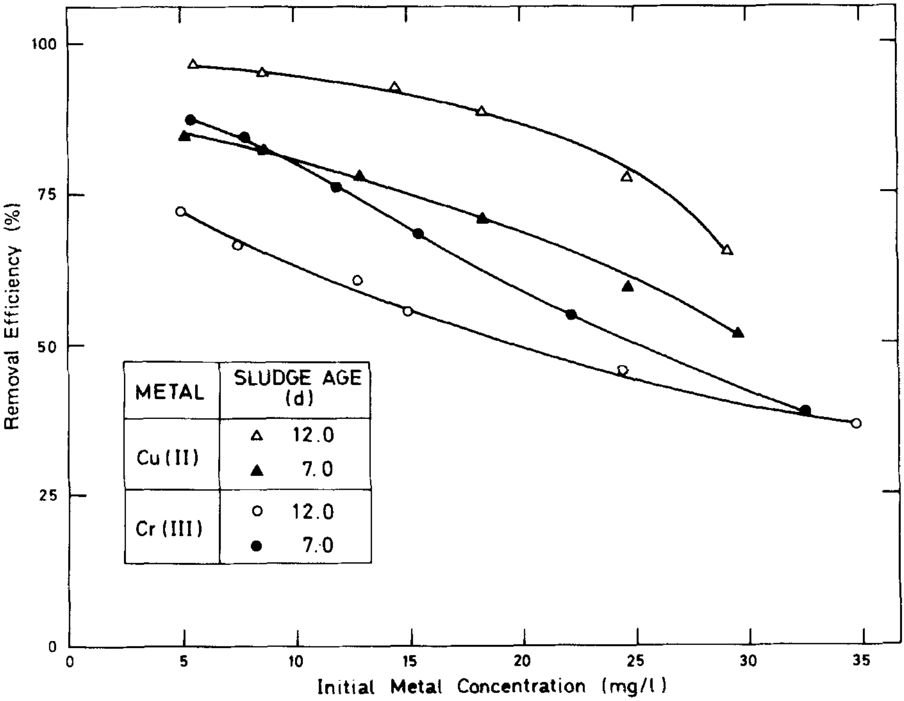

FIG. 1. Metal removal efficiency for two sludge ages.

higher concentrations decreases. Such a phenomenon may be described by the Langmuir isotherm.

The fitting to the adsorption models mentioned above corroborates that the Langmuir model is the best one for reproducing the experimental results, with relative deviations lower than 5% in all cases. The equations obtained by application of that model are listed in Table 1.

The affinity parameters, calculated by means of the three principal models, the conditional stability constant (*K*), and the effective capacity of complexation (*L*) are reported in Table 2.

It is seen that all models agree that there is an increase in binding stability of Cu^{2+}-activated sludge when the sludge age increases. No similar relationship is observed for Cr^{3+} where the highest binding stability appears with the 7-day sludge, and this effect is less than with Cu^{2+}.

The discrepancy of values obtained by different models is due to the different hypotheses they start from, but these values are in total

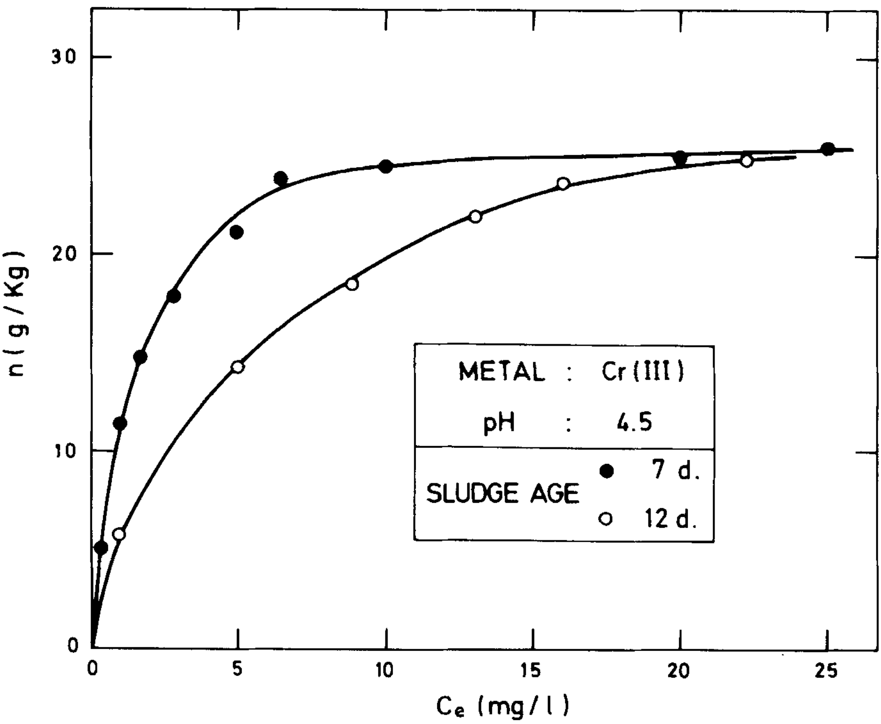

FIG. 2. Adsorption isotherm of Cr^{3+}.

agreement with the ones obtained by other authors when they applied the same model.

The Rudd, Sterrit, and Lester model shows two values of the conditional parameters of complexation determined at high and low metal concentrations. The reason is that these authors consider that the complexation was controlled mainly by stronger binding sites at low

TABLE 1

Metal	θ_c (d)	Equation	Coefficient correlation
Cu^{2+}	7	$1/n = 0.0290 + 0.0658(1/C_e)$	0.994
Cu^{2+}	12	$1/n = 0.0250 + 0.0143(1/C_e)$	0.999
Cr^{3+}	7	$1/n = 0.0368 + 0.0459(1/C_e)$	0.998
Cr^{3+}	12	$1/n = 0.0348 + 0.1486(1/C_e)$	0.998

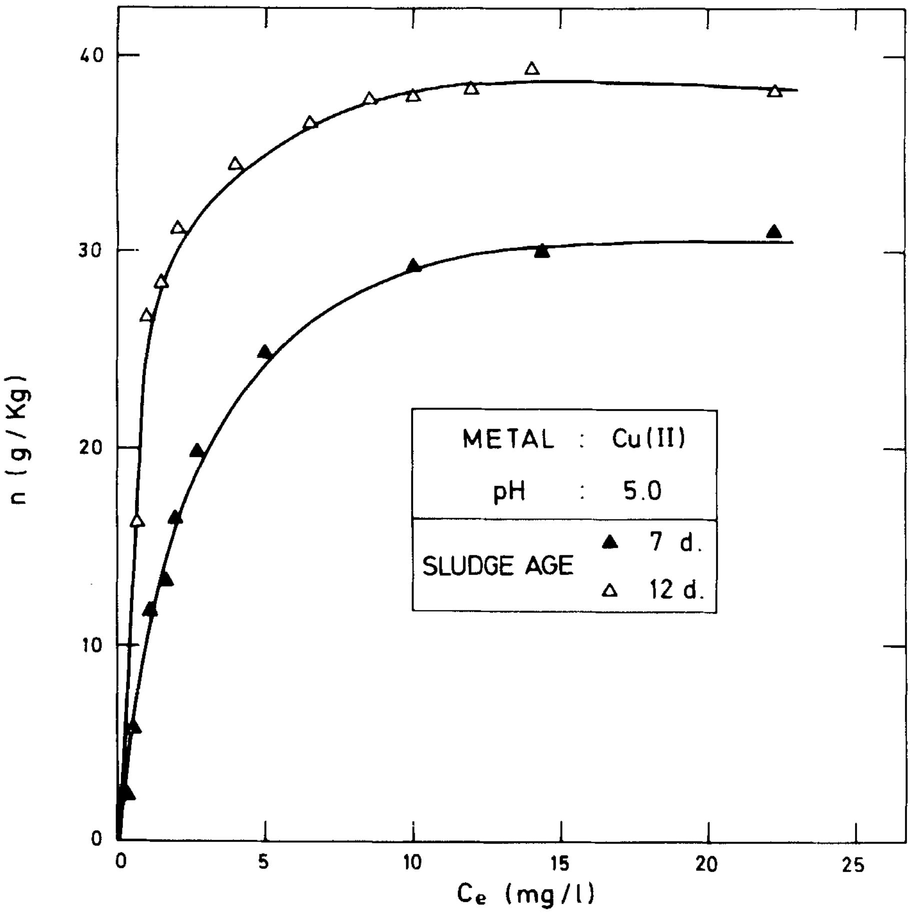

FIG. 3. Adsorption isotherm of Cu^{2+}.

metal concentrations whereas at high metal concentrations the stronger sites became fully occupied and the weaker sites started to affect the complexation, thus causing the decrease seen in the conditional stability constant.

TABLE 2
Complexation Parameters of Systems Cu^{2+}-Activated Sludge and Cr^{3+}-Activated Sludge

Metal	θ_c (d)	lg $K^{a\,d}$	L^a (mmol/g)^d	lg $K^{a\,d}$	L^a (mmol/g)^e	lg K^b	L^b (mmol/g)	lg K^c
Cu	7	7.22	0.038	6.25	0.283	5.99	0.53	7.5
	12	7.90	0.078	6.70	0.315	6.60	0.63	8.1
Cr	7	6.87	0.096	6.14	0.280	6.05	0.52	7.8
	12	6.040	0.164	5.90	0.241	5.50	0.55	7.3

[a]Lester et al. method.
[b]Nelson method.
[c]Sarzanini method.
[d]Low metal concentration.
[e]High metal concentration.

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