

Adsorption kinetics of cadmium chelates on activated carbon

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Abstract

Extensive experiments were performed to investigate the adsorption (equilibrium) isotherms of cadmium on activated carbon in the presence of the following chelating agents: ethylenediaminetetraacetic acid (EDTA), citric acid and nitrilotriacetic acid (NTA). The extent of adsorption was found to be a function of solution pH and cadmium chelate species distribution. A relationship between pH and the parameters of the Freundlich and Langmuir models is discussed.

1. Introduction

Heavy metals such as Cd, Ni, Cu, Zn, etc. are common pollutants found in a variety of industrial wastewaters. Metal plating/metal finishing/metal processing industries are obvious sources of these heavy metals. The wastewaters from these metal industries may contain complexing ions such as ethylenediaminetetraacetate (EDTA), tartrate, ammonia, etc. Activated carbon adsorption has been shown effective for the removal of organic and inorganic pollutants from wastewaters [1–5]. Poor adsorption may be exhibited for heavy metals, but adsorption can be improved substantially with the presence of organic complexing agents [6, 7].

Schindler et al. [8] have reported the adsorption of Fe(III), Cu(II), Cd(II) and Pb(II) onto silica surfaces and developed a model of surface complex formation at the silica–water interface. Elliott and Huang [9] used γ -Al₂O₃, SiO₂ and TiO₂ to remove copper complexed with various ligands. Huang and Ostovic [10] studied the adsorption of Cd(II) with and without ligands (nitrilotriacetic acid (NTA) and EDTA) using three different kinds of activated carbon. The authors proposed a surface complex formation model to describe the adsorption of cadmium ions at the carbon–water interface and observed the improvement of cadmium adsorption in the presence of chelating agents. Huang [11] also conducted an adsorption study dealing with cadmium-containing wastewaters in the presence of the complexing agents:

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tetrafluoroborate and cyanide ions. In this investigation, major factors affecting the extent of removal, such as pH, particle size, mixing rate, carbon types, carbon-to-cadmium ratio, temperature and ionic strength were studied. Benjamin and Leckie [12] proposed a conceptual model for metal–ligand surface interaction during adsorption. The model describes complexed metal–ligand systems as metal-like or ligand-like according to an increasing or decreasing adsorption capacity with respect to pH. Jevtitch and Bhattacharyya [13] studied the effect of surface and species charge on the separation of metal chelates by activated carbon. A relationship between the adsorption capacity, surface charge of activated carbon, and the average species charge for various cadmium ligands system was presented. Bhattacharyya and Cheng [14] also presented activated carbon adsorption equilibrium and kinetics of heavy metal chelates from single and multicomponent systems. An extensive experimental investigation was conducted to establish the adsorption behavior of several metals from single and two metal systems in the presence of complexing agents. The extent of adsorption was found to be a function of metal and ligand types, ligand-to-metal ratio, pH, and metal chelate species distribution. Corapcioglu and Huang [15] investigated the adsorption characteristics of Cu(II), Pb(II), Ni(II) and Zn(II) onto a hydrous activated carbon surface. Carbon type, pH and surface loading are the most important factors affecting the extent of metal removal. Specific

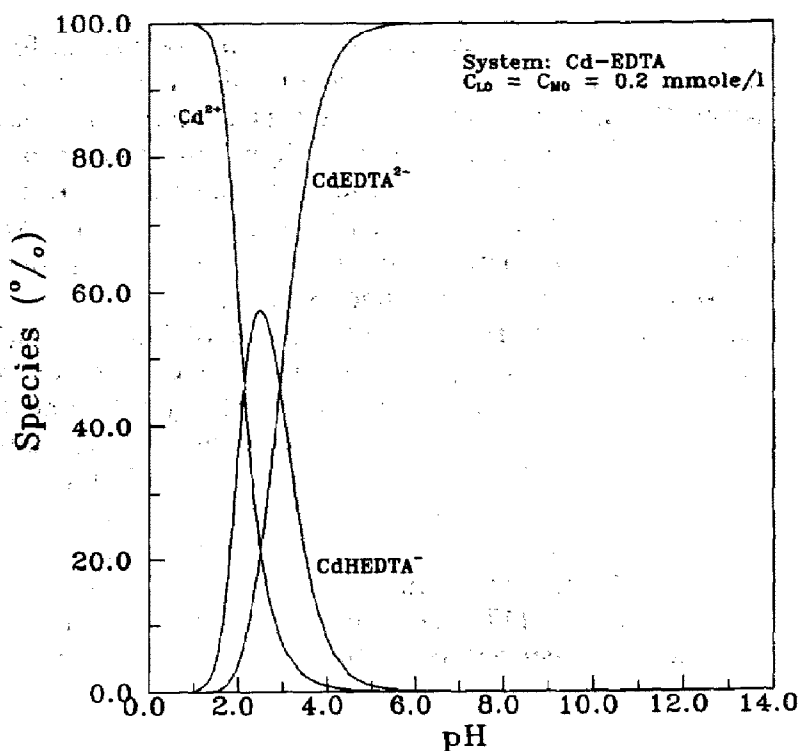


Fig. 1. Species distribution of Cd-EDTA as a function of pH.

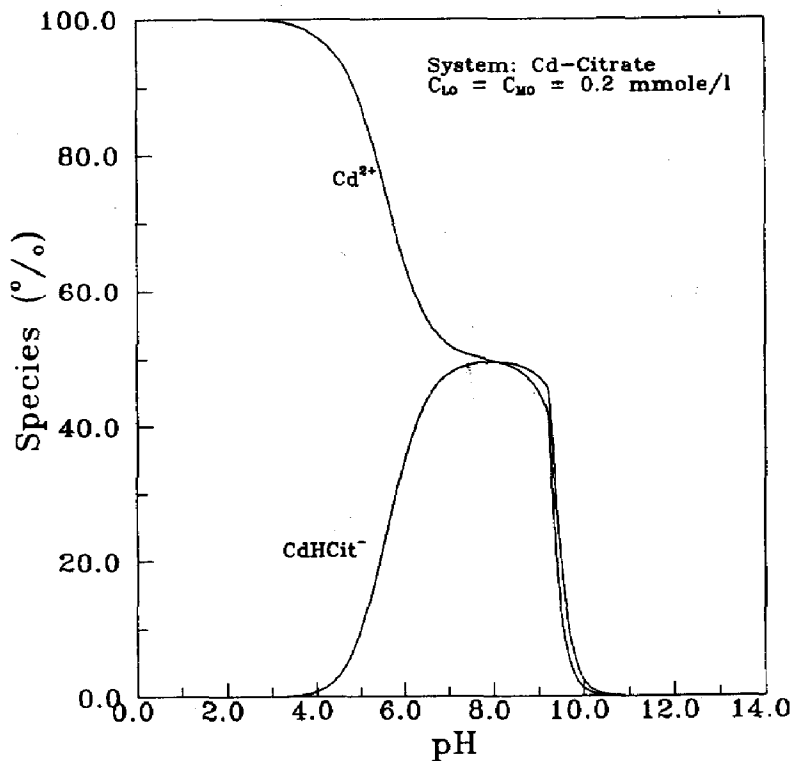


Fig. 2. Species distribution of Cd-citrate as a function of pH.

chemical bonding, probably hydrogen bonding, provided the sole energy needed for adsorption.

The formation and the stability of metal (M)–ligand (L) complexes are influenced by the degree of ionization of the ligand molecules and its functional groups (such as amino, carbonyl, carboxylic, etc.). In solutions containing metal ions and ligands, generally various species may exist at equilibrium such as: ML, ML_2 , MHL, MH_2L , MHL_2 , MH_2L_2 , MOHL, $M(OH)_2L$, and $M(OH)L_2$, etc. In this investigation, the primary interests are in the characteristics of metal–ligand complex formation and their effects on adsorption behavior. The Freundlich and Langmuir isotherms were used to correlate the parameters of models with the solution pH values. Extensive experiments with activated carbon were conducted using cadmium–ligand systems (Cd^{2+} –EDTA, Cd^{2+} –citrate, and Cd^{2+} –NTA). An attempt was made to study the relationship between metal–ligand distribution and solution pH values, and the degree of fit for different equilibrium isotherm models. At low pH solutions, the predominant species in most systems are free metal ions. However, most metal ions form metal chelates at higher pH conditions with chelating agents. Therefore, removal of metal ions by adsorption in the presence of complexing agents is expected to be more effective at the pH ranges where metal ions are chelated. The equilibrium species distribution of Cd–EDTA, Cd–citrate, Cd–NTA as a function of solution pH are shown in Figs. 1–3.

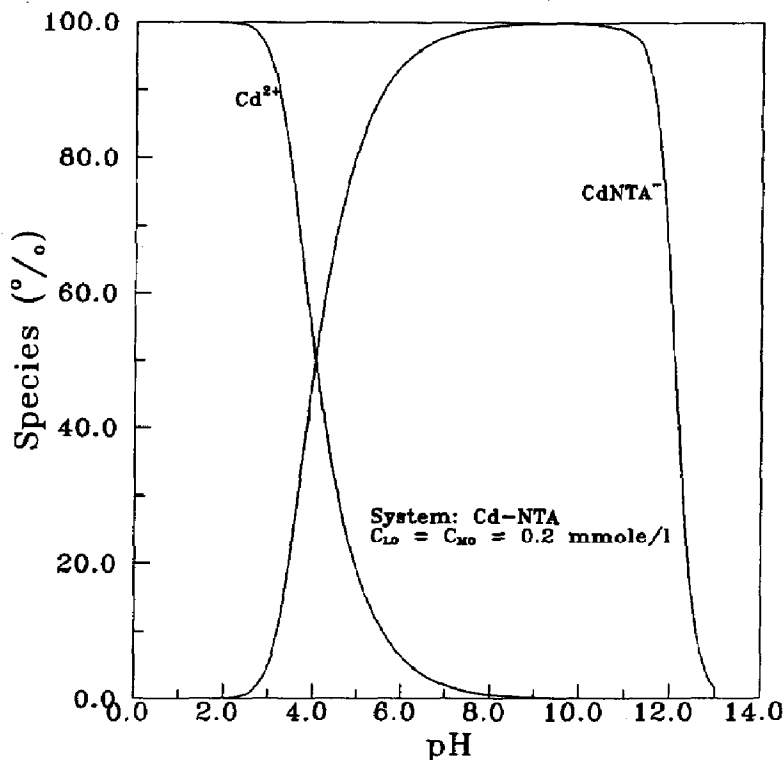


Fig. 3. Species distribution of Cd-NTA as a function of pH.

2. Experimental

Commercial activated carbon Norit PK 3–5 was used as received without further treatment. The characterization of Norit PK 3–5 given by the manufacturer [16] and the pore size distribution of this carbon detected by the Barrett–Joyner–Halenda (BJH) method (Micromeritics ASAP 2000) are shown in Table 1. The surface charge, σ_0 , of the activated carbon was determined by direct titration with NaOH and H₂SO₄. All solutions were prepared from certified reagent grade chemicals. Standard acid and base (1 N H₂SO₄ and NaOH) were prepared fresh every week for pH adjustment. Experimental solutions of cadmium and chelating agents were prepared from 100 mM stock solutions. Stock solutions were prepared fresh every week. All solutions were prepared with double distilled water.

Batch adsorption experiments were performed for all equilibrium studies. Stock metal and chelating agent solutions were diluted to obtain required initial 0.2 mM cadmium–ligand concentrations with 1:1 molar ratio of ligand to metal. A 80 ml sample solution was then transferred to a 250 ml flask. Various amounts of activated carbon were added to the flask. The solutions were mixed using an isothermal shaker bath maintained at 25.0 °C ± 0.5 °C. The pH of the sample solution was adjusted with 1 N NaOH or 1 N H₂SO₄ to preselected pH values. In this investigation, the preselected pH values ranged from 7 to 11.

Table 1
Characterization of activated carbon [17]

Physical properties and specification	NORIT PK 3–5	Pore size distribution average diameter (Å)	Cumulative pore volume (cm ³ /g)
Bulk density (g/l)	250	1664.0	0.021
Ash content (%)	6	1300.5	0.089
Moisture (as packed) (%)	2	1005.1	0.248
Iodine adsorption (mg/g)	800	716.0	0.382
Total pore volume (cm ³ /g)	1.2	306.3	0.409
Surface area (BET) (m ² /g)	750	104.5	0.434
pH value	9–10	65.6	0.470
Particle size:			
> 4.75 mm (%)	2	40.4	0.541
> 4.00 mm (%)	24	32.0	0.577
> 3.40 mm (%)	62	25.3	0.587
> 2.80 mm (%)	90	20.5	0.600
BJH Cumulative desorption pore volume of pores between 17.0 and 3000.0			0.600

Table 2
Nominal experimental condition for the adsorption experiments

System	Concentration range (mM)	Molar ratio (L/M)	pH	Carbon dosage (gm/l)
Cd ²⁺	0.01–0.2	0	1.5–3.5	5–175
Cd–EDTA	0.01–0.2	1	1.5–3.5	5–175
Cd–EDTA	0.01–0.2	1	6.5–11.0	5–112.5
Cd–citrate	0.01–0.2	1	6.5–11.0	1.25–12.5
Cd–NTA	0.01–0.2	1	6.5–11.0	5–112.5

Type of carbon: NORIT PK 3–5.

After mixing for a 24 h period, the equilibrium pH values were measured and recorded. The sample was filtered before dilution and analyses were made. The initial and residual concentrations of cadmium were determined by the atomic adsorption method (Varian Spectra AA-20). Table 2 lists the nominal experimental conditions for the adsorption experiments to be performed in this investigation.

3. Results and discussion

Activated carbon surfaces have been reported in the literature to behave as a diprotic acid after the hydration of the surface functional groups " $\equiv \text{CO}^-$ " [17]. The surface charges of activated carbon are a function of the types of carbon and the dispersed solution characteristics. Since the solution characteristics are a function of ionic strength, this effect must be considered in the surface charge determination. The ionic strength was calculated using species distribution curves. For various experimental systems, the ionic strength varied from 10^{-2} to 10^{-1} M. The surface charge of NORIT PK 3–5 as a function of pH is presented in Fig. 4. The pH of zero point of charge (independent of ionic strength) was found to be 8.20 ± 0.05 .

Cadmium adsorption in the absence of ligand was performed using NORIT PK 3–5 as the adsorbent at 25 °C and pH 1.5, 2.5, and 3.5. Poor adsorption of cadmium was observed and found to be independent of pH. Cadmium ion and activated carbon surface both carry positive charges at low pH values which may explain the poor adsorption of cadmium ion on the surface of the activated carbon. Comparative adsorption experiments were performed with Cd–EDTA and Cd–NTA at 25 °C and pH 1.5 ~ 3.5. The experimental data also show poor adsorption of cadmium and the same behavior as the adsorption of Cd without ligand. Experimental results indicate

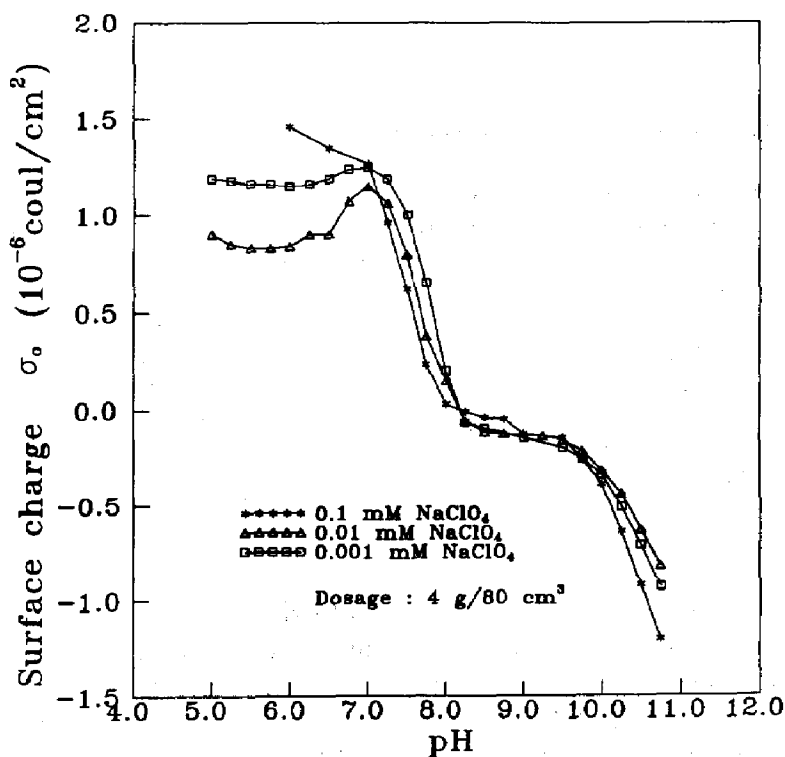


Fig. 4. Effect of pH on surface charge characteristics of activated carbon in single electrolyte solutions.

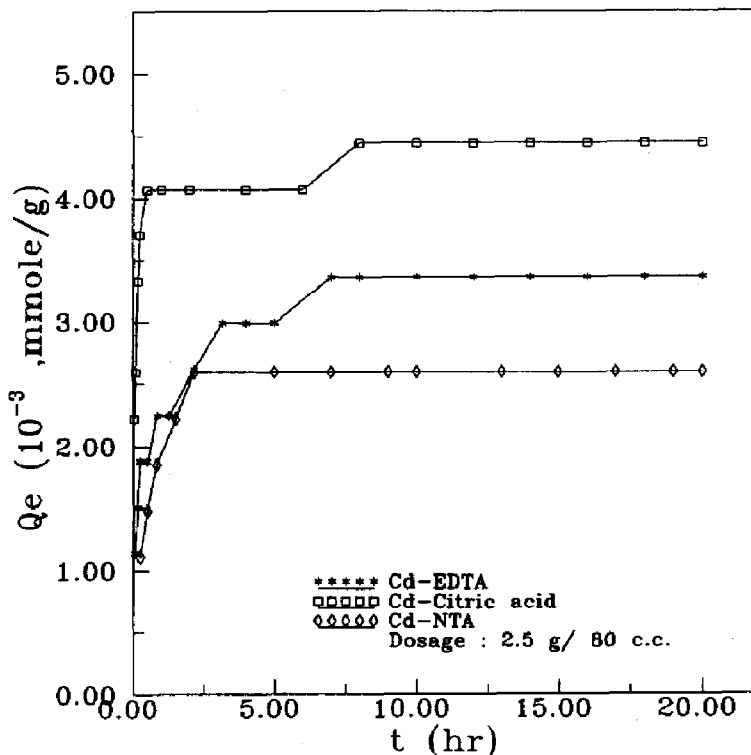


Fig. 5. Effect of ligand type and contact time on removal of cadmium by activated carbon at pH 9.50.

that cadmium hydroxide precipitates for solution pH values greater than 8.0. Thus, adsorption data at higher pH values for cadmium without ligands may not be significant. This result indicates that cadmium ion does not complex with ligands at low solution pH values (such as 1.5–3.5) and was compatible with the product distribution as shown in Fig. 1.

Several experiments were conducted in order to normalize the procedure for the determination of the adsorption isotherm and to study the kinetic behavior. In Fig. 5, the kinetic tests were performed using cadmium–EDTA, cadmium–citrate and cadmium–NTA solutions. The solution pH was controlled during the kinetic experiment at 9.40–9.50. The results shown in Fig. 5 clearly indicate that no significant changes in adsorption occur after 8 h of contact time for these investigated systems and the removal of cadmium is highly dependent on the type of ligand.

The rates of cadmium–ligand complex uptake by activated carbon were discussed in the light of the adherence of the metal–ligand complex with the functional groups of activated carbon as well as its intraparticle diffusion within the pores of the adsorbent. The removal of Cd–ligand complexes is assumed to follow a first-order rate expression [18], according to the relationship:

$$\log(Q_e - Q) = \log Q_e - (Kt/2.303), \quad (1)$$

where, Q_e is the amount adsorbed at equilibrium and Q is the amount adsorbed at time t . The rate constants of adsorption, K , were calculated from slopes of the linear

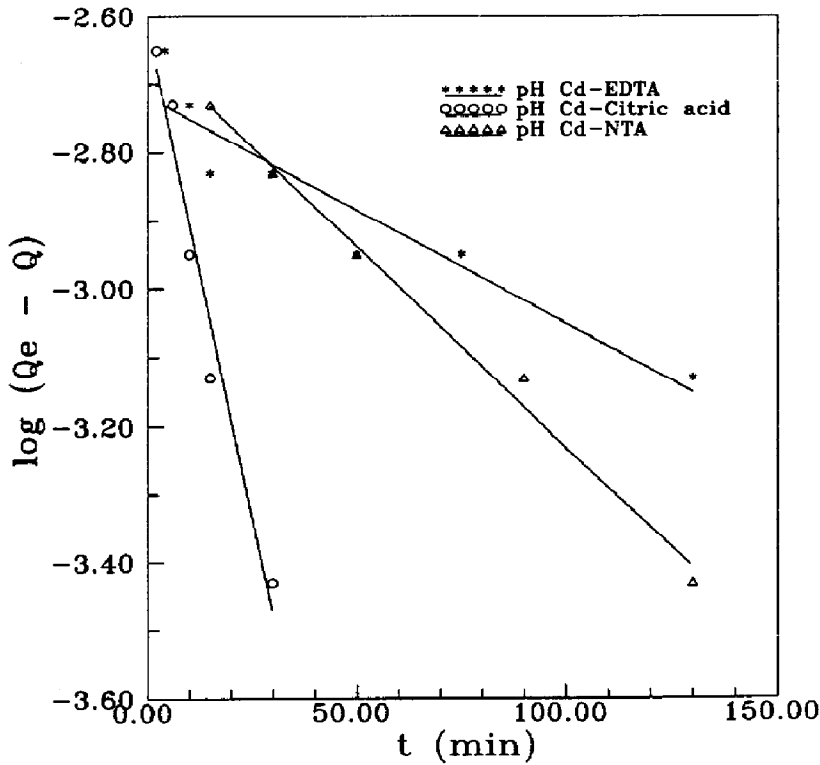


Fig. 6. Plot for rate constants of adsorption at 25°C, pH 9.50 for different Cd-ligand type, based on the first-order reaction kinetics.

plots of $\log(Q_e - Q)$ versus t (Fig. 6) and found to be 6.56×10^{-2} , 7.68×10^{-3} and $1.35 \times 10^{-2} \text{ min}^{-1}$ for Cd-citrate, Cd-EDTA, and Cd-NTA at 25°C, respectively.

The mass transfer coefficient, β_1 , for the adsorption of cadmium on activated carbon was determined using the following relationship [18]:

$$\ln(C_t/C_0 - 1/(1 + mK_c)) = \ln(mK_c/1 + mK_c) - (1 + mK_c)/mK_c \beta_1 S_s t \quad (2)$$

where C_0 is the initial concentration of Cd-L complex, C_t is the Cd-L complex concentration after time t , m is the mass of activated carbon per unit volume of particle free solution, K_c the product of Langmuir constants Q^0 and b , and S_s the outer surface of activated carbon per unit volume of solution. The values of mass transfer coefficients were calculated from the slopes and intercepts of the straight line plots of $\ln[(C_t/C_0) - 1/(1 + mK_c)]$ versus t as shown in Fig. 7 and were tabulated in Table 3.

The Freundlich and Langmuir equations are used to correlate the experimental equilibrium data of Cd-ligand adsorption on activated carbon for an initial cadmium concentration of 0.2 mM and activated carbon amounts ranging from 0.4 to 9 g per 80 mL solution. The values of Freundlich and Langmuir parameters are summarized in Tables 4 and 5, respectively, with relatively good applicability. It was found that the highest adsorption capacity was obtained for the Cd-citrate system. Cd-EDTA and Cd-NTA have similar adsorption capacities on activated carbon.

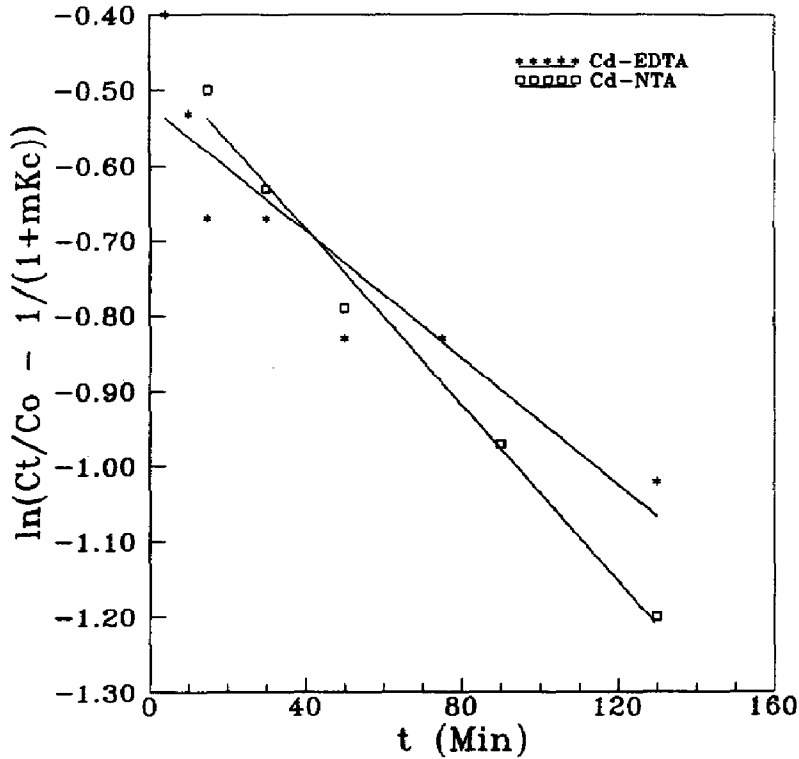


Fig. 7. Mass transfer plot for the adsorption of Cd-EDTA and Cd-NTA at 25°C, pH 9.50.

Table 3
Mass transfer coefficients at 25°C for Cd-EDTA and Cd-NTA systems

System	pH	β_1 (cm/min)	r^a
Cd-EDTA	9.50	1.1×10^{-8}	0.923
Cd-NTA	9.50	1.6×10^{-8}	0.994

^a Correlation coefficient.

The experimental results indicate that Cd-EDTA and Cd-NTA systems show no precipitation of cadmium even at pH close to 11. This represents the complete complexation of cadmium with ligands and is compatible with the species calculation as shown in Figs. 1 and 3. The adsorption capacity of Cd-EDTA, Cd-citrate, and Cd-NTA were determined on NORIT PK 3–5 for various solution pH values to study species and charge influence on adsorption.

The predominant cadmium specie is $\text{Cd}(\text{EDTA})^{-2}$ for solution pH greater than 6.0, better adsorption should occur between pH 6.0–9.0. The experimental results indicate that the poorest adsorption was obtained for pH in the range 10.70–10.80. At

Table 4
Freundlich constants at different pH values for Cd–ligand systems

System	pH	K_a (mmol/g)	1/n	r^a
Cd–EDTA	6.9 ± 0.1	0.0139	0.24	0.995
Cd–EDTA	7.9 ± 0.1	0.0138	0.32	0.964
Cd–EDTA	8.85 ± 0.05	0.0256	0.64	0.979
Cd–EDTA	9.55 ± 0.05	0.0048	0.17	0.948
Cd–EDTA	10.75 ± 0.05	0.0072	0.45	0.996
Cd–citrate	6.90 ± 0.05	0.0656	0.52	0.978
Cd–citrate	8.80 ± 0.05	0.2013	0.70	0.992
Cd–NTA	6.90 ± 0.05	0.0216	0.45	0.992
Cd–NTA	8.80 ± 0.05	0.0268	0.60	0.985
Cd–NTA	9.50 ± 0.05	0.040	0.71	0.994
Cd–NTA	10.75 ± 0.05	0.043	0.75	0.991

^a Correlation coefficient.

Table 5
Langmuir constants at different pH values for Cd–ligand systems

System	pH	Q^0 (mmol/g)	b (l/mmol)	r^a
Cd–EDTA	6.9 ± 0.1	8.39×10^{-3}	94.22	0.995
Cd–EDTA	7.9 ± 0.1	7.89×10^{-3}	51.23	0.996
Cd–EDTA	8.85 ± 0.05	8.72×10^{-3}	16.74	0.970
Cd–EDTA	9.55 ± 0.05	3.64×10^{-3}	81.52	0.992
Cd–EDTA	10.75 ± 0.05	3.51×10^{-3}	27.08	0.994
Cd–citrate	6.90 ± 0.05	0.0256	2.71	0.988
Cd–citrate	8.80 ± 0.05	0.0780	9.92	0.885
Cd–NTA	6.90 ± 0.05	7.54×10^{-3}	65.87	0.996
Cd–NTA	8.80 ± 0.05	0.0103	17.21	0.990
Cd–NTA	9.50 ± 0.05	0.0116	14.32	0.975
Cd–NTA	10.75 ± 0.05	0.0130	10.67	0.894

^a Correlation coefficient.

that pH the surface charge of the activated carbon is negative and repulses Cd(EDTA)²⁻ anions. The adsorption capacity of cadmium was observed to increase at lower pH values 6–9. At this pH range the surface charge of the activated carbon is more positive and the positive surface charges increase with the decreasing pH values. Owing to the stronger attraction forces existing between the negatively charged species Cd(EDTA)²⁻ and the more positively charged surface sites, the adsorption capacity of cadmium was observed to increase at lower pH. The same results were observed in the study of Jevtitch and Bhattacharyya [13]. Meanwhile in the work of

Bowers and Huang for the adsorption of Cu–EDTA onto γ - Al_2O_3 also showed this similar tendency [19].

The adsorption of Cd–citrate was performed at various solution pH levels from 6 to 10. The maximum removal of cadmium was found at pH 9.40–9.50, because cadmium precipitates as $\text{Cd}(\text{OH})_2$ even in the presence of citrate as solution pH greater than 9.0. A higher adsorption of Cd–citrate complex was observed at pH 8.75–8.85 than pH 6.85–6.95. The surface sites of activated carbon are more positively charged with the decreasing pH values. However, the higher degree of the partial complexation of metal–ligand makes the more Cd^{2+} cations existing and results in a lower adsorption capacity with decreased pH values. The similar adsorption tendency was obtained in the investigation of Jevtitch and Bhattacharyya [13].

The adsorption of Cd–NTA was studied for four different pH values: 6.85–6.95, 8.80–8.90, 9.45–9.55 and 10.70–10.80. The higher cadmium removal of $\text{Cd}(\text{NTA})^-$ complex was obtained at pH 10.70–10.80 may be due to the partial precipitation of cadmium hydroxide. The adsorption of cadmium was observed to be better at pH 8.80–8.90 than at pH 6.85–6.95. According to the calculation of species distribution, both Cd^{2+} and $\text{Cd}(\text{NTA})^-$ species are present for $\text{pH} < 8.0$, and the Cd^{2+} concentration increased with decreasing solution pH. The positive charged surface of the activated carbon repulsing Cd^{2+} cations results in the lower adsorption of cadmium at lower pH. This characteristic electrostatic interaction between the surface sites and the species was also shown in the study of Elliot and Huang [9] for the adsorption of Cu^{2+} –NTA onto the γ - Al_2O_3 system.

4. Conclusion

It is clear that chelate formers, such as EDTA, citric acid, and NTA, can greatly enhance cadmium adsorption due to the formation of cadmium chelate species in the solution. Adsorption equilibrium of these chelates can be explained by species charge and carbon surface charge characteristics. The surface charge of the activated carbon is a function of solution pH values. The species distribution is highly dependent on solution pH as well as type and amount of chelating agent present. The effectiveness of adsorption decreases for a metal–ligand anion at higher pH values when the surface of the activated carbon becomes negatively charged. With the lower pH values, the opposite effect is observed. Meanwhile as a metal–ligand anion adsorbed on the positive sites of the activated carbon, the positive surface charges decrease simultaneously and thus enhance the adsorption of Cd^{2+} . This adsorption characteristics was observed in the adsorption of Cd^{2+} –EDTA. However, for the Cd^{2+} –citrate and Cd^{2+} –NTA these two metal complexes, a lower adsorption was observed with the decreasing pH values in the pH levels from 6 to 9. This is because at lower pH values and the species concentration (0.2 mM), the increasing degree of partial complexation of cadmium with citrate and NTA with the decreasing pH levels results in the concentration of Cd^{2+} cations increase. The stronger repulsive forces between the more positively charged surface sites and the increased Cd^{2+} cations results in the adsorption capacity of cadmium decrease at lower pH values. Several attempts made

to correlate the adsorptive capacity of Cd^{2+} with charge parameters do not obtain any satisfactory relationship. It will be the purpose in the latter work.

Meanwhile, a certain adsorption of Cd^{2+} complexes of EDTA was observed at $\text{pH} > \text{pH}_{zpc}$. This suggests the presence of specific chemical interaction between the chelated heavy metals and the surface groups on the activated carbon. The surface groups may interact with the chelated heavy metal by the formation of an electron donor–accepter complex of the chelate and the active sites. Although, the exact mechanism between the chelated heavy metals and the surface groups is quite complex, more work needs to be done. However, the experimental results indicate that the charge barrier between the carbon surface and solute species plays a predominant role during adsorption.

5. Nomenclature

b	Langmuir constant (l/mmol)
C_0	the initial concentration of Cd–L complex (mM)
C_t	the Cd–L complex concentration after time t (mM)
K	the rate constant of adsorption (min^{-1})
K_a	Freundlich constant (mmol/g)
K_c	the product of Langmuir constants Q^0 and b
m	the mass of activated carbon per unit volume of particle free solution (g/l)
$1/n$	Freundlich constant
Q	the amount adsorbed at time t (mmol/g)
Q_c	the amount adsorbed at equilibrium (mmol/g)
Q^0	Langmuir constant (mmol/g)
S_s	the outer surface of activated carbon per unit volume of solution (m^2/l)
t	the experimental time (min or h)
β_1	the mass transfer coefficient (cm/min)
σ_0	the surface charge of the activated carbon (C/cm^2)

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