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Effect of the impregnation of carbon cloth with ethylenediaminetetraacetic acid on its adsorption capacity for the adsorption of several metal ions

Abbas Afkhami *, Tayyebeh Madrakian, Azadeh Amini, Ziba Karimi

Faculty of Chemistry, Bu-Ali Sina University, Hamadan 65174, Iran

Abstract

Effect of loading of C-cloth with ethylenediaminetetraacetic acid (EDTA) on the adsorption capacity for the adsorption of several metal cations was studied. The concentration of ions in the solution was monitored using atomic absorption spectrometry. The adsorption isotherm data for the cations were derived at 25 °C and treated according to Langmuir and Freundlich models and was found that for most of the investigated cations Langmuir model was more successful. Adsorption capacities determined from Langmuir isotherms. Loading of the adsorbent with EDTA increased the adsorption capacity for the adsorption of all of the investigation ions.
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1. Introduction

The transition metals and their ions are of particular interest in many application areas. Environmental contamination due to heavy metals is caused by several industries, metal plating, mining, painting, and car radiator manufacturing, and also by agricultural sources such as fertilizers and fungicidal sprays [1]. Therefore, removal or modification of these ions from wastewaters and ground waters is of significant importance from an environmental point of view.

Different technologies have been developed to remove metal ions species from waters: precipitation, ion exchange, membrane separation, but adsorption has been shown to be an economical alternative for removing trace metals from water [2–5]. Activated carbon is used as an inert porous carrier material for distributing chemicals on the large hydrophobic internal surface, thus making them accessible to reactants. Activated carbon materials are versatile adsorbents that can be applied in both gas and liquid phase applications due to their excellent physical and chemical properties. Activated carbons can adsorb small but significant quantities of metal species from aqueous solutions. High-area carbon cloth, which has the advantage of having a very

large specific surface area, e.g., $2500 \, \text{m}^2 \, \text{g}^{-1}$, has been used for the successful adsorptive removal of various chemical species [6–15].

With regard to the characteristics of the adsorbent, its surface chemistry has been recognized as a key parameter in the control of the adsorption process [16–18]. The adsorption capacity and adsorption kinetics depend on the surface properties of adsorbent. To increase the potentially low adsorption capacity of any adsorbent, a number of modifications including immobilization of a chelating agent on the adsorbent surface have been employed [19]. The adsorption capacities and the feasible removal rates must be substantially boosted by the modification techniques.

Ethylenediaminetetraacetic acid (EDTA) is the most widely used of the aminopolycarboxylic acids. EDTA is a chelating agent, forming coordination compounds with most monovalent, divalent, trivalent and tetravalent metal ions. It combines with metal ions in a 1:1 ratio regardless of the charge on the cation.
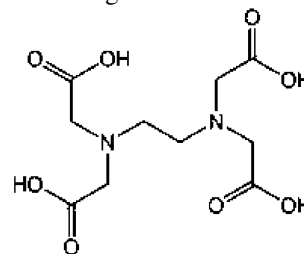
* Corresponding author. Fax: +98 811 8272404.
  E-mail address: afkhami@basu.ac.ir (A. Afkhami).

The aim of this work is to investigate the effect of loading of C-cloth with chelating agent EDTA on the adsorption capacity of C-cloth for the adsorption of metal cations.

2. Experimental

2.1. Reagents

The C-cloth used in this work was obtained from Spectra Corp., coded as Spectracarb 2225 having a specific area of $2500\,m^2\,g^{-1}$. $Cu(NO_3)_2 \cdot 3H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $Bi(NO_3)_3 \cdot 5H_2O$, $CoCl_2 \cdot 6H_2O$, $SnCl_4 \cdot 5H_2O$, $Pb(NO_3)_2$, $AgNO_3$, $NiCl_2 \cdot 6H_2O$, $Cd(NO_3)_2 \cdot 4H_2O$, $Sr(NO_3)_2$, $K(SbO)C_4H_4O_6$, $O.5H_2O$, $Fe(NO_3)_3 \cdot 6H_2O$ and Na_2EDTA were reagent grade materials. Triply distilled deionized water was used for making up the test solutions from which adsorption at the C-cloth was measured.

2.2. Treatment of C-cloth

It is well known [5,6,12–15] that Spectra Corp. C-cloth initially contained some traces of elutable ions as indicated by conductometric measurements. Hence, a deionization cleaning procedure was applied to avoid desorption of ions during adsorption studies [6]. A ~2 g C-cloth sample was first placed in a flow-through washing cup and eluted with a total of 5 L of warm (60 °C) conductivity water in a kind of batch operation over 2 days. Nitrogen gas was bubbled continuously through the washing cup to avoid possible adsorption of CO_2 that might have been dissolved in the water. The out-flow water from each batch was tested conductometrically for completeness of the washing procedure. The washed C-cloth modules were then dried under vacuum at 120 °C and kept in a desiccator for further uses. For the impregnation of C-cloth with EDTA, the C-cloths were submersed in a $0.15\,mol\,L^{-1}$ Na_2EDTA solution for 1 h. The C-cloth was then washed with triply distilled deionized water and used. The loaded C-cloth was tested for leaching EDTA. A piece of C-cloth was place in distilled water and EDTA concentration was monitored spectrophotometrically. The results showed that leaching EDTA is negligible.

2.3. Determination of adsorption isotherms

The adsorption isotherms of the investigated cations on the carbon cloth were determined on the basis of batch analysis. Carbon cloth pieces were allowed to equilibrate with solutions of cations with known initial concentrations. The concentrations after the equilibration period were measured by flame atomic absorption spectrometry. The amount of each cation adsorbed per unit mass of adsorbent, N_f, was calculated by the following equation:

$$N_f = \frac{V(C_0 - C_s)}{m} \tag{1}$$

where V is the volume of the solution of cations in L, C_0 and C_s the initial and equilibrium concentrations, respectively, in

$mmol\,L^{-1}$ and m is the mass of carbon cloth in g. Then Eq. (1) gives N_f in mmol adsorbate adsorbed per g carbon cloth.

3. Results and discussion

3.1. Adsorption behavior of cations

Adsorption of each ion was investigated separately. Ions from solutions with different concentrations of cations were allowed to become adsorbed on the C-cloth. Adsorption of the ions Co^{2+}, Cu^{2+}, Bi^{3+}, Fe^{3+}, Pb^{2+}, Sn(IV), Zn^{2+}, Ag^+, Cd^{2+}, Ni^{2+}, Sr^{2+}, and Sb^{3+} on both the unmodified carbon cloth (adsorbent I) and EDTA loaded C-cloth (adsorbent II) was studied. Figs. 1 and 2 show several typical diagrams for the variation in the concentration of cations with time. The decrease in the concentration of ions with time is due to their adsorption on C-cloth. As Figs. 1 and 2 show the rate of adsorption on adsorbent II is faster than that on adsorbent I. The figures also show that the amount of cations adsorbed on adsorbent II after 60 min is greater than that
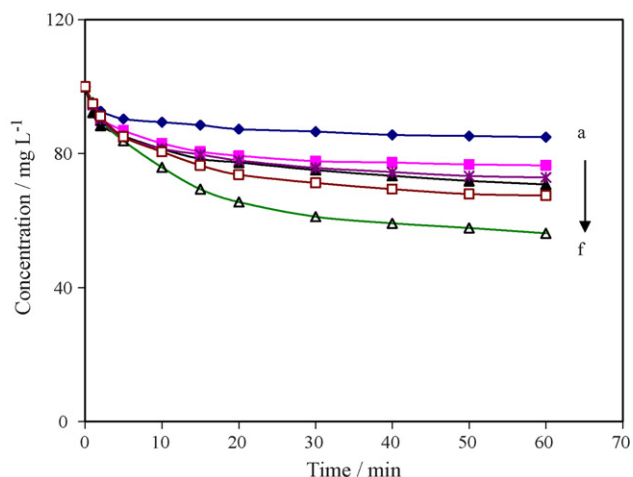

Fig. 1. Adsorption behavior of (a) Co(II), (b) Cu(II), (c) Bi(III), (d) Fe(III), (e) Pb(II) and (f) Sn(IV) on adsorbent I.
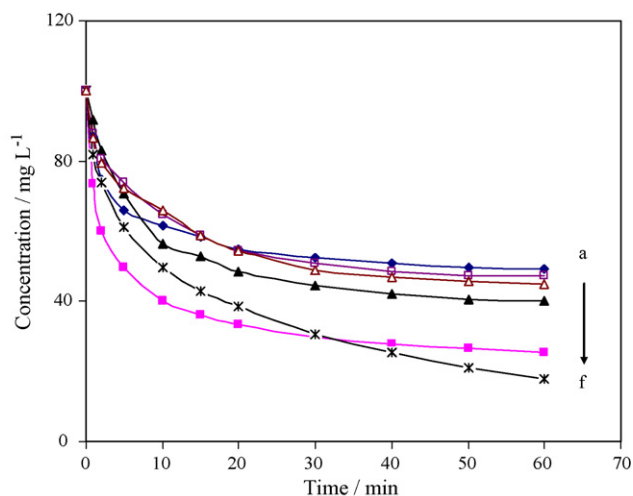

Fig. 2. Adsorption behavior of (a) Co(II), (b) Pb(II), (c) Sn(IV), (d) Fe(III), (e) Cu(II) and (f) Bi(III) on adsorbent II.

adsorbed on adsorbent I. The concentration of Co^{2+}, Cu^{2+}, Bi^{3+}, Fe^{3+}, Pb^{2+} and $Sn(IV)$ in the solution decreased only by 15, 24, 27, 29, 33 and 44% of their initial concentrations, respectively, by adsorption at adsorbent I after 60 min. But their concentration decreased by 51, 74.5, 82, 60, 53 and 55% for Co^{2+}, Cu^{2+}, Bi^{3+}, Fe^{3+}, Pb^{2+} and $Sn(IV)$, respectively, by adsorption on adsorbent II after 60 min. This indicates loading of EDTA on C-cloth caused a significant increase in the adsorption rate and adsorption capacity of adsorbent for the adsorption of all the investigated cations.

The oxygenated groups including –OH groups and lactone groups are present in the C-cloth surface [20,21]. Adsorption of the cations on unmodified C-cloth might occur due to surface complex formation and exchange between metal ions and acidic functional groups according to the equation:

$$n(\equiv S\text{--}OH) + M^{n+} \leftrightarrow (\equiv S\text{--}O)_n M + nH^+ \qquad (2)$$
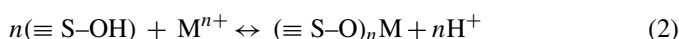
However, these groups cover only a small fraction of the carbon surface area. Modification of carbon with EDTA increases the number of active sites and thus increases the covered surface area.

When a modifier is immobilized at the surface of activated carbon, the removal mechanism changes. The impurities are not only removed by adsorption on the surface of the plain carbon but it could be removed by a surface attraction/chemical bonding phenomenon on the newly added chemicals. The chemical formula of EDTA consists of hydrophobic and ionic groups. The hydrophobic groups were adsorbed onto the surface of activated carbon while the ionic groups rest in the bulk solution and act as chelating group. Metal ions are sorbed due to chelation via the N and COO^- groups.

3.2. Adsorption isotherms

The adsorption isotherms for some investigated ions from water on both C-cloths are shown in Figs. 3 and 4. The number of mmol adsorbed per gram of adsorbent (N_f) *versus* the equilibrium concentration of cations are illustrated. The isotherm data were treated according to Langmuir and Freundlich equations [22].
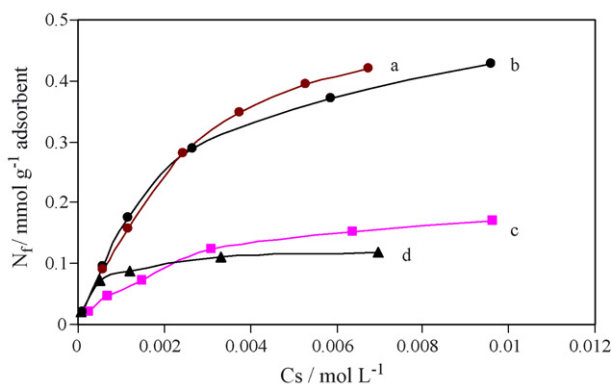
Fig. 3. Adsorption isotherms at 25 °C for adsorption of (a) Cu(II), (b) Fe(III), (c) Co(II) and (d) Cu(II) on adsorbent I.
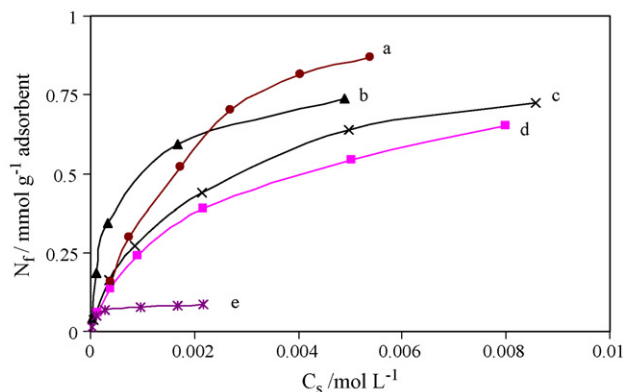
Fig. 4. Adsorption isotherms at 25 °C for adsorption of (a) Sn(IV), (b) Cu(II), (c) Fe(III), (d) Co(II) and (e) Pb(II) on adsorbent II.

Langmuir's model does not take into account the variation in adsorption energy, but it is the simplest description of the adsorption process. It is based on the physical hypothesis that the maximum adsorption capacity consists of a monolayer adsorption, that there are no interactions between adsorbed molecules, and that the adsorption energy is distributed homogeneously over the entire coverage surface.

The general form of Langmuir isotherm is

$$\frac{N_f}{N_s} = \frac{KC_s}{(1 + KC_s)} \qquad (3)$$

where K is a constant and C_s is the equilibrium concentration of the cation solution, N_f represents the number of mmol of cation adsorbed per gram of adsorbent (mmol g^{-1}) at equilibrium concentration, C_s, and N_s is the maximum amount of solute adsorbed per gram of surface (mmol g^{-1}) which depends on the number of adsorption sites. The Langmuir isotherm shows that the amount of cations adsorbed increases as the concentration increases, up to a saturation point. As long as there are available sites, adsorption will increase with increasing cation concentrations, but as soon as all of the sites are occupied, a further increase in concentrations of cations does not increase the amount of cations on adsorbents.

After linearization of the Langmuir isotherm, Eq. (3), we obtain:

$$\frac{C_s}{N_f} = \left(\frac{C_s}{N_s}\right) + \left(\frac{1}{KN_s}\right) \qquad (4)$$

The parameters of this equation for the investigated cations were calculated and are given in Tables 1 and 2.

The Freundlich empirical model is represented by

$$N_f = K_f C_s^{1/n} \qquad (5)$$

where C_s is the equilibrium concentration (mmol L^{-1}), N_f the amount adsorbed at equilibrium (mmol g^{-1}), and K_f (mmol$^{1-1/n}$ L$^{1/n}$ g^{-1}) and $1/n$ are Freundlich constants depending on the temperature and the given adsorbent–adsorbate couple. n is related to the adsorption energy distribution, and K_f indicates the adsorption capacity.

Table 1
Parameters of Langmuir and Freundlich isotherm equations, regression coefficients (r) and normalized percent deviation (P) for the adsorption of metal cations on adsorbent I at 25 °C

Cation	Langmuir					Freundlich			
	N_s (mmol/g)	K (L/mol)	r	P	ΔG (kJ/mol)	K_f (mmol/g^{-1}) (L mmol)$^{1/n}$	$1/n$	r	P
Bi^{3+}	0.0908	3298.97	0.9997	1.75	19.87	2.039	0.500	0.9603	21.14
Cd^{2+}	0.168	76.68	0.9991	6.36	10.72	0.172	0.0502	0.9749	6.53
Co^{2+}	0.2162	382.54	0.9987	2.66	14.59	3.083	0.5896	0.9848	6.05
Ag^+	1.320	12.93	0.9996	5.56	6.34	1.52	0.326	0.9623	10.95
Cu^{2+}	0.1271	2084.98	0.9998	2.77	18.74	1.103	0.4027	0.9502	19.58
Ni^{2+}	0.3201	7.14	0.9977	16.29	8.85	0.282	0.0732	0.9555	3.14
Fe^{3+}	0.5430	384.10	0.9990	3.17	14.60	13.020	0.6777	0.9781	20.64
Sb^{3+}	0.933	11.82	0.9997	3.28	6.11	0.866	0.0376	0.9502	6.23
Sn^{4+}	0.6527	284.95	0.9961	2.89	13.86	11.719	0.6423	0.9879	7.65
Sr^{2+}	0.3011	21.37	0.9987	3.85	7.58	0.273	0.1080	0.9985	1.62
Pb^{2+}	0.0451	10631	0.9997	6.04	22.28	0.328	0.3045	0.9541	12.96
Zn^{2+}	0.3940	250.22	0.9984	4.39	13.54	13.202	0.7638	0.9939	8.94

Table 2
Parameters of Langmuir and Freundlich isotherm equations, regression coefficients (r) and normalized percent deviation (P) for the adsorption of metal cations on adsorbent I at 25 °C

Cation	Langmuir					Freundlich			
	N_s (mmol/g)	K (L/mol)	r	P	ΔG (kJ/mol)	K_f (mmol/g^{-1}) (L mmol)$^{1/n}$	$1/n$	r	P
Bi^{3+}	0.441	4201.52	0.9986	5.80	20.46	40.77218	0.6471	0.9891	16.46
Cd^{2+}	0.348	172.07	0.9990	4.03	12.72	0.358	0.081	0.9759	10.05
Co^{2+}	0.797	493.042	0.9986	1.00	15.21	12.87001	0.5897	0.9985	11.57
Ag^+	1.910	10.11	0.9995	29.23	5.73	6.190	0.830	0.9770	12.74
Cu^{2+}	0.6983	2349.94	0.9993	5.14	19.04	15.794	0.5197	0.9585	27.98
Ni^{2+}	0.961	10.83	0.9990	1.64	5.89	0.753	0.342	0.9532	16.18
Fe^{3+}	0.864	576.39	0.9981	5.38	15.59	17.604	0.6189	0.9795	19.371
Sb^{3+}	1.476	58.91	0.9990	3.70	10.09	1.133	0.1253	0.9751	22.70
Sn^{4+}	1.329	377.07	0.9962	2.78	14.55	29.928	0.6513	0.9872	9.07
Sr^{2+}	1.980	36.94	0.9979	5.11	8.91	1.470	0.163	0.9902	2.22
Pb^{2+}	0.0886	10190.2	0.9999	3.18	22.83	0.967	0.3632	0.9506	22.73
Zn^{2+}	0.401	463.39	0.9952	5.80	15.056	11.12728	0.6775	0.9895	14.66

The linearized form of Freundlich adsorption isotherm equation is

$$\ln N_f = \ln K_f + \left(\frac{1}{n}\right) \ln C_s \qquad (6)$$

The parameters of this equation for the investigated cations were calculated and are given in Tables 1 and 2.

Among the studied cations, the adsorption capacity of two adsorbents I and II for the adsorption of Zn^{2+} was the same. The ratio of adsorption capacity of adsorbent II to the investigated cations, except for Zn^{2+}, to that of adsorbent I was in the range 1.4–6.6. The increase in the adsorption capacity for EDTA loaded C-cloth was expected, because as described above, modification of carbon cloth with EDTA increases the covered surface area. The increase in covered surface area also chelate formation between EDTA and metal ions can increase the adsorption capacity. Loading of the adsorbent with EDTA increased the adsorption capacity for the adsorption of Ag^+, Sb^{3+}, Fe^{3+}, Pb^{2+}, Sn^{4+}, Cd^{2+}, Ni^{2+}, Co^{2+}, Bi^{3+}, Sr^{2+} by the factors of 1.45, 1.58, 1.59, 1.96, 2.04, 2.07, 3.00, 3.69, 4.86, 5.49, 6.58, respectively (Fig. 5).

Tables 1 and 2 also show the values of correlation coefficient, r, for the fit of experimental isotherm data to Langmuir and Freundlich equations. The values of correlation coefficients are all close to each other and are mostly >0.95. Therefore, it is very difficult to decide which model represents the experimental data better on the basis of values of regression coefficients. There are also several reports in the literature that the correlation coefficients for fitting of adsorption data to both Langmuir
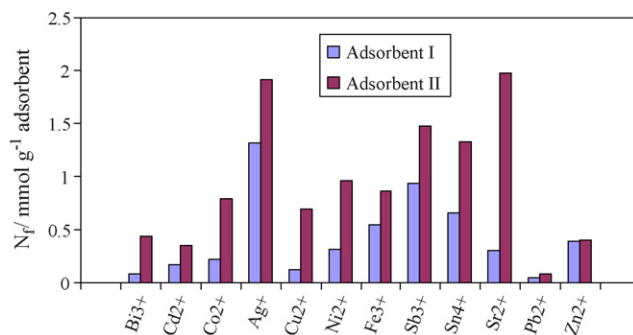

Fig. 5. Comparison of the maximum adsorption capacity for the adsorption of cations by adsorbents I and II.

and Freundlich equations were also found to be mostly >0.98 [23–25]. The parameter normalized percent deviation [26] or the percent relative deviation modulus, P [27,28] as a better criterion for the assessment of experimental isotherm data was also calculated using the following equation:

$$P = \left(\frac{100}{N}\right) \sum \left(\frac{N_{f(expt)} - N_{f(pred)}}{N_{f(expt)}}\right)$$

where $N_{f(expt)}$ is the experimental N_f at any C_s, $N_{f(pred)}$ the corresponding predicted N_f according to the equation under study with the best fitted parameters and N is the number of observations. The lower the P value, the better is the fit. The calculated P values for the fit of isotherm data of the investigated cations on both adsorbents to the two isotherm equations are given in Tables 1 and 2. It is generally accepted that when the P value is less than 5, the fit is considered to be excellent [27]. Most of the P values for Freundlich model are higher than 5 with the exceptions of Ni^{2+} on adsorbent I and Sr^{2+} on both adsorbents. But most of the P values for Langmuir model are lower than 5 with the exceptions of Ag^+, Cd^{2+}, Ni^{2+} and Pb^{2+} on adsorbent I, and Ag^+, Cu^{2+}, Fe^{3+} and Zn^{2+} on adsorbent II.

4. Conclusion

Activated carbon cloth is known for its effectiveness in removing chemicals from water and wastewater. Loading of C-cloth with EDTA provides a more efficient sorbent for the adsorption of metal cations. Modification of C-cloth with EDTA causes a significant increase in the rate and the extent of the adsorption of metal cations. Procedures based on adsorption of some cations at EDTA loaded high-area C-cloth are shown to be effective for removal of them from aqueous solutions. Langmuir model is more successful than Freundlich model in representing experimental isotherm data for the adsorption of the most of the ions on both C-cloths.

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