Attachment of benzo-crown ethers onto activated carbon cloth to enhance the removal of chromium, cobalt and nickel ions from aqueous solutions by adsorption

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ABSTRACT

This work consists of two stages. In the first stage, the adsorption of some monobenzo- and dibenzo-crown ethers onto activated carbon cloth (ACC) was investigated. Adsorption isotherm data were derived at 30 °C. Then the ACC surface was modified by saturating it with crown ethers. In the second stage, the adsorption of three metal ions, Cr(III), Co(II) and Ni(II), onto both the ACC and the ACC modified with crown ethers was investigated. The enhancement of adsorption of the ACC upon modification with crown ethers was examined for the three ions. The effects of the type and cavity size of crown ethers, the size and form of the ions on the extent of adsorption were discussed in terms of interactions of adsorbate species with the ACC surface. All the isotherm data were treated according to Langmuir and Freundlich models. Generally, Freundlich model was found to represent the experimental isotherm data better than Langmuir model.

1. Introduction

Metal ions are among the important pollutants in wastewaters as they are being discharged from several industries. Chromium, cobalt and nickel ions are among common metal ion pollutants. Electroplating, leather tanning, metal finishing and mineral color industries discharge chromium in their wastewaters [1]. Nickel may enter the water from various industries such as mining, electroplating, pigments, ceramic, battery and accumulator manufacturing [1,2]. Nickel ions cause cancer of lungs, nasal sinus and bone. Acute poisoning of nickel causes headache, dizziness, nausea and vomiting, chest pain, tightness of the chest, dry cough and shortness of breath, rapid respiration, cyanosis and extreme weakness [3,4]. Cobalt also appears in wastewaters of many industries and it can produce variety of undesirable effects like nausea, vomiting, asthma, damage to heart, causing heart failure, damage to thyroid and liver on human beings [1,5,6].

Organic pollutants are biodegradable, whereas metal ions are non-biodegradable. So, metal ions should be removed from wastewaters before discharging to the environment. There are various methods to remove metal ions from wastewaters such as chemical precipitation, ion-exchange [4,7,8], membrane filtration [9], liquid extraction, reverse osmosis, electrochemical operation [3], flotation [10], electrodialysis [11] and adsorption [12–15].

Crown ethers are capable of forming complexes with positive ions. Each crown ether binds different ions, depending on the size of its cavity and the size of the ion. Crown ethers are commonly used in organic synthesis. They are known as phase transfer agents [16]. These compounds are toxic, thus they should be removed from waters.

Adsorption is a very popular technique in the removal of organic and inorganic pollutants from waters. Activated carbon is one of the most widely used adsorbents for the adsorption of pollutants. It exists mainly in powder, granular or cloth (fiber) forms. Recently, activated carbon cloth (ACC) has received considerable attention as a potential adsorbent for water treatment applications. It has several unique characteristics compared to conventionally used powder or granular activated carbons. These materials are composed of thin fibers of the order of ten microns in diameters leading to greater adsorption rates and hence contributing to the minimization of the reactor size. The cloth or fiber form of activated carbon also makes the handling of adsorbents much easier [17,18].

The adsorption of metal ions onto the various forms of activated carbon is studied extensively. Hu et al. [13] investigated the adsorption of chromium from aqueous solutions by three commercial activated carbons and determined the effect of temperature and solution pH on the adsorption process. Removal of cobalt by 10 commercial activated carbons was studied by Netzer and Hughes

[12]. They optimized the various process variables and indicated that there was a significant difference in the ability of different commercially available activated carbons to adsorb cobalt from aqueous solutions. Park and Jung [19] reported the adsorption behaviors of Cr(III) and Cr(VI) onto the electroless Cu-plated activated carbon fibers. They mentioned that the adsorption of Cr(III) ions was increased with the introduction of Cu on activated carbon fiber, whereas the adsorption of Cr(VI) ions was decreased. Trivalent chromium removal from wastewater using ACC was studied by Mohan et al. [20]. Brasquet et al. [21] and Kadirvelu et al. [22] investigated the adsorption of Ni(II), Pb(II) and Cu(II) onto two different commercial ACC. Moreover, adsorption properties of various ions from aqueous solutions onto ACC were also reported by Babic et al. [23,24].

There is limited number of studies on the removal of crown ethers from water onto various adsorbents in the literature. Rochester and Strachan [25] reported the adsorption of benzo-15-crown-5 from water onto the carbon surfaces (a nonporous carbon and three porous carbons). Azizian and Yahyei [26] used the granular activated carbon for the removal of 18-crown-6 from aqueous solutions by adsorption. They reported that granular activated carbon was a suitable adsorbent for 18-crown-6 and the best temperature for the adsorption of this crown ether was 25 °C.

The aim of the present study is to determine the adsorption behaviors of some crown ethers and metal ions onto the ACC. We also aimed at investigating the possibility of enhancement of adsorption of ions onto the ACC by modifying its surface with crown ethers.

The selected ions are chromium, cobalt and nickel and the selected crown ethers are of two groups. The first group includes some monobenzo-crown ethers; benzo-12-crown-4 (B12C4), benzo-15-crown-5 (B15C5) and benzo-18-crown-6 (B18C6), and the second group includes some dibenzo-crown ethers; dibenzo-15-crown-5 (DB15C5), dibenzo-18-crown-6 (DB18C6), dibenzo-21-crown-7 (DB21C7), dibenzo-24-crown-8 (DB24C8) and dibenzo-30-crow-10 (DB30C10).

2. Materials and methods

2.1. Materials

The ACC used in the present work was obtained from Spectra Corp. (MA, USA) coded as Spectracarb 2225. Although the full details of its mode of preparation are regarded as proprietary, it originates from pyrolysis of phenolic polymer fibers followed by heat treatment in O_2-free N_2 between 800 and 900 °C for some hours. In this respect, it differs from other fibrous carbon materials derived by pyrolysis of rayon [27].

B12C4, DB15C5, DB24C8, DB30C10 were purchased from Fluka, B15C5, B18C6 from ABCR, DB18C6 and DB21C7 from Aldrich. The molecular structures of these crown ethers are given in Fig. 1. $Cr(NO_3)_3 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$ and $NiSO_4 \cdot 6H_2O$ used as Cr(III), Co(II) and Ni(II) ion sources, respectively, were obtained from Merck. All other chemicals used in this study were reagent grade. Deionized water was used in adsorption experiments.

Benzo-12-crown-4
B12C4

Benzo-15-crown-5
B15C5

Benzo-18-crown-6
B18C6

Dibenzo-15-crown-5
DB15C5

Dibenzo-18-crown-6
DB18C6

Dibenzo-21-crown-7
DB21C7

Dibenzo-24-crown-8
DB24C8

Dibenzo-30-crown-10
DB30C10
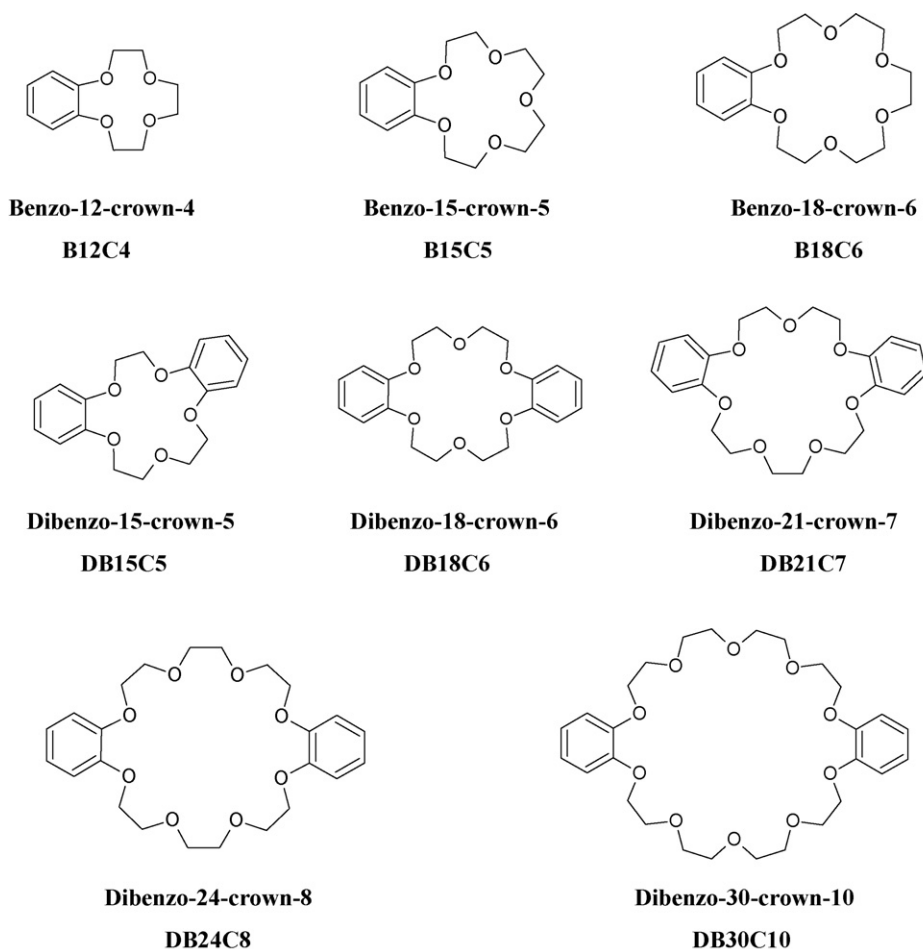
Fig. 1. Names, chemical structures and abbreviations of crown ethers.

Table 1
Properties of the ACC [29–33].

Specific surface area	$1870\,\mathrm{m^2\,g^{-1}}$
Total pore volume	$0.827\,\mathrm{cm^3\,g^{-1}}$
Micropore volume	$0.709\,\mathrm{cm^3\,g^{-1}}$
Mesopore volume	$0.082\,\mathrm{cm^3\,g^{-1}}$
Average fiber diameter	$17\,\mu\mathrm{m}$
Carbon content	95.14%
Hydrogen content	0.37%
Oxygen content	4.49%
Nitrogen and sulfur content	0%
$\mathrm{pH_{PZC}}$	7.4
Total acidic group content	$0.25\,\mathrm{mmol\,g^{-1}}$
Carboxylic group content	$0.093\,\mathrm{mmol\,g^{-1}}$
Lactonic group content	$0.020\,\mathrm{mmol\,g^{-1}}$
Phenolic group content	$0.14\,\mathrm{mmol\,g^{-1}}$
Total basic group content	$0.28\,\mathrm{mmol\,g^{-1}}$

Table 2
Spectral and calibration data for UV spectroscopic analysis of crown ethers. λ_{max}: wavelength of maximum absorption, ε: molar absorptivity, r: regression coefficient.

Crown ether	Solvent	λ_{max} (nm)	ε ($\mathrm{M^{-1}\,cm^{-1}}$)	r
B12C4	H_2O	215	7100	0.9992
	H_2O	273	1900	0.9996
B15C5	H_2O	223	7250	0.9994
	H_2O	274	2570	0.9999
B18C6	H_2O	224	7540	0.9995
	H_2O	274	2600	0.9998
DB15C5	C_2H_5OH	275	5040	0.9956
DB18C6	C_2H_5OH	275	5040	0.9998
DB21C7	C_2H_5OH	275	5045	0.9999
DB24C8	C_2H_5OH	275	5000	0.9992
DB30C10	C_2H_5OH	275	4900	0.9981

2.2. Treatment and properties of the ACC

A washing procedure was applied for the ACC as described previously [27–30]. Several properties of the ACC such as specific surface area, volumes of micropores and mesopores, elemental composition, $\mathrm{pH_{PZC}}$ which is the pH of solution at which net charge on the surface of the ACC is zero, and acidic and basic group contents were determined in our previous works [29–33]. These properties are listed in Table 1. The SEM pictures and electrochemical characterization of the ACC were also reported earlier [34].

2.3. Adsorption isotherms

2.3.1. Adsorption isotherms of crown ethers

The ACC pieces of 17.0 ± 0.1 mg were introduced into the beakers containing deionized water and the beakers were placed in a vacuum desiccator. Vacuum was applied to it in order to remove all air in the pores of the ACC pieces in beakers for about 20 min. Then, the ACC pieces were left in contact with water for 24 h. During this long contact period with deionized water, the pores of the ACC may expand and become more accessible for the adsorbates and water molecules, in the actual adsorption process. The idea of using pre-wetted ACC originated from our previous findings that pre-wetting really enhanced the adsorption process [35].

Crown ether solutions, having a concentration of 2×10^{-4} M and a volume of 50 mL, were introduced into several 100 mL erlenmeyer flasks. Weighed, degassed and pre-wetted ACC pieces were transferred into each erlenmeyer flask containing crown ether solution and allowed to equilibrate. For equilibration, the flasks were kept in Nüve ST 402 shaking waterbath adjusted to 30 °C and to a shaking speed of 150 rpm and kept for 48 h. The solvent was deionized water for monobenzo-crown ethers and ethyl alcohol for dibenzo-crown ethers which were not soluble in water. Preliminary tests showed that the concentration of adsorbates remained unchanged after 16–20 h contact with the ACC. Thus, the allowed contact time of 48 h ensures the equilibration. The concentrations of crown ethers after the equilibration period were measured spectrophotometrically. A Cary 100 UV/Vis. Spectrophotometer was used for the absorbance measurements. Absorbance data were converted into concentration data using calibration relations pre-determined at the wavelength of maximum absorbance for each crown ether. The calibration data for monobenzo- and dibenzo-crown ethers studied are given in Table 2. The ACC piece removed from each erlenmeyer flask was reintroduced into a new crown ether solution (50 mL, 2×10^{-4} M) and again allowed for equilibration. The process of removing ACC from its equilibrated solution and reinserting it into a fresh crown ether solution was repeated several times until no more crown ether has been adsorbed upon reinsertion. The ACC pieces were kept on a course filter paper at room temperature for

about three hours before reinsertion into a fresh, more concentrated crown ether solution. Successive adsorption stages allowed us to obtain more isotherm data points and at the same time to saturate the ACC to crown ethers. At each step the equilibrium adsorbate concentration was measured and the amount of adsorbate adsorbed per unit mass of the ACC, q_e, was calculated from Eq. (1)

$$q_e = \frac{V(C_0 - C_e)}{m} \tag{1}$$

where V is the volume of the adsorbate solution, C_0 and C_e are the initial and equilibrium concentrations, respectively, and m is the mass of the ACC. Cumulative q_e value was calculated at each stage of successive adsorptions by adding the q_e of the previous stage.

The ACC pieces saturated with crown ether solutions were dried at room temperature and kept to be used in the adsorption studies of metal ions. In order to test whether the ACC pieces saturated with crown ethers release some of its crown ethers during adsorption process of metal ions, they were left in deionized water for about 3–4 h. Then, the solution was analyzed for crown ether spectrophotometrically and no crown ether was detected in solution.

2.3.2. Adsorption isotherms of metal ions

The adsorption of Cr(III), Co(II) and Ni(II) ions from aqueous solutions not only onto the degassed and pre-wetted ACC but also onto the ACC modified by saturating with crown ethers as described above was studied. In this way it would be possible to see the enhancement in removal of these ions by crown ether modified ACC.

Batch technique was used to determine the equilibrium adsorption capacities of the washed and pre-wetted ACC and of the ACC saturated with crown ether for metal ions. The adsorbent pieces, which were about 17.0 ± 0.1 mg before saturation with crown ether, were allowed to equilibrate with solutions of metal ions in water with known initial concentrations of 6×10^{-5} M Cr(III), 1×10^{-5} M Co(II) and 2×10^{-5} M Ni(II) at 30 °C for 48 h. Preliminary tests showed the equilibration time as 20–24 h. The equilibration was allowed in 100 mL erlenmeyer flasks kept in shaking waterbath at a constant shaking speed of 150 rpm. After equilibration period, the residual concentrations of Cr(III), Co(II) and Ni(II) ions in solution were analyzed by Varian Liberty Series II Inductively Coupled Plasma Atomic Emission Spectrometer. Then, the q_e values were calculated using Eq. (1).

3. Results and discussion

3.1. Adsorption of crown ethers

The adsorption isotherm data of monobenzo-crown ethers (B12C4, B15C5 and B18C6) in water and dibenzo-crown ethers (DB15C5, DB18C6, DB21C7, DB24C8 and DB30C10) in C_2H_5OH at
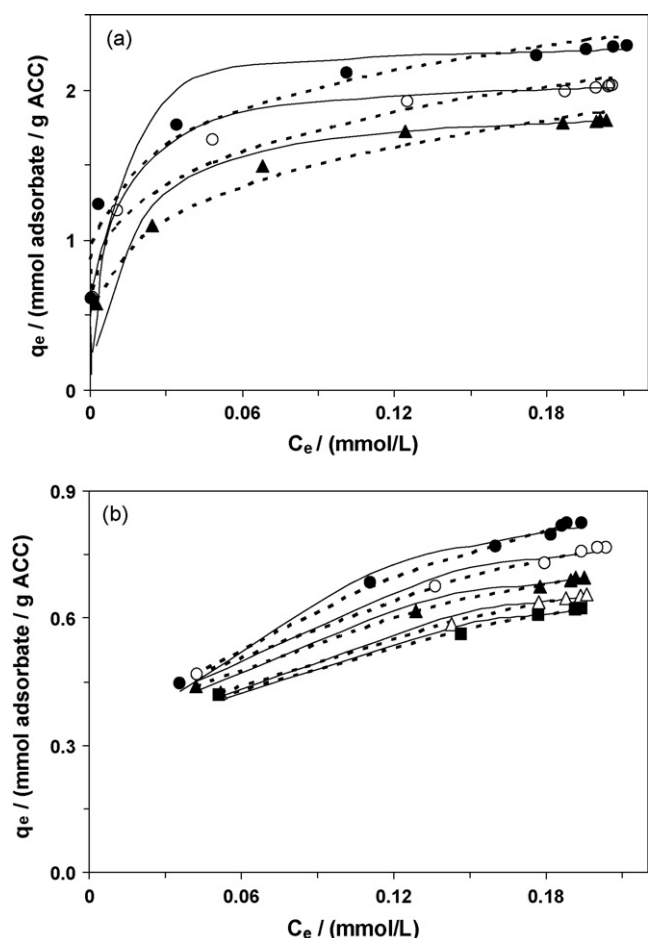
Fig. 2. The isotherm for the adsorption of (a) monobenzo-crown ethers from aqueous solutions at 30 °C [(●) B12C4, (○) B15C5, (▲) B18C6] and (b) dibenzo-crown ethers from ethanolic solutions at 30 °C [(●) DB15C5, (○) DB18C6, (▲) DB21C7, (△) DB24C8, (■) DB30C10]. (—) Langmuir isotherms and (···) Freundlich isotherms.

30 °C are given in Figs. 2(a) and (b), respectively. The isotherm data were treated according to two well-known isotherm equations; Langmuir and Freundlich. The linearized forms of Langmuir and Freundlich isotherm equations can be given in Eqs. (2) and (3), respectively [36]

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{bq_{max}} \tag{2}$$

$$\ln q_e = \ln K_F + (1/n)\ln C_e \tag{3}$$

where q_e is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium, C_e the final concentration at equilibrium, q_{max} the maximum adsorption at monolayer coverage,

b the adsorption equilibrium constant related to the energy of adsorption, K_F the Freundlich constant representing the adsorption capacity and n a constant related to surface heterogeneity. Freundlich constant, $1/n$, is also a measure of the deviation of the adsorption isotherm from linearity. If $1/n$ is equal to unity the adsorption isotherm is linear. This means that the adsorption sites are homogeneous in energy and no interactions take place between the adsorbed species. If the value of $1/n$ is smaller than 1, adsorption is favorable. When the value of $1/n$ is larger than 1, the adsorption interactions become weak and unfavorable adsorption takes place [37].

Freundlich isotherm equation was developed for heterogeneous surfaces. In this case, there is a continuously varying energy of adsorption as the most actively energetic sites are occupied first and surface is continually occupied until the lowest energy sites are filled at the end of adsorption process. Langmuir adsorption isotherm assumes that the adsorbed layer is one molecule in thickness and that all sites are equal, resulting in equal energies and enthalpies of adsorption [36].

The parameters of Eqs. (2) and (3) were obtained by linear regression analysis of the experimental isotherm data and are given in Table 3. The regression coefficients are higher than 0.989 for both isotherm models and for all crown ethers. Thus it was difficult to judge which isotherm model is better for representing the experimental isotherm data of each crown ether. A better criterion for the assessment of experimental isotherm data is a parameter known as normalized percent deviation [38] or in some literature as percent relative deviation modulus, P [39,40] given by the following equation;

$$P = \frac{100}{N}\sum_{i=1}^{N}\frac{|q_{e(pred)} - q_{e(exp)}|}{q_{e(exp)}} \tag{4}$$

where $q_{e(exp)}$ is the experimental q_e at any C_e, $q_{e(pred)}$ the corresponding q_e predicted from the equation under study with the best fitted parameters and N the number of observations. It is clear that the lower the P value, the better is the fit. It is generally accepted that when the P value is less than 5, the fit is considered to be excellent [39]. The present isotherm data were assessed on the basis of P values given in Table 3. It is seen that the P values for Freundlich model are all lower than those for Langmuir model. Thus, it can be concluded that Freundlich isotherm model represents the experimental isotherm data for the monobenzo- and dibenzo-crown ethers under study. Freundlich constant, K_F, representing the adsorption capacity (Table 3) increased in the order DB30C10 < DB24C8 < DB21C7 < DB18C6 < DB15C5 < B18C6 < B15C5 < B12C4. It is apparent that the adsorption capacity of the ACC is higher for monobenzo-crown ethers than dibenzo-crown ethers. It is also seen that the extent of adsorption for each group of crown ethers (monobenzo- and dibenzo-crown ethers) decreases with increasing size of the crown ether.

Table 3
Parameters of Langmuir and Freundlich isotherm equations, regression coefficients (r) and normalized percent deviation (P) values for the adsorption of crown ethers onto the ACC at 30 °C.

Crown ether	Solvent	Langmuir parameters				Freundlich parameters			
		q_{max} (mmol g^{-1})	b (L mmol^{-1})	r	P	K_F (mmol g^{-1}). (L mmol^{-1})$^{1/n}$	$1/n$	r	P
B12C4	H$_2$O	2.325	183.8	0.9992	16.69	3.166	0.1876	0.9887	5.245
B15C5	H$_2$O	2.089	128.7	0.9994	8.173	2.936	0.2175	0.9898	4.562
B18C6	H$_2$O	1.910	74.49	0.9989	8.538	2.792	0.2567	0.9949	3.447
DB15C5	C$_2$H$_5$OH	1.028	19.82	0.9979	1.956	1.500	0.3635	0.9991	0.7053
DB18C6	C$_2$H$_5$OH	0.9256	22.28	0.9981	1.833	1.268	0.3169	0.9997	0.3330
DB21C7	C$_2$H$_5$OH	0.8347	24.81	0.9989	1.381	1.142	0.3017	0.9998	0.2334
DB24C8	C$_2$H$_5$OH	0.8159	20.06	0.9984	1.179	1.115	0.3263	0.9996	0.2951
DB30C10	C$_2$H$_5$OH	0.7607	22.36	0.9976	1.445	1.020	0.3024	0.9983	0.6372

Table 4
Parameters of Langmuir and Freundlich isotherm equations, regression coefficients (r) and normalized percent deviation (P) values for the adsorption of Cr(III), Co(II) and Ni(II) onto the ACC and onto the ACC modified with crown ethers at 30 °C.

Ion	Adsorbent	Langmuir parameters				Freundlich parameters			
		q_{max} (mmol g^{-1})	b (L mmol^{-1})	r	P	K_F (mmol g^{-1}). (L mmol^{-1})$^{1/n}$	$1/n$	r	P
Cr(III)									
	ACC	0.1324	3.295	0.9983	1.268	0.1485	0.6760	0.9975	2.723
	ACC-(B12C4)	0.1432	5.432	0.9399	10.47	0.1639	0.5242	0.9648	9.714
	ACC-(B15C5)	0.1637	5.793	0.9915	5.149	0.2000	0.5464	0.9947	3.645
	ACC-(B18C6)	0.2202	3.475	0.9928	3.081	0.2544	0.6740	0.9959	4.068
	ACC-(DB15C5)	0.1386	7.037	0.9931	3.953	0.1712	0.5002	0.9981	1.821
	ACC-(DB18C6)	0.1256	9.713	0.9827	6.715	0.1677	0.4666	0.9739	8.020
	ACC-(DB21C7)	0.1721	2.574	0.8213	13.80	0.1602	0.6556	0.9485	13.14
	ACC-(DB24C8)	0.1220	4.904	0.9946	2.952	0.1444	0.5767	0.9998	0.822
	ACC-(DB30C10)	0.08747	8.420	0.9722	11.97	0.09797	0.3955	0.9183	10.06
Co(II)									
	ACC	0.05258	24.61	0.9869	11.75	0.09383	0.4299	0.9848	6.523
	ACC-(B12C4)	0.1302	11.40	0.9476	12.27	0.2600	0.6075	0.9949	5.542
	ACC-(B15C5)	0.1166	10.39	0.8903	17.28	0.1930	0.5634	0.9795	11.32
	ACC-(B18C6)	0.1097	8.458	0.7932	21.59	0.1667	0.5758	0.9673	14.18
	ACC-(DB15C5)	0.06638	19.34	0.9897	8.554	0.1130	0.4384	0.9909	4.176
	ACC-(DB18C6)	0.05809	22.48	0.9974	4.013	0.1057	0.4379	0.9786	6.791
	ACC-(DB21C7)	0.04371	21.71	0.9926	7.831	0.07116	0.4011	0.9903	3.583
	ACC-(DB24C8)	0.04085	19.82	0.9781	12.77	0.06097	0.3827	0.9756	5.982
	ACC-(DB30C10)	0.03435	22.60	0.9769	14.10	0.04762	0.3336	0.9614	6.384
Ni(II)									
	ACC	0.03892	42.56	0.9750	10.99	0.08438	0.4066	0.9867	5.103
	ACC-(B12C4)	0.1514	12.56	0.8801	11.23	0.3371	0.5990	0.9782	7.752
	ACC-(B15C5)	0.1187	14.25	0.8239	16.19	0.2127	0.4996	0.9222	13.01
	ACC-(B18C6)	0.1063	15.93	0.8684	14.80	0.1965	0.4893	0.9382	11.47
	ACC-(DB15C5)	0.05245	29.59	0.9987	0.8458	0.09290	0.3697	0.9934	1.751
	ACC-(DB18C6)	0.03815	29.46	0.9953	2.148	0.08868	0.4675	0.9909	3.541
	ACC-(DB21C7)	0.03256	21.31	0.9827	4.765	0.07318	0.5075	0.9719	6.001
	ACC-(DB24C8)	0.02609	23.26	0.9683	7.379	0.06568	0.5348	0.9625	8.097
	ACC-(DB30C10)	0.02480	21.29	0.9940	2.453	0.06173	0.5390	0.9875	4.765

3.2. Adsorption of metal ions

The adsorption isotherm data of metal ions Cr(III), Co(II) and Ni(II) onto the ACC and onto the ACC saturated with monobenzo-crown ethers are shown in Fig. 3(a), (b) and (c), respectively. The isotherms for the adsorption of Cr(III), Co(II) and Ni(II) onto the ACC and onto the ACC saturated with dibenzo-crown ethers are given in Fig. 4(a), (b) and (c), respectively. The isotherm data were treated according to Langmuir and Freundlich isotherm equations (Eqs. (2) and (3), respectively). The calculated Langmuir and Freundlich parameters, regression coefficients and P values (Eq. (4)) for Cr(III), Co(II) and Ni(II) adsorption are given in Table 4. Regression coefficient values of Langmuir and Freundlich equations are generally very close to 1 for the two models. Thus, again the P values were determined for a better assessment and included in Table 4. It is seen that P values are lower for Cr(III) and Co(II) for Freundlich model than Langmuir model. This result indicates that, generally, Freundlich model represents the experimental isotherm data of metal ions better than Langmuir model.

Adsorption capacity of the original washed ACC for the three ions studied, as determined by q_{max} and K_F parameters (Table 4), is seen to decrease in the order Cr(III) > Co(II) > Ni(II). These ions are probably being attached to the surface of the ACC via interactions with carboxylic and phenolic groups possibly present on the surface. The above order is more or less maintained for the ACCs saturated with monobenzo- and dibenzo-crown ethers with a few exceptions. The size and charge of ions, cavity of crown ethers and the type of crown ether (monobenzo or dibenzo derivative) play important roles in determining this order of extent of adsorption. Of course the forms of ions under the experimental conditions are also important in their interactions with the ACC surfaces.

The stability constants for the various hydroxo species of the three metal ions are given in Table 5. Speciation diagrams drawn

using these stability constants are shown in Fig. 5(a) for chromium, in Fig. 5(b) for cobalt and in Fig. 5(c) for nickel. The initial pH values of solutions of all three metal ions were measured to be 6.0 and remained in the range of 5.5 and 6.0 during the whole course of adsorption. It is seen from Fig. 5 that at pH 6 chromium is found 33% in Cr(OH)$^{2+}$ form and 67% in Cr(OH)$_2^+$ form while cobalt and nickel are mainly found as divalent monatomic ions. Thus chromium is expected to be adsorbed onto the surface of the ACC not only through ionic interactions but also through hydrogen bonding interactions. This explains the greatest extent

Table 5
Stability constants of various chromium, cobalt and nickel hydroxo species.

Metal ion	Equilibrium	$\log K$ (at 25 °C and zero ionic strength)
Cr(III)		
	$Cr^{3+} + OH^- \rightleftharpoons Cr(OH)^{2+}$	10.0[a,b,c,d]
	$Cr^{3+} + 2 OH^- \rightleftharpoons Cr(OH)_2^+$	18.3[a,b,c,d]
	$Cr^{3+} + 3 OH^- \rightleftharpoons Cr(OH)_3$	24.0[a,b,c,d]
	$Cr^{3+} + 4 OH^- \rightleftharpoons Cr(OH)_4^-$	28.6[a]
Co(II)		
	$Co^{2+} + OH^- \rightleftharpoons Co(OH)^+$	4.3[e]
	$Co^{2+} + 2 OH^- \rightleftharpoons Co(OH)_2$	8.4[e]
	$Co^{2+} + 3 OH^- \rightleftharpoons Co(OH)_3^-$	9.7[e]
	$Co^{2+} + 4 OH^- \rightleftharpoons Co(OH)_4^{2-}$	10.2[e]
Ni(II)		
	$Ni^{2+} + OH^- \rightleftharpoons Ni(OH)^+$	4.1[c,e]
	$Ni^{2+} + 2 OH^- \rightleftharpoons Ni(OH)_2$	8.0[e]
	$Ni^{2+} + 3 OH^- \rightleftharpoons Ni(OH)_3^-$	11[e]

[a] Ambrose et al. [41].
[b] Vinokurov and Bondar [42].
[c] Salbu and Steinnes [43].
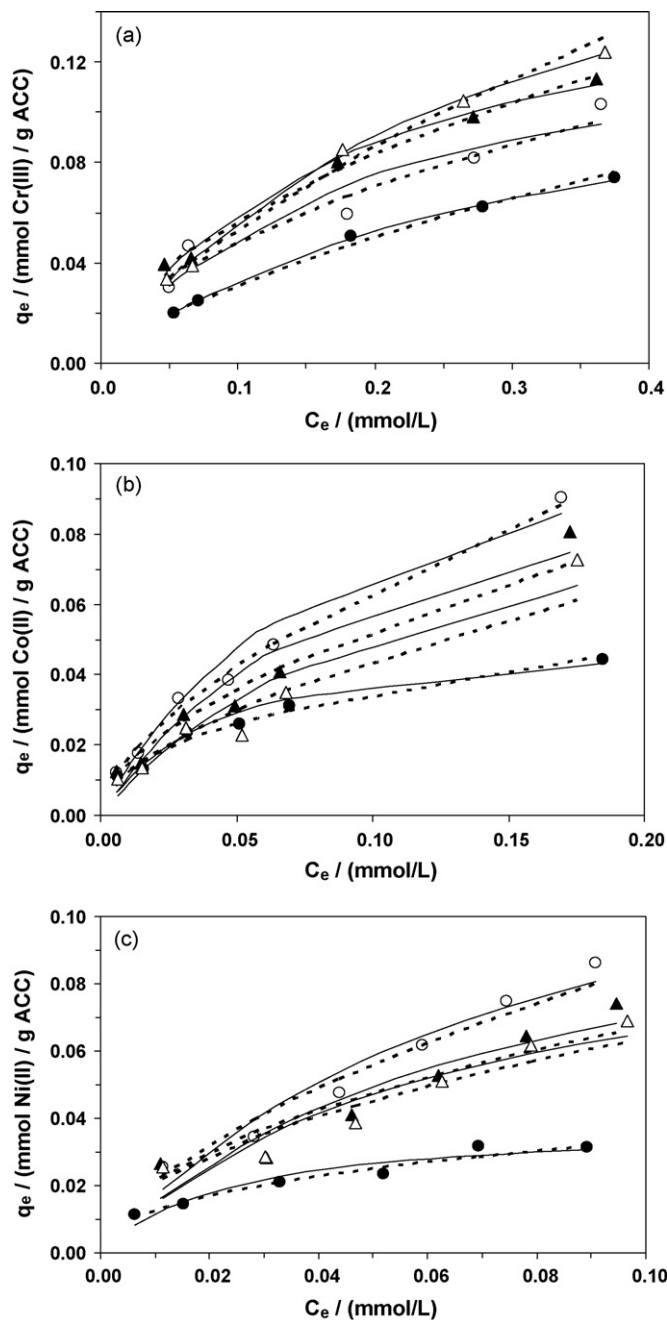[d] Kutz [44].
[e] Martell and Smith [45].

Fig. 3. The isotherm for the adsorption of (a) Cr(III), (b) Co(II) and (c) Ni(II) onto the ACC: (●), ACC-(B12C4): (○), ACC-(B15C5): (▲), ACC-(B18C6): (△). (—) Langmuir isotherms and (···) Freundlich isotherms.

ACC-(B18C6) > ACC-(DB21C7) > ACC-(B15C5) > ACC-(B12C4) > ACC-(DB15C5) > ACC > ACC-(DB18C6) > ACC-(DB24C8) > ACC-(DB30C10). On the other hand, the magnitude of the term K_F, which represents the adsorption capacity according to Freundlich model, decreases in the following order for chromium (Table 4): ACC-(B18C6) > ACC-(B15C5) > ACC-(B12C4) > ACC-(DB15C5) > ACC-(DB18C6) > ACC-(DB21C7) > ACC > ACC-(DB24C8) > ACC-(DB30C10).

Similar trends in q_{max} or K_F values for the adsorption of cobalt and nickel ions can be deduced from Table 4.

In general, it is clear that monobenzo derivatives of crown ethers are more effective in enhancing, via modification of the ACC surface, the extents of adsorption of all three ions than dibenzo derivatives, irrespectiv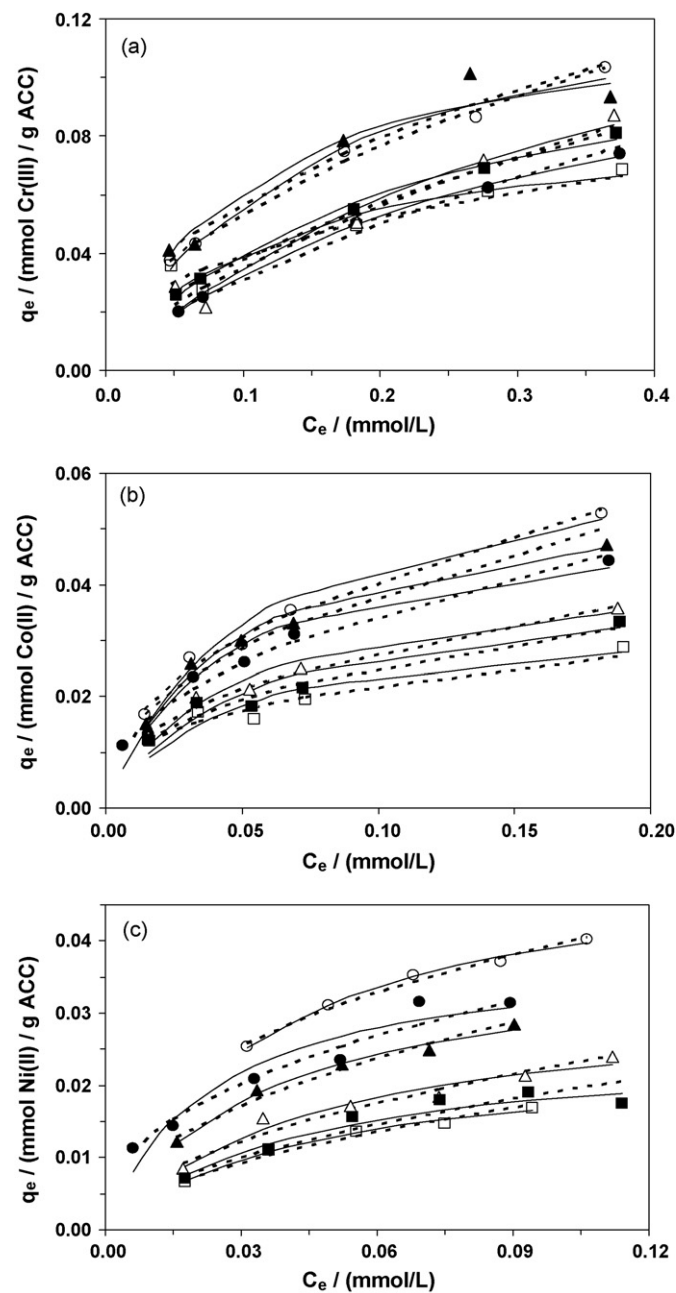e of cavity sizes. This is probably due to the attachment of adsorption observed for chromium among the three ions studied.

Radii of metal ions and sizes of cavities of crown ethers are important in the enhancement of adsorption of metal ions upon saturating of the ACC surface with crown ethers. Diameters of the ions of interest and cavities of crown ethers are given in Table 6.

It is seen from Fig. 3(a) that the extent of adsorption of chromium is enhanced upon modifying ACC surface with monobenzo-crown ethers. This enhancement is the greatest with B18C6 and then decrease in the order B18C6 > B15C5 > B12C4. The enhancement is less with dibenzo-crown ethers.

q_{max} values, representing the adsorption capacity according to Langmuir model, for chromium decrease in the following order for the ACC modified with different crown ethers:

Fig. 4. The isotherm for the adsorption of (a) Cr(III), (b) Co(II) and (c) Ni(II) onto the ACC: (●), ACC-(DB15C5): (○), ACC-(DB18C6): (▲), ACC-(DB21C7): (△), ACC-(DB24C8): (■), ACC-(DB30C10): (□). (—) Langmuir isotherms and (···) Freundlich isotherms.
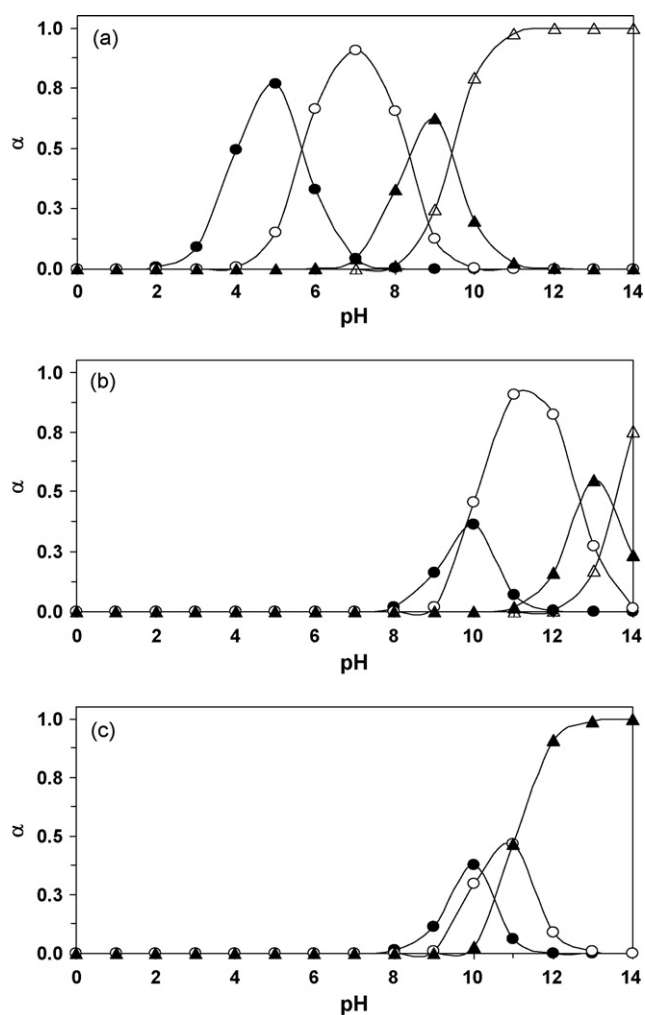
Fig. 5. Relative concentration of species (α) as a function of pH for (a) chromium where (●) is for $Cr(OH)^{2+}$; (○) is for $Cr(OH)_2^+$; (▲) is for $Cr(OH)_3$ and (△) is for $Cr(OH)_4^-$, (b) cobalt where (●) is for $Co(OH)^+$; (○) is for $Co(OH)_2$; (▲) is for $Co(OH)_3^-$ and (△) is for $Co(OH)_4^{2-}$ and (c) nickel where (●) is for $Ni(OH)^+$; (○) is for $Ni(OH)_2$ and (▲) is for $Ni(OH)_3^-$.

of monobenzo-crown ethers onto the ACC surface mainly through the benzene ring. In this way, they occupy less space on the surface and their cavity becomes rather flexible above the surface and can attach the ions more easily. This orientation does not avoid the direct attachment of ions onto the ACC surface while creating additional attachment cites for ions via the cavities of crown ethers. On the other hand, dibenzo-crown ethers are attached onto the ACC surface through both benzene rings, occupying more space on the surface and providing less flexible cavity for the attachment of ions. This causes less enhancement in ion removal from solution.

Table 6
The cavity diameters of crown ethers and diameters of ions.

Crown ether or ion	Cavity or ionic diameter (Å)
All 14-crown-4	1.2–1.5[a]
All 15-crown-5	1.7–2.2[a]
All 18-crown-6	2.6–3.2[a]
All 21-crown-7	3.4–4.3[a]
Cr(III)	1.38[b]
Co(II)	1.48[b]
Ni(II)	1.44[b]

[a] Izatt et al. [46].
[b] Conway [47].

Even smaller extent of adsorption compared to unmodified ACC is observed in cases when the size of dibenzo-crown ether is too big, e.g. ACC-(DB18C6), ACC-(DB24C8) and ACC-(DB30C10).

The best adsorption capacity was achieved by modifying the ACC with B18C6 for chromium and with B12C4 for cobalt and nickel which is consistent with the size of ionic species and cavity diameters of crown ethers. Since chromium is expected to be mainly in $Cr(OH)^{2+}$ or $Cr(OH)_2^+$ forms, their size is larger than the ionic size of Cr(III) given in Table 6. Thus, they do not fit to the cavity of crown ether but they are attached strongly to etheric centers through ion-dipole and hydrogen bonding interactions. B18C6 has the greatest number of etheric –O– centers among the monobenzo-crown ethers studied.

4. Conclusions

The adsorption capacity of the ACC was found to be greater for monobenzo-crown ethers than dibenzo-crown ethers. The extent of adsorption of crown ethers onto the ACC was observed to increase with the size of crown ether within each group; monobenzo- and dibenzo-crown ethers. Adsorption capacity of the ACC was greater for Cr(III) ions than for Co(II) and Ni(II) ions both in unmodified form and in the form modified with crown ethers. This was attributed to the H-bonding interactions between the ACC surface functional groups and Cr(III) ions that are found to exist in $Cr(OH)^{2+}$ or $Cr(OH)_2^+$ forms in the solution at the pH studied, in addition to the normal ionic interactions. The extent of adsorption of ions onto the ACC was enhanced by modification of the ACC surface with monobenzo-crown ethers. The best adsorption capacity was achieved by modification with B18C6 for chromium and with B12C4 for cobalt and nickel ions among the benzo-crown ethers studied.

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