Adsorption (2007) 13: 61–71
DOI 10.1007/s10450-007-9001-0

Mixed silica and alumina hosted carboxylate oxide for removal of chromium species from wastewater

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Received: 14 February 2006 / Revised: 20 December 2006 / Accepted: 16 January 2007 / Published online: 7 April 2007

Abstract Increasing in the use of various chromium species over the past few decades has inevitably resulted in an increased flux of their metallic substances in aquatic life. Therefore, experimental work was developed to improve the physical and chemical characteristics of the prepared mesoporous SiO_2–Al_2O_3 mixed oxides via a sol–gel process. The effective key parameter on the properties of the materials was achieved by the addition of carboxylate functional group such as Alph-hydroxyl isobuteric acid (AHIBA) during the gelation process and prior the calcinations step. Better performance of these carboxylate resins are attributed to the complexing ability of the carboxylate groups toward polyvalent chromium species which is added to the normal sorption properties of the oxides. Urea has been used as a means of producing an aluminum precipitate that is easier to filter than that produced by rapid addition of base. Introduction of Al and Si salts together to form mixed oxide modified the way of their substitution in the hosting resin than when they were separately added. The data revealed that mesoporous materials with very narrow pore diameter distribution (micron-sized) and high surface area were obtained. The surface areas and pore size distributions were mainly depend on SiO_2 content. Systematic investigations were carried out on the set of the prepared mixed oxides with different porosity, cross-linking degree and exchange loading to find out the best sorbent for chromium removal. The final objective in all cases was aimed at determining feasible and economically reliable solution to the environmental problems related to the tannery industry.

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Keywords Modified silica and alumina · Cr(III) · Cr(VI) · Wastewater

1 Introduction

Silica (SiO_2) is wide spread in the earth's crust and is one of the abundant minerals. It is the main component in many composite materials utilized in glass industry, white ware ceramics, various bricks, and abrasives. The most common forms of silica are basically sodium, potassium and aluminum silicates (Chakraborty and Das 2003). The recent development in advanced material technology started to improve the properties of alumina, especially by incorporation of a second phase within the matrix developing the matrix composites to fulfill effective requirement properties (Saegusa 1997). For this reason preparation conditions of the polymeric resin powders are considered as one of the most important factors affecting the processing.

Many author show that the preparation conditions as well as preparation techniques are receiving a new research emphasis because of their recognized relationship with the physical and chemical characteristics of the end product (Hirano et al. 1992; Ibrahim et al. 1999a, 1996; Blendell et al. 1984). To get the desired properties of the prepared oxide, different techniques are practiced such as co-precipitation, impregnation, thermal decomposition of carbonates, solid state reaction, oxidation on flame, and precipitation from aqueous solutions. Micro-emulsion technique was used also to prepare the oxide materials showing that superiority of sol-gel over other tailored techniques. The preparation of ultrafine, ultrapure and extrahomogenous oxide powders was achieved by sol-gel polymeric method (Rongjun et al. 1999; Ibrahim et al. 1999a). The sol-gel technique achieved higher purity, homogeneity and submicron powder size over conventional methods. In this technique metal organic compounds are thermally or hydrolytically decompose to form inorganic nonmetallic oxide powder that applied in different fields. It offers unlimited flexibility because of their wide variety of organic compounds that become available in the recent years (Zhao et al. 2003).

Hydrolysis step processed from colloidal sol best fit the common definition of a sol, (a stable dispersion of colloidal particles in a liquid). This process is used to prepare hydrous metal oxides of uniform particle shape and size from metal salts or metal alkoxides (Yoldas 1975; Blendell et al. 1984). A great variety of metal alkoxides are now commercially available. On preparation of multicomponents sol-gel bodies where all constituents are alkoxides, steps must be taken into consideration for the frequent occurrence of differing hydrolyzes rate. If one component hydrolyses much more rapidly than the others, the polymerized clusters of that component can form and the chemical homogeneity obtained in the solution is lost (Yoldas 1975). Gel technology allows the synthesis of homogeneous, fine grained material for processing and offers control of chemical purity and crystallinity. The gelation process influences pore volume and pore size.

Another route for gelation processing is that known as Pechini's method, which is based on the chelation process between mixed cations in the form of chlorides, nitrates, carbonates, or hydroxides with a hydroxycarboxylic acid, e.g. citric acid (Lessing 1989). In this case the active sites for the reaction are increased. It is believed that the crosslinked resin may provide more homogeneous mixing of the cations and less tendency for segregation during charring and calcination.

1.1 Chromium waste

As a result of the civilization-technology activities, a large amount of toxic materials have been discharged and continue entering the environment. Industrial waste is the major source of metal pollution in aqueous systems (Petruzzlli et al. 1995). The major industrial sources of chromium in the aquatic environment are electroplating, metal- finishing and coating industrial effluents, machining, stamping, foundry, recycling of batteries and radiators and sewage as well as wastewaters treatment plant discharge.

With the help of this concept it is now possible to treat various wastes that contain dangerous and toxic elements (Mohammed and Sirwal 2003). Various technologies for chromium removal and control in industry wastewaters are based on precipitation and co-precipitation method coupled with pre-or post-oxidation, reduction or concentration (Rhyner et al. 1995; SenGupta 1995). As opposed to precipitation method, which is "destructive" toward pollutant, "conservative" technologies allow for removal, recovery and recycling of persistent pollutants by various prepared resins, thus taking advantage of the economic revenue associated with the commercial value of the recycled products (Petruzzelli et al. 1994; Macchi et al. 1991). Chromium, recovered as chromate from the resin spent regeneration eluates could be ready for reuse in the plating industry or in the same tannery industry after reduction to Cr(III) (Jardine et al. 1999).

2 Experimental

2.1 Reagents and solutions

All chemicals used in this work are of analytical grade of E. Merck or BDH. Aqueous solutions were prepared with double distilled de-ionized water. Standard stock solution (1000 ppm) of Cr(III) and Cr(VI) were prepared by dissolving requisite amounts of their salts, Cr_2O_3 and potassium dichromate, respectively, in 2–5 ml of hydrochloric acid (39%) and moderate heating was applied. Each solution was quantitatively dissolved in double distilled de-ionized water containing 5% of nitric acid. Mixed working standards containing different concentrations proportional to the respective detection limits were prepared by the dilution of the stock solutions for calibration.

2.2 Sampling

Locally the tannery processes contain different five steps including, hide preservation, beam house operation, tanning, wet finishing (retanning, neutralization, dyeing and fat liquoring) and final finishing. Two investigated samples were collected from the effluents discharged from located tannery in Cairo. The first sample was collected from the original tannery bath while the second sample was collected from the final drain of final finishing step. Each sample was filtered and then subjected to ion chromatographic (IC) measurement.

2.3 Preparation of mixed oxides powders

Performance of metal oxide components is dependent on the microstructure development, which in its turn is a reflection of the physical and chemical characteristic of the starting powders and their behaviour during processing. Surface activity of ultrafine oxide powders is one of the major driving forces during solid state process. Conditions of the polymerization reaction taking place between urea and formaldehyde to form the respective resin, pH, concentration, temperature and sequence of addition of the different reactants

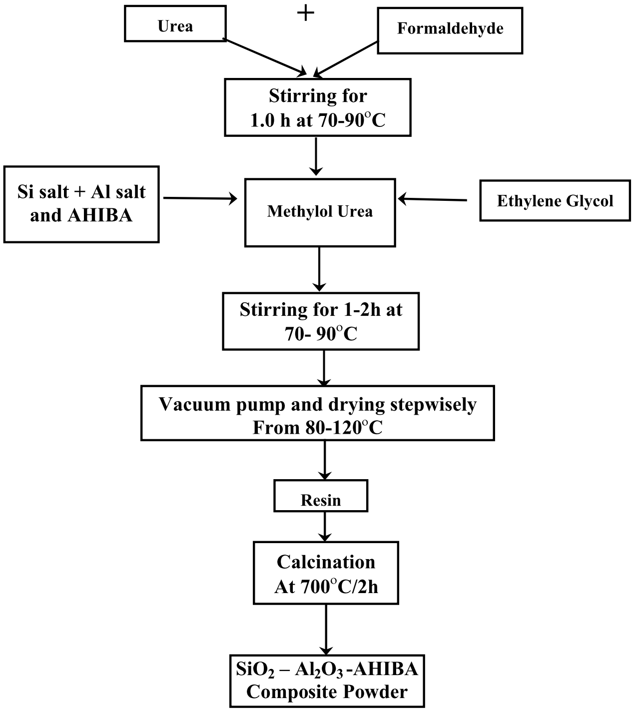


Fig. 1 Flow chart of preparation of SiO_2–Al_2O_3–AHIBA composite powders by sol-gel polymeric method

were previously described (Mostafa 1997; Hassan 2004; Rodríguez Avendaño et al. 2005).

In the present work, aluminium chloride and/or silicon tetrachloride precursors were introduced during resin formation. Upon heating, urea decomposes slowly producing CO_2 and NH_4^+. The particles initially nucleated grow uniformly and few new particles are formed. Ethylene glycol was found to be an appropriate alcohol to terminate the reaction and to obtain a clear transparent gel. The ratio 1:2:1 of urea, formaldehyde, and aluminum chloride, respectively was investigated to prepare Al_2O_3 powder. The ratios 1:2:1:1 and 1:2:1:2 of urea, formaldehyde, aluminum chloride, and silicon tetrachloride, respectively were tested to prepare SiO_2–Al_2O_3 powder. 0.075 M of AHIBA was added to each oxide during the gelation process as shown in Fig. 1. Temperature was ranged between 60 °C and 70 °C during resin formation. Two pH levels were found to be appropriate, alkaline (8–9) to start with resin formation and highly acidic (1–2) to complete the reaction. The time needed varied between 1 h and 2 h, for the change in the reaction media from watery, to a viscous gel without any signs of precipitation to give a clear transparent gel at the end.

The reaction was carried out under reflux conditions with continuous stirring. Products of the reaction were removed under reduced pressure using a pump. The gels produced were slowly dried at 120 °C. The calcination occurred in a stream of air at 700 °C/2 h. The preparation of Al_2O_3 summarized in the flow chart, Fig. 1. The reaction is completed in a highly acidic condition at pH 1–2. The Al precursor used, aluminium chloride, is a highly acidic salt which satisfies the required pH and acts as a catalyst for the resin formation.

Table 1 Surface area and pore volume of the various metal oxide powders

Sample	Surface area (m^2/g)	Pore volume (Cm^3/g)
MO	33.2	2.06×10^{-2}
MOXC-1	40.5	3.22×10^{-2}
MOXC-2	310.4	3.90×10^{-1}

The first metal oxide (MO) is used to refer to aluminum oxide only where as the other two metal oxides MOXC-1 and MOXC-2 are used to refer to aluminum/silica mixed oxide. The silica percentages were 1 and 2% in MOXC-1 and MOXC-2 respectively. The abbreviation C means that these metal oxide is cross linked with carboxylic acid group of AHIBA. Bridging of the carboxylate groups with the necessary crosslinking take place to develop the sorption capacity of the polymeric oxide.

2.4 Physico-chemical characteristic of prepared powders

Meanwhile, the powders obtained after calcination at 700 °C were characterized using Quantachrome system model 2.1 (2003), NOVA-type for measuring surface area and total pore volume. Also, the particle diameter of the prepared powders were determined using laser diffraction particle size analyzer, Shimadzu, model salt 2001, Japan.

The total surface areas of the different prepared composites were measured using standard volumetric method by nitrogen adsorption at 273 K and outgas temperature of 150 °C for 2.0 hours.

As shown in Table 1, the pore surface area and pore volume measured for the different powders display the increase in the proportion of micro-capillary and micro-pores with increase in the number of substituted silica in the resin. This was confirmed by measurement of the average particle diameter of each powder. As shown in Fig. 2, the average particle diameter (micro meter) (X-axis) was determined at the corresponding values at 50% of the Normalized Particle Amount (NPA%) (Y-axis). It was found that the average particle diameters at the corresponding values at 50% of NPA were 85, 7 and 5 μm for MO, MOXC-1 and MOXC-2 respectively.

2.5 Ion chromatographic analysis of Cr(III) and Cr(VI)

A Dionex 2000I, high performance ion chromatograph equipped with ultraviolet and visible spectrophotometer detector was used. Constant injection loop of 50 μl capacity

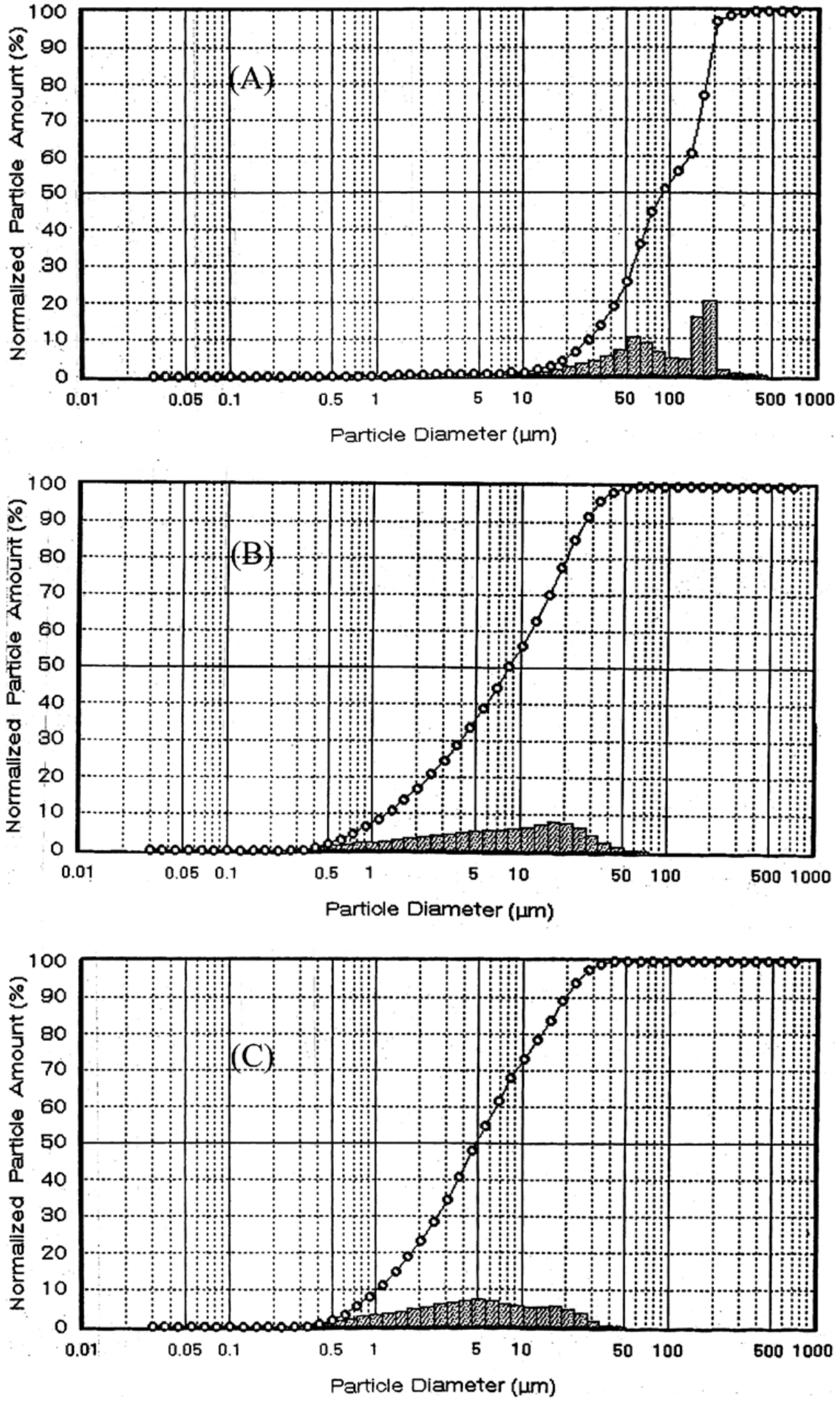


Fig. 2 Particle size distribution of various metal oxides; MO (**A**), MOXC-1 (**B**) and MOXC-2 (**C**)

was used throughout the whole study. Ion pac CS5A analytical column containing sulfonated function group resin was used for cation exchange. This column was operated in conjunction with ion pac CG5A guard column. Both CS5A and

CG5A columns are compatible with pH 0–14 fluents. The retained chromium species on the column were eluted with 2 mM pyridine 2,6-dicarboxylic acid (PDCA) dissolved in phosphate buffer solution.

Post column derivatization reaction was obtained by adding the coloring reagent containing 2 mM of 1,5 diphenyl carbon hydrazide (DPC) to the eluted metal ions to form a light-absorbing complex. The post column reagent delivery was significantly improved by using post column membrane reactor. This contains a semi-permeable membrane, which is permeable for certain reagents. Furthermore, for the operation of a membrane reactor a pressurized container was required, from which the reagent solution reaches the membrane reactor pulsation- free. The reagent diffuses into the interior of the membrane where mixing with the column effluent took place followed by UV-VIS spectrophotometric detection at wavelength 520 nm. Data acquisition and processing were done using Dionex AI-450 computer software for automatic system control including time events of both detector and gradient program as well as to control the run conditions. Separation and quantification method of chromium species was previously developed in our laboratories by ion chromatographic technique (Borai et al. 2002; Mohammed et al. 2002) and applied throughout the present work.

3 Results and discussion

3.1 Addition of AHIBA during gelation process

The general requirement for the acid to progress the gelation process as well as removal efficiency are: (a) the anion of the acid must be very weakly complexing with either aluminum or silicon ions at relatively low concentration. (b) The acid should have relatively low tendency for formation of Al/Si bonding through oxygen or hydroxide group. (c) The acid must also be sufficiently strong to produce the necessary change effect that required for chromium chelation and help for chromium removal. These requirement are available for a very few acids such as AHIBA and trichloroacetic acid.

Yoldas (1975), stated that the gellation process was performed only when the acid concentration was in the range of 0.03–0.1 M. In the present work, gel- formation was performed at constant acid concentration (0.075 M) of AHIBA for MOXC-1 and MOXC-2 oxides.

The addition of aluminium chloride and/or silicon tetrachloride to urea/formaldehyde mixture may be acombined by incorporating the Al/Si into the bridging chain that formed between methylol groups and imido groups of neighbouring molecules. Addition of AHIBA and HCl (acidic media pH = 1–2) leads to activate the imido hydrogen (NH) which leads to promotion of Al/Si substitution in the structure of the polymeric resin. Accordingly, the presence of AHIBA is therefore, expected to increase the degree of crosslinking and hence improve the chromuim metals removal.

Looking to the obtained particle size as shown in Fig. 2 and surface area measurement (Table 1), it was observed that the addition of AHIBA introduce a significant reduction in the average particle size from 85 (Fig. 2A) to 5 (Fig. 2C) micro meter for MO and MOXC-2, respectively. Also the addition of AHIBA changed significantly the measured surface area from 33.2 to 310.4 m^2/g for MO and MOCX-2 respectively, which expected to demonstrate a relatively high enhancement in chromium removal. Chelation of chromium ion with carboxylate resin in acidic media proceeds according to the following reaction (see Scheme 1).

3.2 Adsorption studies

Batch technique was applied in this work to study the adsorption of the prepared oxides towards chromium species. This technique depends on mixing of a particular weight of the powder with a certain concentration of each of Cr(III) and Cr(VI). The influence of critical variable such as shaking time, solution pH, chromium ion concentration and resin weight were tested to evaluate the behavior of different resins as a function of metal ion speciation.

The mixture is checked well till equilibrium is reached. The phases were separated and aliquots of the aqueous solution were withdrawn then subjected to IC measurement. The percent uptake was determined from the ratio of the concentration change to the initial concentration.

3.2.1 Effect of shaking time

The effect of shaking time on chromium species distribution is used as orientation maps for insights into reaction kinetics. The sorption kinetics of Cr(III) and Cr(VI) on the three oxide materials are studied at different time intervals ranged from 5 minutes to 3 hrs. As shown in Figs. 3 and 4, the equilibrium time for Cr(III) is reached after 120, 150 and 120 minutes while the equilibrium time for Cr(VI) is reached after 120, 75 and 30 minutes for the three investigated oxide MO, MOXC-1 and MOXC-2, respectively. For

Scheme 1

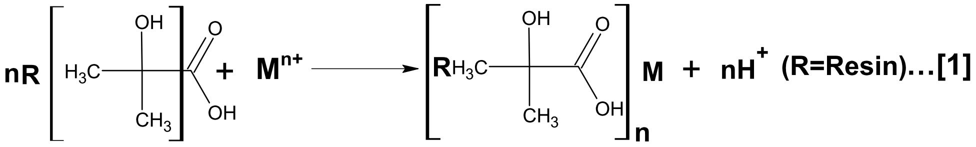


Fig. 3 Effect of shaking time on distribution constant of Cr(III)

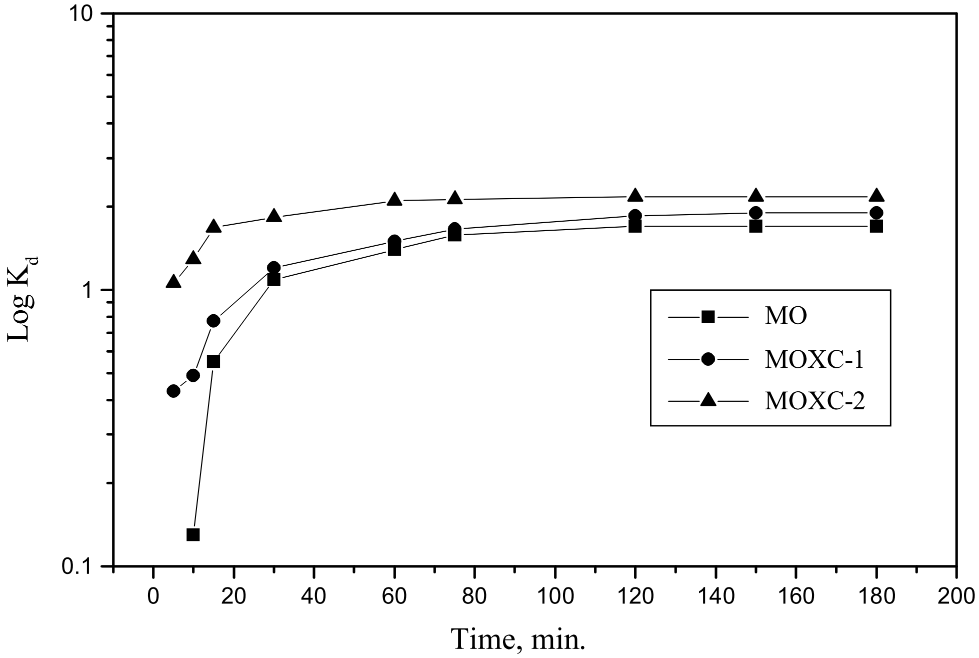
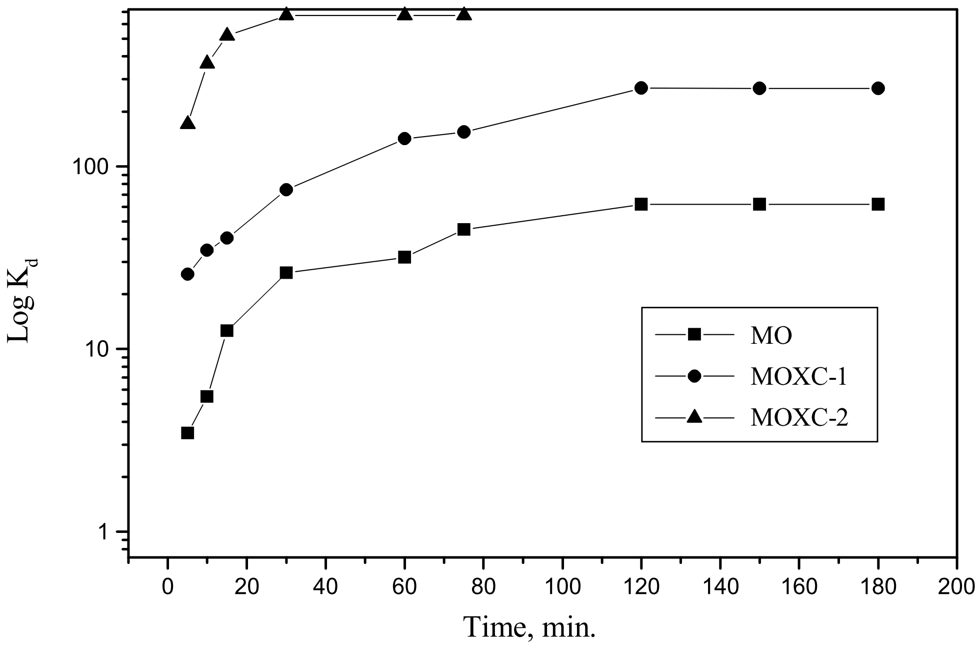


Fig. 4 Effect of shaking time on distribution constant of Cr(IV)



the adsorption of Cr(VI) on MXOC-2, it is observed that the uptake starts rapidly when the shaking starts and increases over time until a steady state is attained after 30.0 min. The kinetic data indicates that there is no significant change in the distribution ratio after this time up to 30 min.

Another important aspect of kinetic order was related to the chemical composition of the prepared oxides which contributing to the chemical speciation of polyvalent chromium complexes in system. However, this was not true in thermodynamic equilibrium, it is leading to a steady equilibrium. Trivalent chromium breaks through the metal oxides by adsorption process inside the pores cavity, as non-exchangeable polynuclear complex, furthermore chromate species bind strongly to the carboxylated oxides.

3.2.2 *Effect of volume/weight ratio*

The effect of volume to weight ratio (V/M) on the distribution coefficient of both Cr(III) and Cr(VI) are studied in the range from 25 to 500 ml/mg. This is to evaluate the optimum resin weight that could be used to achieve a high extraction capability with a minimum resin weight. As shown

Table 2 Effect of volume/weight ratio on the distribution coefficient and corresponding uptake percentage of Cr(III)

V/M ratio	MO		MOXC-1		MOXC-2	
	K_d	Uptake (%)	K_d	Uptake (%)	K_d	Uptake (%)
25	272	91.58	738	96.72	1667	98.5
50	126	71.59	412	89.17	644	92.8
71.4	64	47.25	217	75.2	337	82.5
100	51	33.8	79	44.15	148	59.67
167	34	16.94	44	20.88	95	36.31
500	19	3.66	37	6.89	63	11.2

Concentration of Cr(III) = 20 ppm

Table 3 Effect of volume/weight ratio on the distribution coefficient and corresponding uptake percentage of Cr(VI)

V/M ratio	MO		MOXC-1		MOXC-2	
	K_d	Uptake (%)	K_d	Uptake (%)	K_d	Uptake (%)
25	514	95.36	1305	98.12	7385	99.6
50	277	94.7	709	93.4	3468	98.5
71.4	205	74.2	412	85.2	1838	96.26
100	62	38.3	268	72.82	670	87.0
167	58.8	26.0	135	44.75	470	73.8
500	27.3	5.2	79	13.64	272	35.2

Concentration of Cr(IV) = 20 ppm

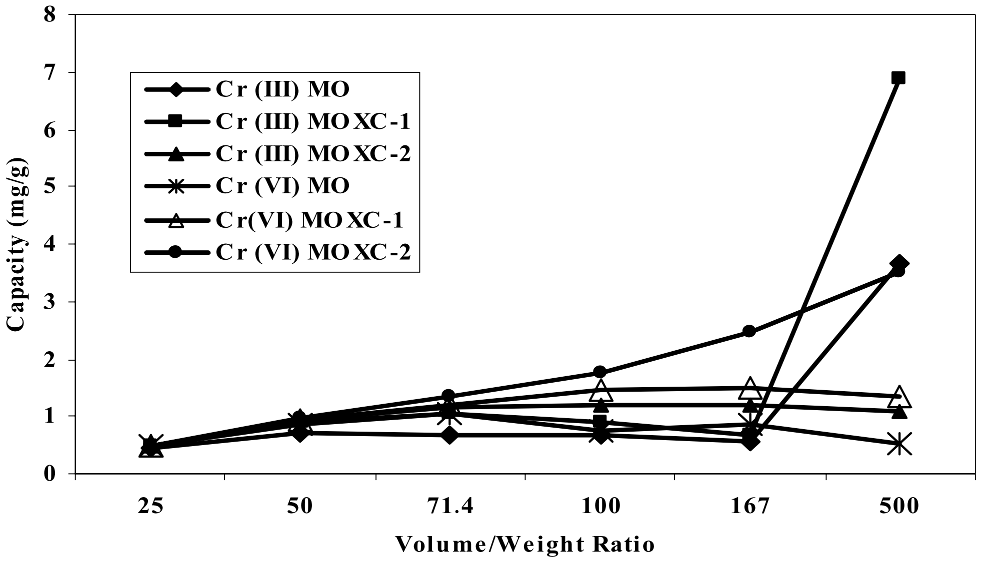


Fig. 5 Effect of V/M ratio on the adsorption capacity of Cr(III) and Cr(VI)

in Tables 2 and 3, the distribution ratios increases as V/M decreases from 500 up to 71. Starting from V/M equal 50 to 25, the distribution ratios reach to steady values. Thus, the optimum V/M ratio was obtained at 50. As shown in Fig. 5, lowering in V/M from 500 to 50 gives significant capacity change while insignificant change in capacity values was observed between $V/M = 50$ to 25.

3.2.3 *Effect of pH*

Hydroxide ion plays a determinant role in the chromium uptake from wastewater solution. Accordingly, sufficiently high pH is required for permanent activation of the resin carboxylate groups, but sufficiently low pH is necessary to minimize in situ precipitation of chromium metal ions in the form hydroxides due to metal hydrolysis and/or chromium oxidation rather than resin extractability. As shown in Table 4, the uptake percentage of three resins towards Cr(III) decreases by increases the pH-value from 2 to 7 due to activation of the exchange reaction (Equ. 1) then decreases by further increasing to pH = 10 due to metal hydrolysis. In this case the chromium oxidation reaction is thermodynamically favored over the competitive side reaction with the resin. Different behavior of Cr(IV) was observed due to

Table 4 Effect of pH on the uptake percentage of Cr(III) and Cr(VI)

pH	Uptake (%)					
	Cr(III)			Cr(VI)		
	MO	MOXC-1	MOXC-2	MO	MOXC-1	MOXC-2
2.0	7.6	14.2	18.8	14.9	32.5	46.3
3.0	16.1	19.9	25.1	18.6	47.6	57.8
4.0	19.2	33.4	39.5	23.4	54.6	61.9
5.0	34.4	53.1	46.5	29.8	69.4	77.6
7.0	33.8	44.2	59.6	38.3	72.8	87.0
9.0	21.0	27.4	41.3	58.1	77.5	89.9
10.0	14.1	17.3	33.6	66.4	83.4	92.1

$V/m = 100$, concentration of Cr(III) and Cr(IV) = 20 ppm

pH change. The uptake of Cr(IV) increases by increases the pH value from 2 to 10. This is mainly accumulated due to: (a) promotion of the exchanging efficiency of the carboxylated resins, (b) increases the reactivity of Cr(IV) in the more alkaline media, (c) low solubility of Cr(IV) in the oxidized form at relatively high acidic media. Thus, maximum uptake percentage of Cr(III) was obtained in neutral medium (pH = 7) while the maximum uptake percentage of Cr (IV) was obtained in alkaline medium (pH > 7).

3.2.4 *Effect of metal ion concentration*

The isothermal sorption capacity of the three oxide materials were determined using the batch process, by equilibrating 50 mg of the resin sample with 5 ml of aqueous solution containing various concentration of Cr(III) and Cr(VI) metal ion separately, ranged from 5 to 3000 ppm for both Cr(III) and Cr(VI). The concentration range of the metal ions was selected to be mimic to their concentration in the tested tannery bath. The loading capacity of the resin for chromium metal ion was calculated by mass balance of the difference between the metal ion concentration before and after sorption.

As shown in Tables 5 and 6, the distribution coefficients of Cr(VI) ion were found to be significantly high using MOXC-2 as compared with that of MO and MOXC-1. The distribution coefficients obey the following sequence:

MOXC-2 > MOXC-1 > MO.

The high charge-density of the hexavalent chromium ion is preferentially bound to the resin functional group due to the strong electro-selectivity effect of the resin. As a consequence, an increase in the selectivity order for hexavalent chromium over trivalent chromium is evidenced by the inflexions of the chromium breakthrough curves.

As demonstrated in the isothermal capacity curve, Fig. 6, the shape of the breakthrough curves confirms the selectivity sequence of carboxylate group toward all the polyvalent chromium species. In addition to the adsorption process of the mixed oxide by either the oxygen or the hydroxide group, both chromium metal ions are preferentially retained by the resin carboxylate groups, given the strong electroselectivity effect.

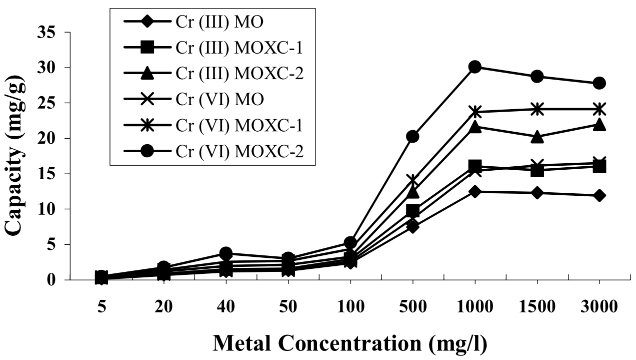


Fig. 6 Isothermal capacity curve of Cr(III) and Cr(VI) on silica/alumina hosted resins

3.2.5 *Effect of temperature*

The effect of temperature on the sorption of Cr(III) and Cr(VI) was studied in the range from 5–45 °C to test the thermodynamic parameters that affect the kinetic behaviour of each metal ion species. Table 7, showed that an increase in the sorption process with the increasing in the temperature for both Cr(III) and Cr(VI). The data obtained were found to obey the Arrhenius equation. The values of the free enthalpy change (ΔH) calculated from the slopes of the obtained straight lines are given with the free energy change (ΔG) and entropy change (ΔS) for the investigated ions, Cr(III) and Cr(VI), respectively. Comparing the thermodynamic parameters for Cr(III) and Cr(VI), it could be observed that the negative values of ΔG revealed the spontaneous nature of both Cr(III) and Cr(VI) sorption. The obtained negative values of ΔH indicated that the exothermic reaction of the sorption process for Cr(VI) is rather than of Cr(III). Insignificant differences in the negative ΔS values were obtained, which indicated the increase in the ordering of both systems with similar magnitude.

Table 5 Effect of metal concentration on the distribution coefficient and corresponding uptake percentage of Cr(III)

Metal conc	MO		MOXC-1		MOXC-2	
(ppm)	K_d	Uptake (%)	K_d	Uptake (%)	K_d	Uptake (%)
5	63	38.6	181	64.6	290	74.35
20	51	33.8	79	55.15	148	59.67
40	42	29.6	59.7	37.4	99.7	49.92
50	36.8	26.9	46.5	31.76	75.9	43.15
100	31.4	23.9	40.9	29.02	48.6	32.71
500	17.5	14.9	24.2	19.48	33.0	24.8
1000	14.2	12.4	19.0	16.0	27.6	21.64
1500	8.9	8.2	11.5	10.3	15.5	13.4
3000	4.1	3.96	5.6	5.33	7.9	7.32

$V/m = 100$

Table 6 Effect of metal concentration on the distribution coefficient and corresponding uptake percentage of Cr(VI)

Metal conc	MO		MOXC-1		MOXC-2	
(ppm)	K_d	Uptake (%)	K_d	Uptake (%)	K_d	Uptake (%)
5	76	43.18	397	97.75	2520	96.2
20	62	38.3	268	72.82	670	87.0
40	46	31.5	175	63.63	216	68.37
50	38	27.54	115	53.48	156	60.9
100	35	25.9	77	43.5	109	52.15
500	21	17.36	39	28.05	68	40.48
1000	18.2	15.39	31.1	23.7	43	30.07
1500	12.1	10.8	19.1	16.06	23.6	19.09
3000	5.8	5.4	8.7	8.0	10.2	9.2

$V/m = 100$

Table 7 Thermodynamic functions for the sorption of Cr(III) and Cr(VI)

Loaded material	Cr(III)			Cr(VI)		
	$-\Delta H$ kJ/mol	$-\Delta G$ kJ/mol	$-\Delta S$ kJ/mol/K	$-\Delta H$ kJ/mol	$-\Delta G$ kJ/mol	$-\Delta S$ kJ/mol/K
MO	63.2	9.7	0.18	51	10.3	0.14
MOXC-1	51.7	10.8	0.14	43.5	14.3	0.10
MOXC-2	57.4	12.6	0.23	107	19.3	0.29

The obtained thermodynamic parameters are in a good agreement with all the previous practical work, which confirmed that the exchange reaction of Cr(VI) with the resin is thermodynamically favored over than that of Cr(III).

3.3 Column investigation

Previous experiments showed that the exchange kinetics of Cr(III) was relatively slower than that of Cr(VI), therefore, the loading step was carried out at low flow rate of 0.75 ml/minute. The two samples were loaded separately on a glass column having 15 mm internal diameter, 25 cm length and packed with 2.0 gram of the prepared MOXC-2. Elution process was performed by passing 80 ml of PDCA through the column then chromium species were measured by IC system.

IC chromatographic measurement of the original concentration of both Cr(III) and Cr(VI) in the tannery bath (first sample) revealed that their concentration were 3145 ± 24 and 26.2 ± 3.8 $\mu g\,ml^{-1}$ respectively, whereas, their concentration in the final drain (second sample) were 1155 ± 15 and 7.6 ± 1.2 $\mu g\,ml^{-1}$, respectively.

The detected concentrations of the eluted Cr(III) and Cr(VI) were 87.4 and 0.93 $\mu g\,ml^{-1}$, in the tannery bath and 6.7 and 0.18 $\mu g\,ml^{-1}$, in the final drain, respectively. These indicated that the removal column efficiency are around 97.2 and 96.4% for Cr(III) and Cr(VI) in the tannery bath, respectively.

Table 8 Adsorption capacities of various adsorbents used for Cr(IV) removal

Adsorbent	Capacity (mg/g)	Reference
Sawdust	4.44	Bryant et al. (1992),
	10.1	Dikshit (1989),
	16.05	Zarraa (1995)
Chitosan	27.30	Udaybhaskar et al. (1990)
Cetyl-amended zeolite	0.65	Santiago et al. (1992)
EHDDMA-amended zeolite	0.42	Santiago et al. (1992)
Bentonite	0.51	Ahan et al. (1995)
Wollastonite-fly ash mixture	0.27	Panday et al. (1984)
Zeolite	0.65	Santiago et al. (1992)
Bauxite	0.52	Edrem et al. (2004)
Iron(III) hydroxide-loaded sugar beet pulp	5.12	Altundogan (2005)
Bagasse fly ash (sugar industry waste)	4.35	Gupta and Imran (2004)
Sorel cement	21.41	Hassan et al. (2006)
Si-Al carboxylate mixed oxide	30.07	The present work

Table 9 Adsorption capacities of various adsorbents used for Cr(III) removal

Adsorbent	Capacity (mg/g)	Reference
Activated Carbon Fabric (ACF)	12.2	Mohan et al. (2006)
Agricultural activated Carbon (ATFAC)	39.5	Mohan et al. (2006)
Mixed aluminosilicate-activated carbon	92.0	Shawabkeh (2006)
Treated sand filtration	11.0	Baig et al. (2003)
Chinese Reed Plant	1.85	Namasivayam and Holl (2004)
Tetrabutyl ammonium iodide-activated carbon	9.5	Lotfi and Nafaa (2002)
Sodium diethyl dithiocarbamate (SDDA)	6.84	Lotfi and Nafaa (2002)
Si-Al carboxylate mixed oxide	22.0	The present work

Column experimental data shows the high capabilities of the prepared hosted carboxylate mixed oxide not only for removal of Cr(III) and Cr(IV) but also for pre-concentration of both species from the tannery wastewater.

For comparison with other materials, Tables 8 and 9 show a set of cation exchange materials with different porosity, cross-linking degree and exchange loading to find out the best sorbent for chromium removal. The tables show more dramatic data for high removal total capacity of the new prepared carboxylate mixed oxide towards hexavalent chromium ion (30.07 mg/g). Similarly, the calculated total capacity towards trivalent chromium ion was found to be 22.0 mg/g. These high removal efficiencies are mainly attributed to the complexing ability of the immobilized carboxylate group.

The reaction kinetic in column process was also related to the chemical composition of the prepared oxides. In general, strong cation resins manifested poor performance toward chromium removal from segregated wastes of tanning operations. Accordingly, their use was misleading.

In column experiments, the data shows that the exchange kinetic was relatively rapid at the loading flow rate of 1.0 ml/min., thus, the regeneration step was carried out fast at the elution flow rate of 1.0 ml/min. Better kinetic performance of our resin is attributed to the complexing ability of the carboxylate group toward polyvalent metal species which is added to the normal ion exchange properties of the resin. This interpretation is in a good agreement with various previous works (Eisenman 1983; Janauer et al. 1985).

4 Conclusion

Sol-gel processing of mixed metals oxides has become an interesting investigations area because of its advantages compared with conventional wet chemical methods. The advantages of the prepared carboxylated mixed Al/Si oxides can be summarized as, the high surface area of dried gel results in a very high reactivity. Also, sol-gel processes can provide a means of convenient preparation method for highly homogeneous particles**.** Better insight into the above aspects might improve or simplify the basic concept of chromium removal process.

With the help of the carboxylated mixed Al/Si oxides it is now possible to treat the segregated tannery wastewaters that contain dangerous and toxic chromium ions which leads to formation of detoxified wastewater residue and minimized the environmental impact of various industrial activities. In conclusion, the environmental impact of the tannery industry is highly blamed due to the presence of hazardous pollutant such as chromium ions.

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