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Article

On the Active Adsorption of Chromium(III) from Alkaline Solutions Using Multi-Walled Carbon Nanotubes

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The paper constitutes a contribution and an advance in the treatment of wastewater contaminated by chromium. These waters are present in various sectors of the metallurgical industry (pickling liquors, effluents from electroplating processes among others)

Abstract: The present investigation deals with the adsorption of chromium(III) from alkaline media using multi-walled carbon nanotubes. The adsorption of Cr(III) has been studied under various experimental conditions: stirring speed of the aqueous solution, initial metal and adsorbent concentrations, NaOH concentration in the aqueous solution, and temperature. The rate law indicated that chromium adsorption is well represented by the particle diffusion model, whereas the adsorption process fits to the pseudo-second order kinetic model within an exothermic character. Equilibrium data fit to the Langmuir type-2 equilibrium isotherm in an spontaneous process. Chromium(III) can be eluted from metal-loaded nanotubes using acidic solutions, from which fine chromium(III) oxide pigment can be ultimately yielded.

Keywords: carbon nanotubes; chromium; wastewaters; adsorption.

1. Introduction

Nanotechnologies are one of the most important topics in today´s investigations, among them, adsorptive nanomaterials have shown their tremendous potential, and different compositions and configurations of these nanomaterials are being investigated for different applications [1],[2],[3],[4],[5],[6]. These techniques have been extensively used in separation science, i.e. metal recovery from pregnant and waste solutions, winning of precious and strategic metals, and treatment of effluents which included, e.g. toxic metals.

Including in the above, carbon nanomaterials in single-walled, multi-walled and functionalized configurations are gaining considerable importance due to their application in the recovery and separation of metals from aqueous phases [7],[6],[8],[9],[10],[11],[12],[13].

Chromium, is a toxic element [14], especially in its VI oxidation state, but solutions containing chromium(III) are also considered of a hazardous nature due to the real potential of its oxidation to the VI state, thus, its elimination from different aqueous solutions should be considered as a primary target. The recovery and separation of chromium(III) from aqueous solutions with different material and nanomaterials have been reported in the literature, with about 60 papers dealing with it in 2019 [15]; however, the majority of this information is related to the removal of Cr^{3+} from acidic to neutral aqueous pH values, thus, scarce information is available in the literature about the use of carbon nanotubes as adsorbents for Cr(III) separation and/or speciation in alkaline medium.

In the present work, Cr(III) adsorption results, from alkaline aqueous solutions, using multi-walled carbon nanotubes are presented.

2. Materials and Methods

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Multi-walled carbon nanotubes (MWCNTs) were obtained from Fluka, and were used, unless otherwise stated, without further modifications. Their main characteristics are shown in Table 1. Z potential was estimated as indicated in the literature [16].

All chemicals were of AR grade, and used in the experiments directly without any further purification. Other adsorbents used in this work were also obtained from Fluka or Sigma-Aldrich (oxidized-muti-walled carbon nanotubes (ox-MWCNTs), Ionac SR7, Lewatit EP63), except the activated carbon which was generated as described in the literature [17]. Throughout all the experimentation distilled water was used.

All experiments were conducted in a glass reactor at 20º C, except in the experiments performed at various temperatures, by using batch technique. Once the aqueous solution and the carbon nanotubes were put into the reactor and mixed using a four blades glass impeller (25 mm diameter), aliquots were taken at given times in order to analyze the chromium content in the solution by AAS. Metal uptake onto the nanotubes was calculated by the mass balance.

3. Results and discussion

3.1. Influence of stirring speed

The influence of stirring speed was studied in order to optimise uniform mixing of both aqueous solution and adsorbent, and to minimise thickness of the aqueous boundary layer, with the aqueous solution and adsorbent conditions being maintained as follows: Cr(III) 0.01 g L^{-1} in 0.1 M NaOH, and adsorbent dosage of 1g L^{-1}.

Table 1. Characteristics of the multi-walled carbon nanotubes

type	multi-walled
melting range	3652-3697 º C
density	2.1 g mL^{-1}
appearance	dust
purity	98% carbon
dimensions	10±1 nm external diameter
	4.5±0.5 nm internal diameter
	3-6 μm (length)
maximum adsorption	1295 cm^3 g^{-1}
BET	263 m^2 g^{-1}
Z potential	1.22

Results derived from this investigation revealed that the stirring speed had not any influence on the time that the system reached equilibrium (Fig. 1), since for every stirring speed investigated here, at 30 min of contact time, between the aqueous solution and the adsorbent, 85% of the chromium(III), from the solution, were adsorbed onto the carbon nanotubes, whereas equilibrium was reached after 120 min also at all the stirring speeds. However, the stirring speed had an influence on the maximum metal uptake onto the nanotubes (Table 2); as it can be seen from these results, a maximum chromium(III) uptake was achieved at 1000-1500 min^{-1}, this being attributable that at these stirring speeds the minimum of the aqueous layer was reached and adsorption maximizes. A stirring speed of 1000 min^{-1} was kept constant throughout the experiments conducted.

The data at 1000 min^{-1} were used to estimate the rate law in the present system. Experimental results best fit with the particle diffusion model (r^2= 0.962):

$$\ln\left(1-F^2\right)=-kt \quad (1)$$

with rate constant 3.8×10^{-2} min^{-1}.

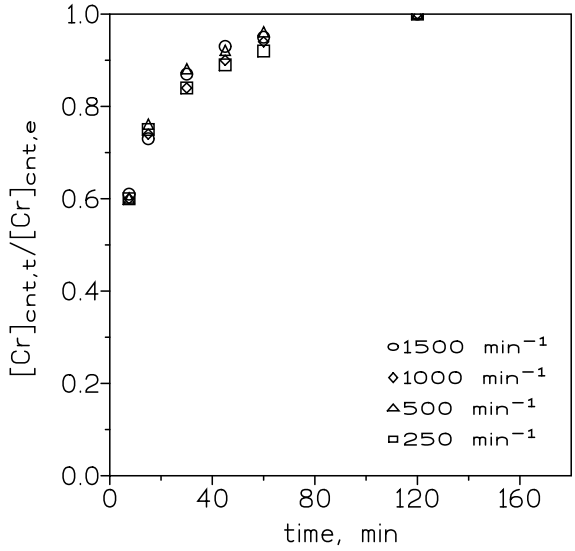

Figure 1. Dimensionless [Cr(III)]cnt,t/[Cr(III)]cnt,e versus time at the various stirring speeds. ([Cr(III)]cnt,t and [Cr(III)]cnt,e are the chromium concentrations in the nanotubes at elapsed time and at the equilibrium, respectively).

Table 2. Chromium(III) adsorption at various stirring speeds (Temperature: 20º C. Time: 2 h)

Speed (min^{-1})	Cr(III) uptake (mg g^{-1} adsorption)
250	6.4
500	7.0
1000	8.4
1500	8.3

In the above expression, F is the factorial approach to the equilibrium, defined as:

$$F=\frac{[Cr(III)]_{cnt,t}}{[Cr(III)]_{cnt,e}} \quad (2)$$

being [Cr(III)]cnt,t and [Cr(III)]cnt,e the chromium(III) concentrations, in the carbon nanotubes, at an elapsed time and at the equilibrium, respectively.

3.2. Influence of the NaOH concentration in the aqueous solution

In order to asses the influence of this variable during the adsorption of chromium(III), NaOH concentration variation studied in the range 0.1 - 0.5 M NaOH were carried out with aqueous solutions contained 0.01 g L^{-1} Cr(III). The adsorbent dosage was of 1 g L^{-1} and the temperature of 20 º C. The results from this experimentation (Table 3) showed that the percentage of metal adsorption (and metal uptake) was dependent of the NaOH concentration of the aqueous solution; increasing the chromium(III) loaded onto the adsorbent from 0.1 to 0.35 M NaOH solutions, and decreasing as the NaOH concentration in the solution was further increased.

Table 3. Influence of the NaOH concentration on chromium(III) adsorption onto the nanotubes.

NaOH, M	Cr(III) adsorption (%)	Metal uptake (mg g^{-1})
0.1	84	8.4
0.2	89	8.9
0.28	96	9.6
0.35	99	9.9
0.43	51	5.1
0.5	37	3.7

3.3. Influence of adsorbent dosage on the adsorption of chromium(III)

The results concerning adsorption of chromium(III) from the aqueous solution containing this metal in 0.1 M NaOH medium, and various adsorbent doses in the range 0.25-4 g L^{-1} , revealed an increase in the percentage of adsorption as the adsorbent dosage was increased (Fig. 2).

Experimental results of the chromium(III) adsorption onto the nanotubes were fit to various kinetics models; from this fit, it is assumed that the pseudo-second order kinetic model best represented the adsorption kinetics for initial carbon nanotubes dosages in the 0.25-4 g L^{-1} range:

$$\frac{t}{[Cr(III)]_{cnt,t}} = \frac{1}{k_2[Cr(III)]^2_{cnt,e}} + \frac{1}{[Cr(III)]_{cnt,e}} t \qquad (3)$$

Table 4 summarized the results from this fit.

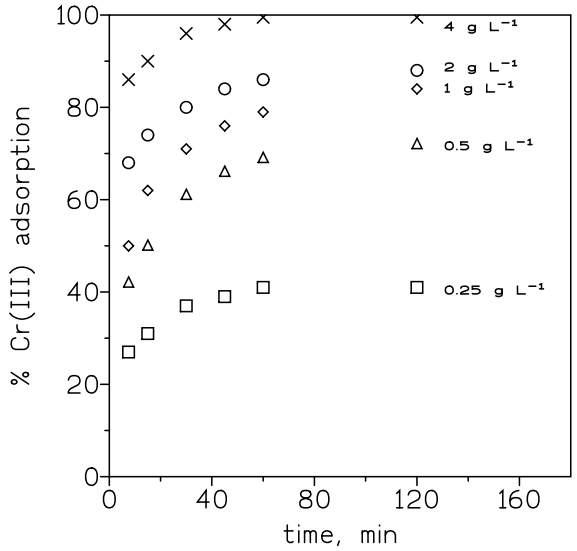

Figure 2. Influence of adsorbent dosage on chromium(III) adsorption. Aqueous solution: 0.01 g L^{-1} Cr(III) in 0.1 M NaOH. Temperature: 20 º C.

Table 4. Parameters for the fit of eq.(3) to various nanotubes doses.

Nanotubes dosage	r^2	k_2,

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(g L^{-1})		(g min^{-1} mg^{-1})
0.25	0.9986	$1.8x10^{-1}$
1	0.9997	$1.8x10^{-2}$
4	0.9998	$1.4x10^{-2}$

The equilibrium data fitted to the Langmuir Type-2 isotherm model (r^2= 0.921):

$$\frac{1}{[Cr(III)]_{cnt,e}} = \frac{1}{[Cr(III)]_{cnt,m}} + \frac{1}{k_L [Cr(III)]_{cnt,m}} \frac{1}{[Cr(III)]_{aq,e}} \quad (4)$$

In the above expression, k_L is the Langmuir constant, [Cr(III)]cnt,m the maximum metal uptake onto the nanotubes, and [Cr(III)]cnt,e and [Cr(III)]aq.e the metal equilibrium concentrations in the carbon nanotubes and in the aqueous solution. The Lagmuir model explained monolayer adsorption onto a surface containing a given and finite numbers of adsorption sites. The relative parameters for this fit are [Cr(III)]cnt,m= 333 mg g^{-1} and kL = $1.4x10^{-2}$ L mg^{-1}. Moreover, by using the next expression:

$$R = \frac{1}{1 + k_L [Cr(III)]^2_{aq,0}} \quad (5)$$

where $[Cr(III)]_{aq,0}$ is the initial metal concentration in the solution (10 mg L^{-1}), it is assumed that the adsorption process is favourable (R= 0.42), since 0<R<1.

3.4. Influence of temperature on the adsorption of chromium(III)

The adsorption of chromium(III) (0.01 g L^{-1}) in 0.1 M NaOH by 1 g L^{-1} of the adsorbent was studied over the range 20-60º C. Under these conditions, increasing temperature gave a decrease in chromium adsorption (84% at 20º C versus 52% at 60º C), and defining the metal distribution coefficient between the adsorbent and the aqueous solution as:

$$D_{Cr} = \frac{[Cr(III)]_{cnt,e}}{[Cr(III)]_{aq,0}} \quad (6)$$

A plot of log D_{Cr} versus 1000/T was linear (r^2= 0.9959), and from this plot, the value of ΔH^o was estimated as -32 kJ mol^{-1}, thus, the adsorption being exothermic, and ΔS^o= -95 J mol^{-1} K^{-1}, indicating a decreasing in the randomness, at the solid-liquid interface, during the adsorption process. The estimated ΔG^o value was -4 kJ mol^{-1}, which represented to an spontaneous adsorption process.

3.5. Chromium(III) removal from the aqueous solution using different adsorbents/ion exchangers: a comparison

Different adsorbents or anion exchange resins were used to compare their chromium(III) adsorption results with that obtained within the present multi-walled carbon nanotubes. In the present case, the aqueous solution was of 0.01 g L^{-1} Cr(III) at 0.1 M NaOH, with an adsorbent dosage of 1 g L^{-1}. The temperature of the experiments was of 20º C. The results from this comparison were summarized in Table 5. It can be seen, that worse results were obtained when the non-functionalized Lewatit EP63 resin was used to remove Cr(III) from the solution, whereas the use of the active carbon allowed to reach near 94% Cr(III) removal, value which was very near to the yield reached with the use of the multi-walled carbon nanotubes.

Table 5. Chromium(III) adsorption using various adsorbents.

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Adsorbent	Functional group	[a]Cr(III) (mg g^{-1})
MWCNTs	none	8.4
Ionac SR7	[b]QAS	7.3
Lewatit EP63	none	1.1
ox-MWCNTs	carboxylic	5.0
Active carbon [18],[19]	none	9.4

[a] At the equilibrium. [b] Quaternary ammonium salt. Ionac SR7 and Lewatit EP63 are resins

3.6. Desorption

Previous experiments demonstrated that at pH 4, a mere 5% of chromium(III) was adsorbed by these nanotubes, thus it seemed logical to approach the desorption process by the use of acidic solutions. Results obtained when 8.4 mg g^{-1} Cr(III)-loaded carbon nanotubes were put into contact with acidic solutions allowed to conclude that, by the use of sulphuric acid solutions (0.1 M onwards), near 85% of the chromium(III) loaded onto the nanotubes, can be desorbed after 30 min of reaction at 20º C. From these solutions, a greenish-fine pigment can be yielded [20].

4. Conclusions

The developed investigation was useful for the recovery of chromium(III) from alkaline conditions, though the adsorption wass dependent upon the NaOH concentration in the aqueous solution. Adsorption of Cr(III) onto multi-walled carbon nanotubes was quick at initial contact times but slow down with increasing contact times. The rate law was well described by the particle diffusion model in an exothermic (ΔH^{o}=-32 kJ mol^{-1}) conducted adsorption process. In the range of carbon nanotubes dosages (0.25-4 g L^{-1}) used in the investigation, adsorptions can be described by the pseudo-second order kinetic model, whereas the Langmuir type-2 isotherm described well Cr(III) adsorption within an spontaneous process. The multi-walled carbon nanotubes used in the investigation performed well, in terms of chromium(III) removal from alkaline medium, with respect of a number of other Cr(III)-potential adsorbents. Acidic solutions can be used to desorb chromium(III) from metal-loaded nanotubes, and Cr(III) can be recovered as a fine pigment.

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