Potential use of CeO_2, TiO_2 and Fe_3O_4 nanoparticles for the removal of cadmium from water

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Abstract

Inorganic nanoparticles (NPs) of cerium oxide (CeO_2), iron oxide (Fe_3O_4) and titanium oxide (TiO_2) were studied for the removal of dissolved cadmium from water at concentrations ranging from 25 to 350 mg/L. Adsorption was the predominant mechanism for sequestration, and particularly efficient cadmium removal was demonstrated for iron oxide NPs. Experimental data were fitted to three different adsorption isotherms: Langmuir, Freundlich and Temkin. The best fit was obtained for the Freundlich isotherm ($R^2 > 0.96$ for all NPs). Adsorption was shown to follow pseudo second order kinetics ($R^2 = > 0.91$ for all NPs). All three NPs showed some removal of cadmium in aqueous solution, but after 72 hours of process, iron oxide NPs showed a higher capacity of cadmium adsorption (101.1 mg Cd/g NP) than cerium oxide nanoparticles (49.1 mg Cd/g NP) or titanium oxide nanoparticles (12.2 mg Cd/g NP). These results demonstrate the potential use of these nanoparticles to remove dissolved cadmium at high concentrations.

Keywords: Cadmium; Adsorption; Nanoparticles; Water Treatment; Adsorption Kinetics; Adsorption isotherm.

1. Introduction

Cadmium is a heavy metal with important adverse and toxic effects when released to the environment. Cadmium can enter the environment from natural processes, but the most important source is from human activities such as metal production, combustion of fossil fuels, or the manufacturing of batteries, dyes and screens, which cause the pollution of soils and waters [1,2]. Cadmium is also detrimental to human health, causing kidney, lung and bone damage [3].

As a result of the publication of new regulations on cadmium, only small quantities of this metal are now released to wastewater from municipal and industrial sources. Nevertheless, this is often in excess of the extremely low recommended limits of cadmium in drinking water: a maximum of 0.003 mg/L is recommended by the World Health Organization [4], and in other countries such as Spain the permissible limit of cadmium is similar (0.005 mg/L) [5].

Several treatments exist to remove cadmium from water, such as chemical precipitation, electrolysis, ionic exchange and membrane technologies [6,7]. Heavy metal adsorption onto nanoparticles (NPs) is an emerging technique for the removal of these pollutants. The high specific surface of NPs, together with a suitable electric charge given by an adequate Z-potential, makes them excellent candidates for the adsorption of heavy metals [8].

The objective of this study is to explore the possibilities of using CeO_2, Fe_3O_4 and TiO_2 NPs for the adsorption of dissolved cadmium. Adsorption isotherms and kinetic models typically used for NPs are also tested to give a base for further studies.

2. Materials and Methods

2.1. Synthesis of Nanoparticles (NPs)

Metal and metal oxide NPs were synthesized in aqueous phase, using milli-Q grade water. All reagents were purchased from Sigma-Aldrich and used as received. All the synthesis procedures are based on previously published studies modified where necessary for scale-up. For CeO_2 NPs a modified method based on Zhang et al. was used [9,10]. For the synthesis of TiO_2 NPs the process of Pottier et al. [11] was adopted. Fe_3O_4 NPs were synthesized by Massart's method [12] modified according to [13]. Physical properties of the NPs are summarized in Table 1. A detailed description of the methodology and the resulting nanoparticles can be found elsewhere [10].

Table 1 here

2.2. Cadmium determination

Calibration curves for cadmium were constructed using 99.995% cadmium (II) chloride using a colorimetric method based on the reaction of cadmium with dithizone to form a complex that is extracted with chloroform [14]. The limit of detection of the method is 0.01 mg of cadmium.

2.3. Adsorption and kinetic experiments

To test the adsorption capacity and to determine the adsorption isotherm of the different NPs tested, eight dilutions of cadmium were prepared at 25, 50, 100, 150, 200, 250, 300 and 350 mg/L. Solutions of TiO_2, Fe_3O_4, and CeO_2 NPs were prepared at 0.64 mg/mL. pH was adjusted to 7.0 with sodium hydroxide (0.1 M) and citric acid (0.15 M) where necessary. Finally, 10 ml of each solution of cadmium were mixed with 10 ml of the NPs solution for 24 hours. The mixture was centrifuged to separate nanoparticles from the liquid solution at 14000 rpm for 20 min. The supernatant was analyzed for residual dissolved cadmium.

Kinetics was measured by analysis of dissolved cadmium at several time points after mixing. Aliquots from a stock cadmium solution (initial concentration 200 mg/L) were mixed with an equal volume of NP solution and analyzed as described above at 0, 0.5, 1, 2, 3, 5, 10, 24 and 48 hours after mixing.

3. Results and Discussion

3.1. Adsorption isotherms

The adsorption of dissolved cadmium by different NPs is presented in Fig. 1. The equilibrium capacity can be calculated according to Equation (1) [15]:

$$q_e = (C_0-C_e)V/m \qquad \text{Eq. (1)}$$

where C_0 and C_e are the initial and equilibrium concentrations of Cd^{2+} (mg/L) respectively, V is the solution volume (L) and *m* is the mass of NPs (g). Adsorption was modeled using the Langmuir, Freundlich and Temkin isotherms [16,17]. The results are presented in Table 2.

Fig. 1 here

Table 2 here

The Freundlich isotherm gave the best fit to the experimental data, which suggests a chemical interaction on a heterogeneous surface. The Freundlich isotherm is described in Equation (2) as:

$$x/m = Kc^{1/n} \quad \text{Eq. (2)}$$

where x is the mass of adsorbate, m is the mass of adsorbent, c is the equilibrium constant of the adsorbate in solution, and K and n are constants. A value of $n \sim 1$ reduces Equation (2) to the linear isotherm typically observed for the adsorption of dyes onto solid adsorbents [16]. From Table 2, it can be observed that the correlation coefficients for the Temkin isotherm are also relatively good, which supports again the presence of a chemical interaction between cadmium and NPs. In contrast the Langmuir isotherm could not be applied because the concentration tested were far from adsorbent saturation (data not shown).

The three types of NP clearly demonstrated sequestration of dissolved cadmium. The highest adsorption (101.1 mg Cd/g NP after 72 h) was observed for iron oxide NPs, more than twice that of the cerium oxide nanoparticles (49.1 mg Cd/g NP) and almost ten times that of titanium oxide nanoparticles (12.2 mg Cd/g NP).

Despite the high capacity of the iron oxide NPs, the lowest equilibrium concentration of dissolved cadmium was achieved by treatment with the titanium oxide NPs. Fig. 1 shows the evolution of the adsorption of cadmium using a solution of 0.64 mg/mL of the different NPs tested at initial concentrations of Cd^{2+} that resulted in maximum percentage removal: 150 mg Cd^{2+}/mL for iron oxide NPs, 100 mg Cd^{2+}/mL for CeO_2 NPs and 25 mg Cd^{2+}/mL for TiO_2 NPs. Maximum removal of ~90% of dissolved cadmium was obtained for titanium oxide NPs.

3.2. Kinetics of adsorption

Two models were proposed to fit the experimental kinetic data: pseudo first-order and pseudo second-order. Pseudo first-order kinetics imply an adsorption site in the NP surface for each cadmium atom, and may be expressed as Equation (3):

$$\log(q_e - q_t) = \log q_e - (k_1/2.303)t \qquad \text{Eq. (3)}$$

where: q_e and q_t (mg/g) are the adsorption capacities at equilibrium (steady state, infinite time) and at any time t, respectively, and k_1 (h^{-1}) is the first-order kinetic constant. In this case, correlation coefficients were very poor (<0.4) and this model was discarded.

The pseudo second-order kinetic model is widely used [16] and it is normally applied to describe chemical adsorption in liquid media. The model is expressed as Equation (4):

$$t/q_t = 1/k_2 q_e^2 + (1/q_e)t \qquad \text{Eq. (4)}$$

where k_2 ($g/mg^{-1}\ h^{-1}$) is the second order kinetic constant and the rest of parameters are the same as those presented in Equation (3).

Although both models assume that the driving force for adsorption is essentially the difference of concentration of cadmium between the bulk liquid and the surface of the NP, the results obtained with the second-order model were in good agreement with the data (R^2=0.981 for CeO_2, R^2=0.995 for Fe_3O_4 and R^2=0.918 for TiO_2, respectively), as observed in Table 3. As expected, the theoretical equilibrium adsorption capacity is similar to that predicted by the model, a fact that has been also observed in the case of the adsorption of lead on NPs [17].

Table 3 here

3.3. Discussion

Iron oxide NPs exhibit significantly higher equilibrium adsorption values than other widely used adsorbents, for example activated carbon (3.37 mg/g) [18], orange peel wastes (43.3 mg/g) [19] or chitin (14.7 mg/g) [1]. Cerium and titanium oxide NPs exhibit lower equilibrium adsorption values, similar to those of orange peel wastes and chitin, respectively

Increased regulatory stringency has stimulated the investigation of a large number of new adsorbents for the removal of cadmium at low concentrations. In many of these studies, biowastes that are otherwise costly to dispose of have been proposed for cadmium sequestration. For instance, Fard et al. [20] tested the direct application of biosolids for the adsorption of cadmium, with a maximum adsorption capacity of the biosolids (q_e) of 46.0 mg/g dry biosolid and an adsorption process that could be represented by the Langmuir isotherm. Similarly, Hamdaoui et al. [21] tested an agricultural waste material (melon peels) to remove cadmium with considerable success and a maximum adsorption capacity of 81.97 mg/g using the Langmuir isotherm. Other studies [22] have also tested vegetal residues for the removal of dissolved cadmium. However, the problem with these processes is that the toxic metal is transferred from a liquid medium to solid wastes, which themselves then present novel disposal challenges. In contrast, the use of nanoparticles facilitates the recovery of both the adsorbent and the pollutant, as has been demonstrated with other toxic dissolved metals such as lead or chromium [10,23]. Further research is clearly needed to explore the reuse of NPs in the adsorption of heavy metals to make adsorption a competitive technology applicable to full-scale processes.

4. Conclusions

The present study is the first critical assessment of the potential for inorganic NPs to sequester dissolved cadmium. The results show that Fe_2O_3 NPs offer the highest specific absorption capacity, while TiO_2 NPs offer the strongest adsorption. Future studies will explore the reuse (desorption of cadmium) of NPs, the number of adsorption/desorption cycles possible without losing adsorption capacity, and possible interferences when other compounds are present. Obviously, a life-cycle analysis of the technology will ultimately be required, although it is noteworthy that all the NPs used in this study are commercially available at low prices. The magnetic properties of iron oxide nanoparticles, which facilitate separation from the liquid medium, make Fe_2O_3 NPs attractive candidates for the removal of dissolved cadmium at acceptable costs, in comparison with other complex and expensive adsorbents.

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Tables

Table 1. Physical properties of synthetic nanoparticles.

Nanoparticle composition	*Shape*	*Z-Potential (mV)*	*Surface coating*	*Concentration (NPs/mL)*	*Concentration (mg/mL)*	*Solvent Conc. (mM)*
Iron oxide (Fe_3O_4)	Irregular	-58	Inorganic TMAOH *	~10^{15}	0.67	TMAOH 1
Cerium oxide (CeO_2)	Irregular	+12	Inorganic HMT*	~10^{16}	0.64	HMT 8.33
Titanium oxide (TiO_2)	Irregular	-42	Inorganic TMAOH *	~10^{16}	1.2	TMAOH 10

* TMAOH: Tetramethylammonium hydroxide
* HMT: Hexamethylenetetramine

Table 2. Parameters for the Freundlich, Langmuir and Temkin isotherms using CeO_2, TiO_2 and Fe_3O_4 NPs.

		Parameter		
Isotherm	NPs	k_F	n	R^2
Freundlich	CeO_2	2.727	0.95	0.968
	Fe_3O_4	2.231	1.087	0.969
	TiO_2	1.845	0.997	0.994
	NPs	q_m (mg/g)	$k_L \times 10^{-3}$ (L/mg)	R^2
Langmuir	CeO_2	1111.111	4.87	0.313
	Fe_3O_4	2000	8.35	0.142
	TiO_2	-5000	-0.36	0.071
	NPs	k_T	b	R^2
Temkin	CeO_2	0.777	5.379	0.801
	Fe_3O_4	0.865	7.733	0.966
	TiO_2	0.897	8.491	0.862

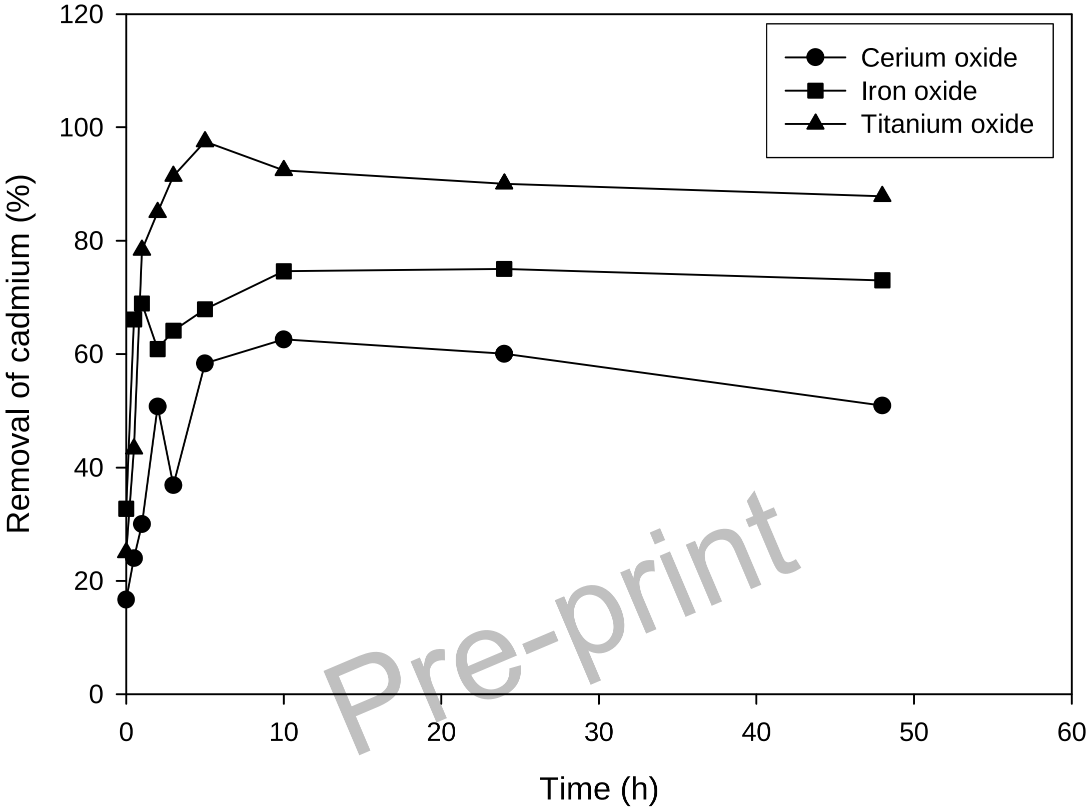
Table 3. Maximum adsorption capacity (q_e) at equilibrium (steady state, infinite time) and pseudo second-order rate constants (k_2) obtained using the pseudo second-order kinetic model. Concentration of NPs of CeO_2, Fe_3O_4 and TiO_2 was 0.64 mg/l and initial Cd^{2+} concentration was 100 mg/l.

NPs	q_e (mg Cd^{2+} /g NPs)	k_2 (g NP/(mg Cd^{2+} h))	R^2
CeO_2	48.30	0.016	0.981
Fe_3O_4	99.57	0.20	0.995
TiO_2	15.83	0.019	0.918

Legends to Figures

Figure 1.- Cd^{2+} adsorption on Fe_3O_4 (squares), CeO_2 (circles) and TiO_2 (triangles) NPs. Conditions were pH=7, temperature=25ºC and initial concentrations of cadmium that produces the highest removal of Cd^{2+} for each nanoparticle (150 mg Cd^{2+}/mL for iron oxide NPs, 100 mg Cd^{2+}/mL for CeO_2 NPs and 25 mg Cd^{2+}/mL for TiO_2 NPs) and for a concentration of nanoparticles fixed at 0.64 mg/mL.

Fig. 1



Removal of cadmium (%)
Time (h)
0
20
40
60
80
100
120
0
10
20
30
40
50
60
Cerium oxide
Iron oxide
Titanium oxide