

USE OF CERIUM OXIDE (CeO₂) NANOPARTICLES FOR THE ADSORPTION OF DISSOLVED CADMIUM (II), LEAD (II) AND CHROMIUM (VI) AT TWO DIFFERENT pHs IN SINGLE AND MULTI-COMPONENT SYSTEMS

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ABSTRACT

Cerium oxide (CeO₂) nanoparticles (NPs) were used for the removal of cadmium (II), lead (II) and chromium (VI) ions in single aqueous solutions and in solutions with mixtures of the three metals. The adsorption studies were carried out at pH 5 and 7 using a systematic factorial experimental design that considered the metal concentration from 1 mg l⁻¹ to 10 mg l⁻¹ and NP concentration from 0.064 g l⁻¹ to 0.640 g l⁻¹. The highest adsorption capacity was obtained in the removal of lead (II) (128.1 mg g⁻¹), followed by cadmium (II) (93.4 mg g⁻¹) and finally chromium (VI) (34.4 mg g⁻¹). Data were fitted to a polynomial function obtaining the best reduced models. The type of system (single, multi-component) did not affect sorption capacity, whilst pH affected the sorption of Cd and Cr, but not that of lead. CeO₂ nanoparticles proved to be effective adsorbents in removing all three heavy metals in multi-component systems, which opens a new window for their use as sorbent materials in complex waters contaminated with mixtures of heavy metals.

Keywords: Adsorption, Cerium oxide, Heavy metals, Multi-component systems, Nanoparticles

1. Introduction

Nowadays, the world is facing a water crisis due to the lack of clean drinking water. With the fast development of various industries, a huge quantity of wastewater has been produced from industrial processes and it has been discharged in soils and water systems (Wang and Peng, 2010). One of the main concerns is the presence of heavy metals such as cadmium, lead and hexavalent chromium, which have been extensively used as target pollutants in research studies due to their high toxicity and also because of the well-documented human health problems associated to these compounds (Förstner, 1984; Tan and Xiao, 2009; Recillas *et al.*, 2011). Water pollution is one of the main health concerns around the world. The world's supply of fresh water is running out and the contaminant levels permitted are getting more stringent. This generates new challenges to meet the quality standards for drinking water (Wang and Peng, 2010), especially when there is a shortage.

Many methods have been used to remove heavy metals from water and wastewater, mainly by chemical precipitation, ionic exchange, membrane separation, biosorption, classical adsorption processes, electrolysis, etc. However, most of them require an extensive processing and imply a high cost. Therefore, it is necessary to develop more efficient remediation strategies that are able to remove heavy metals from contaminated water at very low concentrations (Recillas *et al.*, 2011).

Nanotechnology, which is the engineering of functional systems at the molecular scale, is a promising new technology with diverse applications. Among them, it can offer new products and process alternatives for drinking water purification. Heavy metal adsorption onto nanoparticles (NPs) is an emerging technique for the removal of those pollutants. Nanosized metal oxides such as iron oxides, manganese oxides, aluminum oxides, and titanium oxides are studied for adsorption of heavy metals from aqueous systems (Hua *et al.*, 2012). Among the NPs used for adsorption processes, CeO₂ NPs have been the focus of some of the most significant advances regarding the use of nanomaterials, such as their immobilization on carbon nanotubes for the removal of arsenate (Peng *et al.*, 2005) or the development of a combined adsorbent of Mn-Ce oxide for fluoride removal (Deng *et al.*, 2011), among other recent examples. CeO₂ nanoparticles have been studied also from the point of view of its specific surface area (Ju-Nam and Lead, 2008) showing that nanoparticles are strong sorbents and their properties are strongly size-dependent. When a high specific surface area is combined with other properties, such as an appropriate electrical charge, NPs become excellent candidates for adsorption of heavy metals (Zach-Maor *et al.*, 2011). The use of NPs in adsorption processes presents some problems related to the comparison of CeO₂ NPs with other types of organic and inorganic adsorbents. This is because of the experimental conditions among the different types of adsorbents. In addition, the NPs synthesis can produce NPs with different physico-chemical properties on the surface, and, as a result, different values of adsorption capacities can be found in the literature (Recillas *et al.*, 2010). Even though data on the removal of heavy metals ions from binary and ternary mixtures with different adsorbents such as peat (McKay *et al.*, 1997), fly ash (Visa *et al.*, 2010) or activated carbons (Mohan and Chander, 2001; Mohan and Singh, 2002) have been reported, experimental data on multi-component sorption systems involving NPs are still very limited in the literature. Multi-component systems are characterized by additional features such as the possible interaction effects among different species in solution and the potential interactions on the surface or the competition among the different metal ion species, which depend on the ionic characteristics. Accordingly, no single mechanism can explain the adsorption of complex mixtures of metal ions from aqueous solution onto NPs (Mohan and Chander, 2001).

The aim of this work was to study potential differences of the sorption capacity of CeO₂ NPs with regard to cadmium (II), lead (II) and chromium (VI), dissolved in water, both in single systems (one metal in the solution) as well as in multi-component (all 3 metals mixed together in the solution) systems. This was done so that to study any competitive phenomena in the multi-component systems, as has been found in other studies (Kyzas *et al.*, 2013). The study was performed at two different pHs (5 and 7), which are typical pHs found in environmental systems. A factorial experimental design was used to obtain an empirical equation that can describe the sorption capacities as a function of the initial metal concentration, initial NP concentration and pH.

2. Materials and methods

2.1 Synthesis of nanoparticles

Cerium oxide nanoparticles were synthesized in aqueous phase using milli-Q grade water. All reagents were purchased from Sigma-Aldrich® and used as received. The CeO₂ nanoparticles synthesis was based on Zhang (2004). Briefly, the Ce³⁺ ions from Ce(NO₃)₃ salt are oxidized at basic pH conditions to Ce⁴⁺ using hexamethylenetetramine (HMT). Then, the CeO₂ nanocrystals precipitate and are further stabilized in

aqueous solution with the same reagent (HMT), which forms the double electrical layer to prevent NP agglomeration (Recillas *et al.*, 2010; Recillas *et al.*, 2011).

2.2 Adsorption experiments

For the adsorption studies, cadmium (II) chloride (99.99% of purity, Sigma Aldrich, Spain), lead (II) nitrate (99.99% of purity, Sigma Aldrich, Spain) and potassium dichromate (VI) (99.5% of purity, Panreac, Spain) were used as metal sources, respectively. They were dissolved in deionized water and the corresponding dilutions were carried out. While lead and cadmium are dissolved cations, chromium is present as dichromate anion. However, along the text we will refer to it as Cr(VI). Each of these solutions was mixed with the corresponding suspensions of CeO₂ nanoparticles for single and multi-component systems, with a resultant pH of 7±0.1, and then the mixture was stirred at 130 rpm at room temperature for 24 hours. All the adsorption experiments were performed at equilibrium pH of 5±0.2 and 7±0.1. Solutions were adjusted to pH 5±0.2 by using 10 g l⁻¹ citric acid solution. Final pH measurements were done at the end of the 24 h period; then samples were centrifuged (10,000 rpm) to separate the nanoparticles (solid phase) from the liquid phase. The supernatant was analyzed for residual dissolved heavy metals (non-adsorbed metal). The equilibrium capacity was calculated with the following equation according to Contreras *et al.* (2012):

$$q_t = (C_0 - C_e)V/m \quad (1)$$

where q_t is the sorption capacity (mg metal sorbed / g NP), C_0 and C_e are the initial and equilibrium concentrations of each heavy metal in solution (mg l⁻¹), respectively, V is the solution volume (l) and m is the mass of the NPs (g) placed in the solution.

2.3 Experimental design

In this factorial experimental design, the primary goal was to investigate the simultaneous effects of the initial metal concentration and the initial NP concentration on sorption capacity. Therefore, a three-level central composite full factorial design containing all the possible combinations between the factors (f) and their levels (L) was used, leading to $N=L*f$ experiments, including one four-replicated central point (Dejaegher and Heyden, 2011). The two variables were the initial concentration of metals and the initial NPs concentration.

Table 1. Initial conditions in the adsorption experiments

Exp	Coded concentration values		Actual initial concentrations	
	NPs (g l ⁻¹)	Metal (mg l ⁻¹)	NPs (g l ⁻¹)	Metal (mg l ⁻¹)
1	-1	-1	0.064	1.0
2	-1	0	0.064	5.5
3	-1	1	0.064	10.0
4	0	-1	0.352	1.0
5	0	0	0.352	5.5
6	0	0	0.352	5.5
7	0	0	0.352	5.5
8	0	0	0.352	5.5
9	0	1	0.352	10.0
10	1	-1	0.64	1.0
11	1	0	0.64	5.5
12	1	1	0.64	10.0

The initial metal concentrations selected were: 1 mg l⁻¹, 5.5 mg l⁻¹ and 10 mg l⁻¹, in both the single and the multi-component systems. The initial NP concentrations were: 0.064 g l⁻¹, 0.352 g l⁻¹ and 0.64 g l⁻¹, which

corresponds to the range of metal and NPs concentrations typically found in literature in similar experiments (Recillas *et al.*, 2011).

2.4 Empirical modeling

Empirical modeling was performed in order to assess the effect of 4 parameters, initial sorbent concentration, initial metal concentration, pH and type of sorption system, on the sorption capacity. The generic equation 2 was fitted to the data:

$$q_t = b_1 X_1 + b_2 X_2 + b_3 X_3 + b_4 X_4 \quad (2)$$

where: b_1 , b_2 , b_3 , b_4 are the model coefficients, X_1 is the initial NP concentration (g l^{-1}), X_2 is the initial metal concentration (mg l^{-1}), X_3 is the pH, X_4 is a categorical variable that indicates type of system (1 for single system and 2 for multi-component system) and q_t as earlier defined. A constant was avoided to be included since it has no physical meaning. Interaction terms were not investigated.

According to the methodology presented in Berthouex and Brown (2002), only the significant terms (at $p < 0.05$) should be used in the regression model equation to obtain the best reduced model (BRM). This is done by sequentially removing terms that are not statistically significant and by continuously re-fitting new models until all coefficients become statistically significant. The results obtained from the experimental design were processed with Minitab® v.17 and SigmaPlot® v.11.

2.5 Determination of metals

Cadmium (II) and lead (II) were determined by using a colorimetric method based on the reaction of the metal with dithizone to form a complex that is extracted with chloroform; then the absorbance was measured at 518 nm for cadmium and 510 nm for lead determination (Greenberg *et al.*, 1981). Chromium (VI) was also determined by a colorimetric methodology, using diphenylcarbazide as complexing reagent (Greenberg *et al.*, 1981).

3. Results and discussion

3.1 Adsorption results and isotherms

Figure 1 presents the isotherms for the 3 metals in both systems (single, multi-component) at both pHs (5 & 7). A deviation from the typical adsorption isothermic profile is observed, particularly in the cases of chromium and lead. The presence of two outliers for these metals needs further investigation.

According to Figure 1, a highest adsorption capacity (q_t) was obtained for Cd (II) ($62.0 \text{ mg Cd}^{2+}/\text{g CeO}_2$) when compared with that previously obtained with cerium oxide nanoparticles ($48.3 \text{ mg Cd}^{2+}/\text{g CeO}_2$) at the same pH (Contreras *et al.*, 2012). This may suggest that for low initial concentrations of NPs, better adsorption capacities can be obtained. Although this seems unexpected, a possible explanation could be the fact that when the concentration of nanoparticles in the solution increases, the effective surface area for adsorption becomes lower, due to interaction among ions. Therefore, a relatively low initial concentration of nanoparticles could promote higher adsorption capacities. It is evident that this hypothesis should be confirmed with further specific experiments. For Cd (II), when the pH became more acidic, the adsorption capacities reduced; this could be due to the high concentration of H^+ that also occupy available adsorption sites (Dong *et al.*, 2010). In the case of Pb (II), there is no clear effect of the pH on the adsorption capacity. On the other hand, the Cr (VI) presented a similar behavior to Cd (II). It is well known that Cr (VI) can form several complexes (CrO_4^{2-} , HCrO_4^-) with different affinities for the adsorbent that may result in variable adsorption capacities (Navarro *et al.*, 2006). Lead (II) and chromium (VI) exhibited maximum q_t values of 43.8 mg/g CeO_2 and 21.3 mg/g CeO_2 , respectively, at the single system.

According to Figure 1, higher q_t values were obtained in the multi-component experiments for Cd (II) and Pb (II). Actually, the q_t for lead (128.1 mg Pb²⁺/g CeO₂), obtained in the multi-component system at pH 5, was significantly higher than that obtained in the single component experiments (43.8 mg Pb²⁺/g CeO₂). The adsorption capacities for lead were actually higher when compared with other adsorbents such as coconut (4.38 mg g⁻¹) (Nowack and Bucheli, 2007). In the case of Cr (VI), the adsorption capacity in the multi-component system was slightly higher than that obtained in the single component system. The maximum adsorption capacity was 34.4 mg Cr⁶⁺/g NP, similar to that obtained with maghemite (Hu *et al.*, 2005), and approximately three times higher than that of the EA-200 activated carbon sorption capacity (Recillas *et al.*, 2010). From the results, we can observe that the sorption capacity for cadmium (93.4 mg Cd²⁺/g) was higher in the neutral pH and at the multi-component system. Since Figure 1 does not clearly reveal the effects of the various parameters (initial concentration of metal and NP, pH, type of system) on the sorption capacities, empirical models were built to better investigate that.

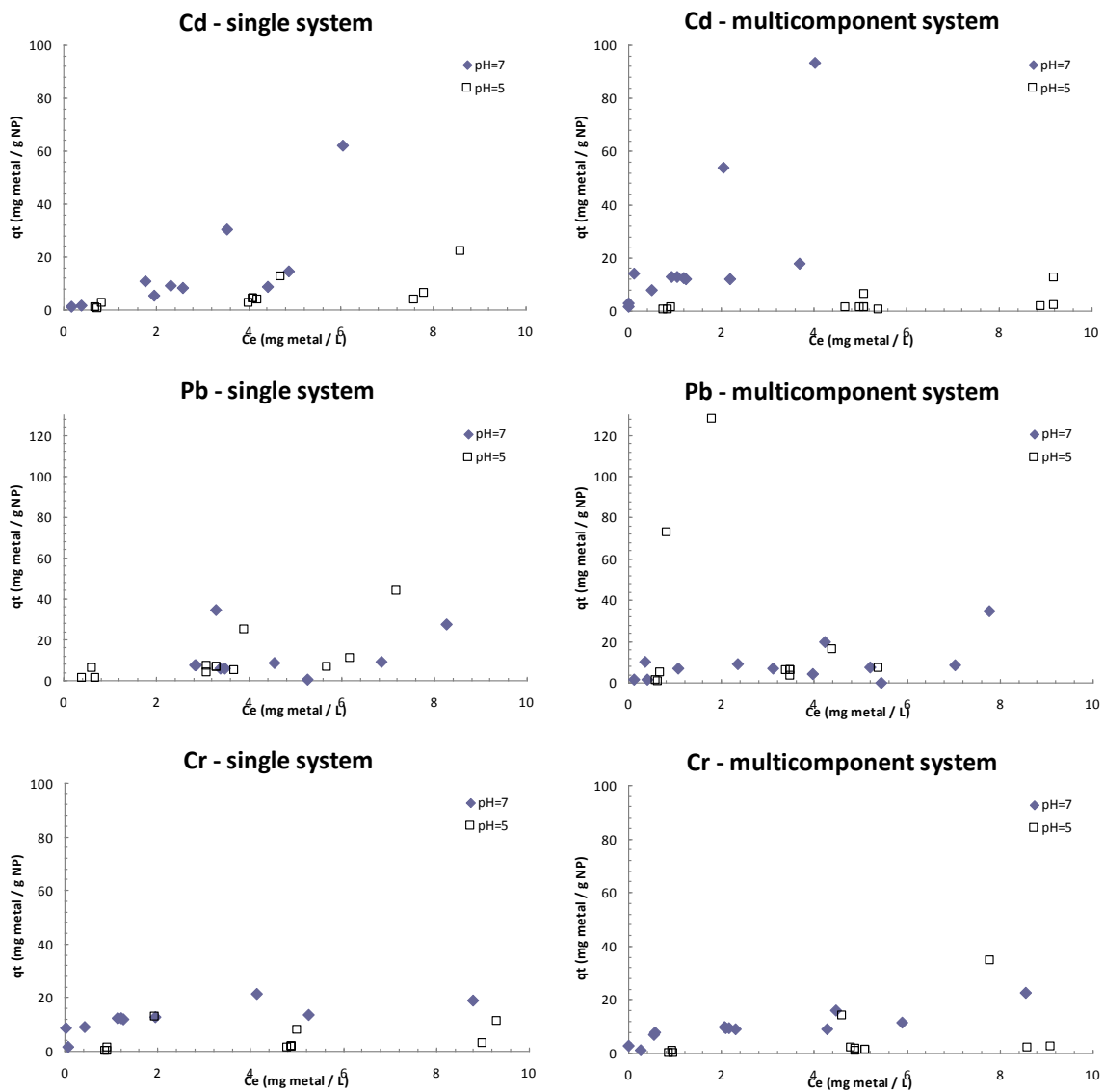


Figure 1. Isotherms for all 3 metals at the single and multi-components systems and at two different pHs (5 and 7)

3.2 Empirical modeling

Empirical modeling was based on equation (2). The fitted equations (best reduced models) for each metal are included in Table 2.

Table 2. Best reduced models to predict sorption capacity as a function of several parameters.

Metal	Best reduced models	R ²
Cd (II)	-46.9 NP + 1.6 M + 3.3 pH	60.4%
Pb (II)	-31.5 NP + 3.9 M	45.6%
Cr (VI)	-17.8 NP + 1.0 M + 1.4 pH	78.5%

NP: initial CeO₂ NP concentration; M: initial metal concentration

All coefficients in the models are statistically significant at $p < 0.05$. According to the equations, the sorption capacity of all three metals was always affected significantly by the initial NP and initial metal concentration. That is, as the initial metal concentration in the solution increased, the sorption capacity increased as well, whilst the opposite was true with the initial NP concentration. Furthermore, it is interesting to note that the system (single, multi-component) did not statistically affect the sorption process with regard to any of the metals (the p -value of that coefficient was always much higher than 0.05). That is, the sorption capacity of all 3 metals was statistically similar in the single and multi-component systems and, apparently, no competitive phenomena existed as have been noted in other multi-component adsorption systems (Kyzas *et al.*, 2013, 2015). Apparently, the sorption sites of the NPs were enough so that not to allow competitive sorption phenomena to occur.

On the other hand, the equations of Table 2 reveal that pH significantly affected the sorption capacities of Cd (II) and Cr (VI), but not of Pb (II). It is reminded that these equations were based on experiments on two pH values only (5 and 7); thus, the effect of pH can be explained only within that range. Therefore, in the case of Cd (II) and Cr (VI), as pH increased from 5 to 7, the sorption capacity increased as well. This can be explained by the speciation of those metals in those pHs and the fact that the abundance of H⁺ (at low pHs) competed with sorption sites. Actually, pH affected more the sorption capacity of Cd (II) than that of Cr (VI). In the case of Pb (II), as was also evident in Figure 1, pH was not a predictor of the sorption capacity.

Figure 2 graphically depicts the original sorption capacities, as a function of initial NP and metal concentrations, as well as the response surfaces that were drawn based on the empirical modeling performed.

4. Conclusions

The results obtained in this study demonstrate that cerium oxide nanoparticles can be effectively used as adsorbents for the removal of dissolved Cd (II), Pb (II) and Cr (VI) in both single and multi-component aqueous systems. Sorption capacity was statistically similar between the two systems (single and multi-component). Both the initial metal and the initial NP concentrations were statistically significant predictors of the sorption capacities of all the three metals. However, pH was found to affect the sorption capacity of cadmium and chromium, but not that of lead.

The maximum sorption capacities recorded in this work were 93.4 mg Cd²⁺/g CeO₂ (multi-component system, pH 7), 128.1 mg Pb²⁺/g CeO₂ (multi-component system, pH 5), and 34.4 mg Cr⁶⁺/g CeO₂ (multi-component system, pH 5).

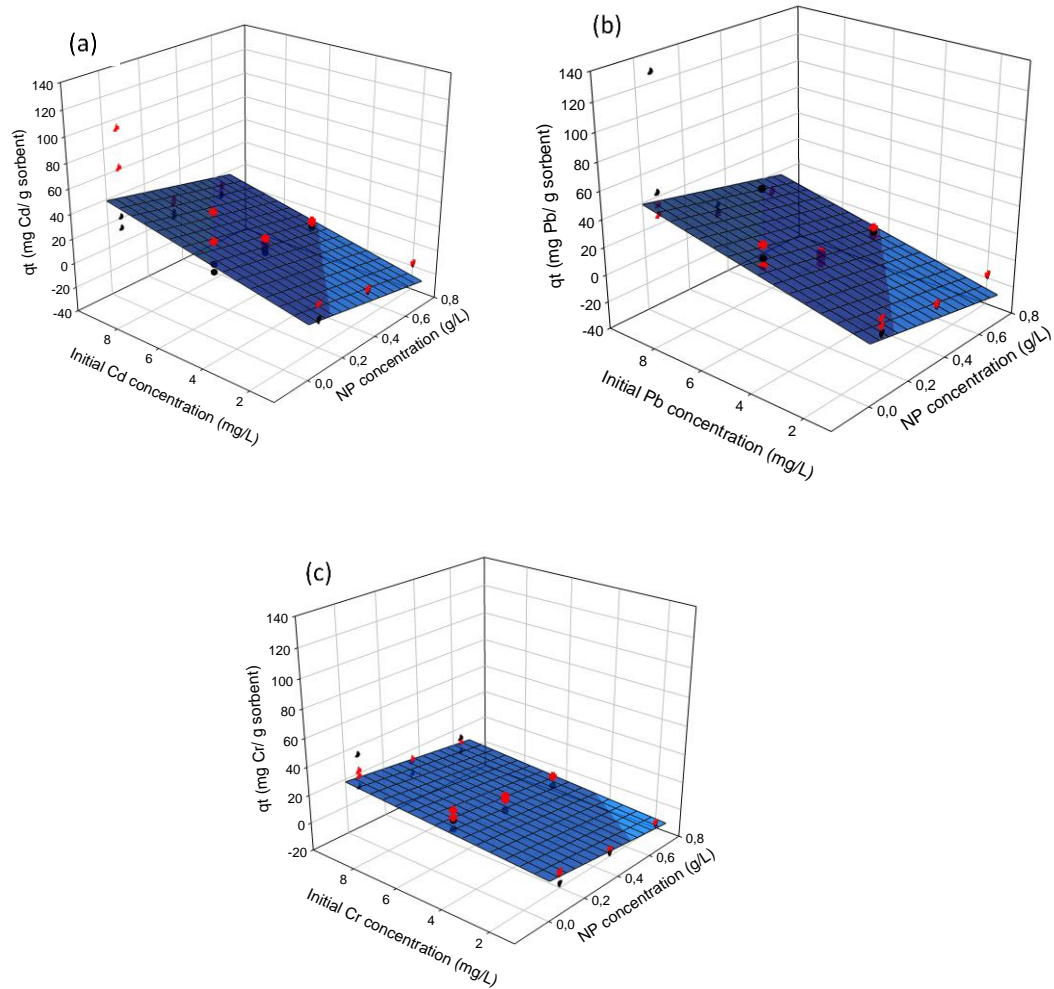


Figure 2. (a): Cd (II) response surface equation $-23.1 \cdot NP + 3.1 \cdot M$, (b): Pb (II) response surface equation $-31.5 \cdot NP + 3.9 \cdot M$, (c): Cr (VI) response surface equation: $6.43 - 15.43 NP + 1.17 M$; Red dots: q_t at pH 7, Black dots: q_t at pH 5, NP: initial nanoparticle concentration (g l^{-1}), M: initial metal concentration (mg l^{-1}).

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