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CHITOSAN/OXIDIZED EXFOLIATED GRAPHITE NANOPLATELETS ADSORPTIVE MATERIALS FOR IMPROVED LEAD ADSORPTION FROM AQUEOUS SOLUTIONS

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Exfoliated graphitic nanoplatelets (xGnP) show adsorption capability and adsorption efficiency for lead removal from water, the adsorption being influenced by the pH value of the solution and the xGnP surface characteristics, which are controlled by their treatment processing. In this work, oxidized exfoliated graphite nanoplatelets entrapped in chitosan/THF adsorptive materials on nylon discs are used as improved adsorbents for Pb(II) removal from aqueous solutions. Preliminary results are presented in terms of sorption capacity, kinetics and reuse.

Keywords: carbon nanostructures, heavy metals, adsorptive materials

1. Introduction

Adsorption is an efficient technique for removal of contaminants from effluents. In comparison with other methods like ion exchange and adsorption on columns, adsorptive porous materials offer certain advantages such removal efficiency and faster kinetics. Exfoliated graphite nanoplatelets (xGnP) [i] have attracted attention since 2009, as a substitute for carbon nanotubes, given the predicted mechanical, structural, thermal and electrical properties of graphite and their similar properties to carbon nanotubes (CNTs), well known as adsorbents [ii]. Structurally, CNTs and graphite are made up of the same building blocks-graphene [iii], therefore the adsorption behavior of xGnP presents great potential for environmental contaminants [iv]. Based on our previous results presented in [v] and in [vi], the study of adsorptive properties of oxidized xGnP was continued by entrapping them in adsorptive materials [vii] prepared with chitosan and tetrahydrofuran (THF).

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As a shortcoming, oxidized xGnP used as adsorbents cannot offer sufficient stability and they are not easily removed from samples after experiments. To overcome this problem, blended chitosan materials present superior mechanical properties supplying a constant and reproducible dispersion of the carbon-based nanostructures in membranes. The obtained materials present better sorption capacities, very good mechanical strength and compact matrices.

Lead is a toxic heavy metal present in the environment, because of its non-biodegradability [viii,ix]. For humans, lead is a neurotoxic metallic element, exposure to high concentrations especially from waters, causing health problems by accumulating in the human body [x].

Based on our knowledge, the preparation of chitosan/oxidized xGnP adsorptive materials has not been reported elsewhere. The distribution of oxygen functional groups, which act as adsorption sites improve at the surface, the biodegradability and the reuse of these disks improving as well.

In the current study, the oxidized xGnP were obtained as in [5] by oxidation with $KMnO_4$ and HNO_3, these nanostructures being already characterized in terms of Boehm's titration and pH of the point of zero charge pH_{PZC}. The objective of this preliminary study was to enhance the sorption capacity, as well as the reusability of these materials for lead adsorption in batch adsorption experiments. The adsorptive materials were characterized through scanning electron microscopy (SEM) and Fourier transformed infrared spectroscopy (FTIR).

2. Experimental

2.1. Reagents

Graphite nanoplatelets xGnP were purchased from xGSciences Inc. (USA). They were synthesized via the chemical reduction of exfoliated oxide nanoplatelets, graphite oxide being produced by the oxidative treatment of graphite [xi].Polyvinyl alcohol (PVA) was purchased from Merck (Germany). Chitosan (95%) was analytical reagent grade purchased from Sigma-Aldrich (UK).
All other reagents were analytical reagent grade. All the solutions were prepared with doubly distilled water.

2.2. Apparatus

The potentiometric and pH measurements were conducting using a potentiometric interface ELITE 8908 with 8 channels (NICCO, UK) with a Metrohm 632 pH–meter equipped with a combined electrode. The potential measurements were carried out at 25 ± 0.1^0C using an Ag/AgCl reference electrode with the following cell assembly: Ag/AgCl | internal solution (10^{-4} M $Pb(NO_3)_2$) || PVC membrane || sample | Ag | AgCl | KCl.

The sensors were washed with doubly distilled water between the measurements, and the potential was recorded when it became stable and then plotted as a logarithmic function of the lead concentration.

The morphology of oxidized xGnP was characterized by scanning electron microscopy using a SEM microscope coupled with an energy dispersive X-ray spectroscope (Philips Quanta Inspect F) at 30 kV and 2000xmagnification.

Fourier transform infrared (FTIR) measurements were performed using a Shimadzu 8400 FTIR spectrophotometer equipped with a KBr beam splitter (KBr, FTIR grade).

2.3. Chitosan/oxidized xGnP preparation

The chitosan/oxidized xGnP adsorptive materials were prepared by casting-evaporation method. 40 mg of oxidized xGnP were dispersed in 2 mL tetrahydrofuran (THF) using a horn sonicator for 30 minutes. Then 20 mg chitosan were added and the mixture was mechanically stirred for 60 minutes to obtain homogeneous membrane casting solutions. The prepared solutions were cast on nylon plates of 20 mm diameter with the same thickness of 1000 µm and dried at room temperature. The obtained disks were then immersed in 1 M NaOH solution for one hour, in order to be insoluble in water. Chitosan plain disks were prepared without oxidized xGnP, too. Both types were washed with distilled water and dried.

2.4. Procedures

Static adsorption

The adsorption of lead ions onto chitosan/oxidized xGnP adsorptive materials was examined using a batch method. Disks were cut in quarters and weighed, then introduced in 25 mL of Pb(II) solutions prepared at various concentrations in the concentration range 10^{-3}-10^{-4} M for 6 hours under stirring. The optimum pH for the adsorption of lead ions on chitosan/oxidized xGnP adsorptive materials was considered in the range 5-6 for all the sample solutions. Batch equilibrium tests were carried out at 25^0C, Pb(II) adsorption on the membranes was calculated by measuring the differences in Pb(II) in solutions before and after equilibration. All the experiments were done in triplicate, the mean value being reported. The maximum deviation was less than 10% (experimental error).

2.5. Porosity

The porosity of the adsorptive nanomaterials was determined using dry-wet method, being calculated as in [xii]:

$$\text{Porosity (\%)} = [(w_1-w_2)/dV]x100$$

Where, w_1 and w_2 are wet and dry membrane mass, d is the density of distilled water at room temperature, and V is wet volume of the membrane.

2.6. Reuse of the adsorptive disks

Quarters of disks were incubated in 25 mL of lead solutions with the initial concentration of 200 mg L^{-1} at 25 ^{0}C and pH 5 for 24 hours. After calculating the amount of lead ion adsorbed, the disks were washed with distilled water and then immersed in 25 mL 30 mM Na_2EDTA solution under stirring for 3 hours.[xiii] The regenerated disks were used for the next adsorption stage as described in the batch experiment. Repeated stages were conducted to evaluate the reusability of the adsorptive materials.

3. Results and discussion

Lead adsorption depends on many factors, such as the surface functional groups, the specific surface area and the composition of the solution. The oxidation treatment by nitric acid can cause a modification of the ion-exchange capacity, different functional groups with acidic nature on the surface dissociating at different pH values. The adsorptive materials based on chitosan/oxidized xGnP allow a homogeneous distribution of the functional groups on the surface. xGnP nanoplatelets, composed of non-polar benzene rings present low affinity toward polar polymeric matrix of chitosan polyvinyl alcohol based membrane, because of the difference in polarity and weakly interfacial interactions between the xGnP and the polymer. The carboxylic groups attached at the margins of xGnP facilitate cations transport to the membrane and cause a better dispersion of the oxidized xGnP in the polar polymeric matrix. Due to this, the ion adsorption on the disk is improved resulting bigger concentration gradients.

3.1. Characterization of adsorptive materials chitosan/ oxidized xGnP

The dispersed oxidized xGnP were characterized using scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) in a previous publication. [xiv] A multilayer structure with curled morphology was observed with overlapped graphene sheets. The FTIR spectra proved the existence of hydroxyl and carboxyl groups at the edges of the nanoplatelets. Stretching vibrations of acidic -OH appear as a broad absorbing peak, confirming the attachment of -OH groups to the graphene structure as a result of the acidification. Oxidized xGnP embedded in chitosan materials increase its porosity and during air drying of the casted layer, the oxygenated groups were homogeneously distributed without overlapping due to their hidrophilicity. Similar observations were done by Salehi et al. [xv] who observed the connection between the hydrophilic nature of the oxygenated groups and the porosity of the disks, by using the dry-wet method.

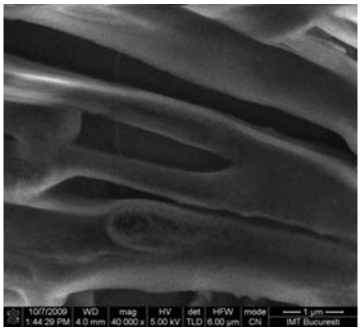

Fig. 1 SEM image of oxidized xGnP embedded in chitosan

The chitosan morphology is presented in Fig. 1, observing that the chitosan surface has a unidirectional aspect already mentioned in the literature [15], no porosity being observed. In this case, the diffusion problems can be avoided and the sorption process takes place fast. The porous materials present a unidirectional porous structure that facilitates the diffusion of metal ions.

3.2. Effect of pH on the adsorption of lead

The pH value of the solution is one of the most important variables, this influence being studied on oxidized xGnP. [5] It was observed that because of the functional groups of chitosan there are more lead adsorption sites, especially the amino groups. It was observed by Rangel-Mendez et al.[xvi] that the chitosan's solubility varies depending on the pH values, diminishing between 3 and 5, increasing at pH values between 5 and 7 and remaining constant at pH values between 8 and 9. A pH value of 5 was selected for this experiment.

It can be also observed that at very low pH values very low adsorption of the metal takes place, this being observed before [xvii].

The surface charge depends on pH of the electrolyte, at the point of zero charge where the net surface charge is zero.[xviii] The effect of the solution pH can be explained by considering the surface charge of xGnP and the degree of ionization and speciation of the sorbate. The increase in the adsorption of Pb^{2+} ions by increasing pH for suggests an ion-exchange mechanism between the H^+ ions and the metal ions at the oxygen-containing functional groups of the xGnP. Below a pH value of 6, Pb^{2+} will exist as a free ion easily interacting with the surface.[xix,xx] Above pH 6 Pb hydroxides will precipitate from the solution. There were also mentioned in the literature unfavorable interactions of these hydroxides with the surface of carbon adsorbents.[xxi,xxii]

3.3. Kinetics

In the figure below, the time profile of adsorption of lead ions on chitosan/oxidized xGnP in THF adsorptive materials in 25 mL of Pb(II) solutions prepared at various concentrations in the concentration range 10^{-3}-10^{-4} M for 6 hours under stirring is presented.

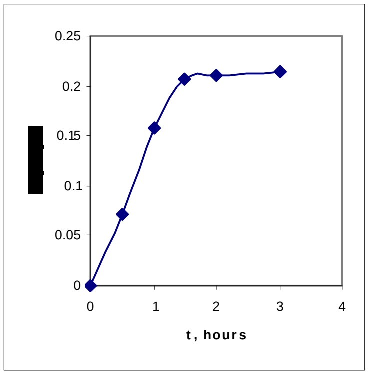

Fig. 2 Effect of the contact time for Pb^{2+} adsorption by adsorptive materials oxidized xGnP/chitosan at T=298 K in 25 mL of 10^{-3} M Pb(II) solution, for 6 hours under stirring

The sorption velocities are fast, the kinetic of adsorption indicating that the adsorption process achieves equilibrium after 60 minutes. The proposed adsorptive materials support favorable mass transport and superior loading capacities. The main sorption mechanisms of metal ions onto xGnP taken into consideration were: electrostatic attraction, sorption-precipitation and chemical interaction between the metal ions and the surface functional groups of xGnP. The most prevalent of them is chemical interaction. The kinetic process could be well-described by the pseudo-second order rate law and the rate constants increase by increasing the temperature.[xxiii,xxiv] The temperature at which a sorption process is carried out influences both the sorption rate and the degree of sorption, because by increasing the temperature the diffusion rate of the metal ions across the external boundary layer will rise based on the decrease of the solution viscosity.

3.4. Adsorption isotherms

The adsorption isotherms for the removal of metal ion on adsorptive materials based on oxidized xGnP/chitosan were studied using quarters of membranes containing 10 mg oxidized xGnP each in lead solutions between 10^{-4} and 10^{-3} M. The adsorption equilibrium data are represented by adsorption isotherms, which represent the relationship between the mass of the solute adsorbed per unit mass of adsorbent q_e, estimated as the sum of oxidized xGnP (in mg) and the mass of chitosan (in mg), corresponding to a quarter of the disk. The

Langmuir and Freundlich equations were used to describe the data obtained from the experiments.

Removal efficiency of the adsorptive disk was of 85% using the material in batch adsorption mode. Removal efficiency in solutions enhances at low initial concentrations of the lead ions

The mechanisms by which the metal ions are adsorbed onto the disks are complicated and appear attributable to electrostatic attraction, sorption and chemical interaction between the metal ions and the surface functional groups of xGnP and chitosan. The chemical interaction between the metal ions and the surface functional groups of xGnP is the major sorption mechanism [xxv], protons in the carboxylic and hydroxil groups of xGnP exchange with the metal ions in the aqueous phase. In acidic media, chitosan favors Lewis acid-base type reactions between the amino groups and the free orbital in the proton. The amino group is protonated as RNH_3^+, the proton being replaced by ion-exchange with Pb^{2+} ions.

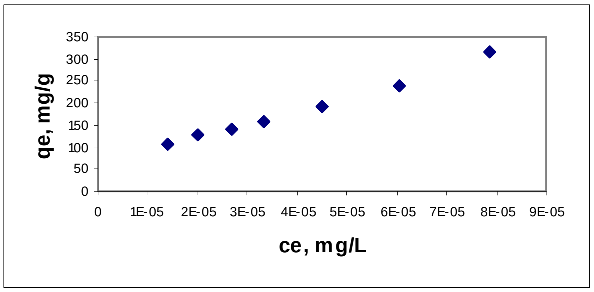

Fig. 3 Adsorption experiment using quarters of disks containing 10 mg oxidized xGnP each in lead solutions between 10^{-4} and 10^{-3} M, at T=298 K, under stirring

Freundlich adsorption isotherm

The adsorption data obtained were fitted to the Freundlich adsorption isotherms [xxvi], which is described by the following equation:

$$\log q_e = \log K_F + 1/n \log C_e \text{ , where}$$

q_e represents the ratio between the mass of the solute adsorbed per unit mass of adsorbent q_e for the solution concentration C_e. The Freundlich isotherm constants K_F and n are constants incorporating the factors affecting the adsorption process like the adsorption capacity and intensity of adsorption. The constants K_F and n were calculated from the Freundlich plots, the values of both constants being presented in Table 1. The values of n between 1 and 10 represent a favorable adsorption in terms of the intensity of adsorption.

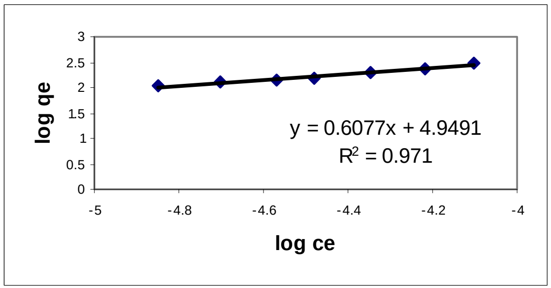

Fig. 4 Linearized Freundlich isotherms for Pb^{2+} adsorption by adsorptive disk oxidized xGnP/chitosan, pH = 5.0, adsorbent concentration 10 mg oxidized xGnP and 5 mg chitosan, contact time 30 minutes, T = 298 K

If the value of 1/n is lower than 1, it indicates a normal Langmuir isotherm, which correlates with our results. 1/n=0.6077and K_F=284.99.

Langmuir adsorption isotherm

The data obtained were fitted to the Langmuir-1 adsorption isotherm applied to equilibrium adsorption assuming monolayer adsorption onto a surface with a finite number of identical sites:

$$C_e/q_e = 1/(q_m K_a) + C_e/q_m,$$

a linear plot of Ce/q_e vs. C_e being employed to determine the value of q_m (mg/g) and K_a(L/mg). The data obtained with the correlation coefficients are presented in Table 1.

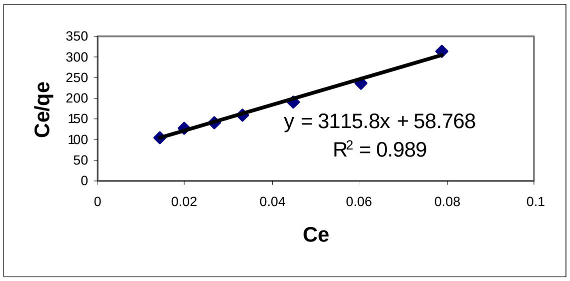

Fig. 5 Langmuir plot for the adsorption of Pb^{2+} on the adsorptive disk oxidized xGnP/chitosan: pH = 5.0, adsorbent concentration 10 mg oxidized xGnP and 5 mg chitosan, contact time 30 minutes, T = 298 K

The value of q_m = 320.94 mg/g obtained from the Langmuir isotherm is consistent with that experimentally obtained of 314.99 mg/g, indicating that the adsorption process is mainly a monolayer one. The chelation adsorption mechanism for Pb(II) on the adsorptive membrane offers a good distribution at the material surface.

Table 1

Parameters of Freundlich and Langmuir adsorption isotherm models for Pb(II) on xGnPs

Langmuir constants		Freundlich constants	
q_m (mg/g)	320.94	K_F	284.99
K_a (L/mg)	0.53	n	1.64
r^2	0.989	r^2	0.971

The Langmuir and Freundlich adsorption constants and the corresponding correlation coefficients are got. The adsorption of Pb(II) is well fitted to the Langmuir isotherm, the 1/n value less than 1 being an indicative of a normal Langmuir isotherm.

3.5 Desorption and reuse

Desorption experiments were performed at different pH values of the solutions. Low values of the pH (acidic pH) are useful for the removal of the adsorbed metal ions. Different acids (HCl and EDTA salts) were used for the regeneration of the chitosan/oxidized xGnP/THF adsorptive material saturated by the Pb(II) ions. Na_2EDTA revealed a better performance for the regeneration of the materials, EDTA being capable of forming Pb(II) complexes. Based on He et al [xxvii], 25 mM Na_2EDTA solution was selected for the regeneration.

The effect of consecutive adsorption-desorption cycles was studied, the results showing that the adsorption capacity of the adsorptive materials for Pb(II) decreases after three regeneration cycles. Therefore, new chitosan/oxidized xGnP/THF membranes were used for further adsorption. The desorption of Pb(II) increased by decreasing the pH of the solution with HNO_3 up to pH = 3 where it reached 95%.

4. Conclusions

The sorption behavior of Pb(II) onto oxidized exfoliated graphite nanoplatelets (xGnP)/chitosan in THF adsorptive materials was studied, preliminary results being presented in this work .

The adsorptive disks present good sorption capability of Pb(II) from aqueous solutions, the sorption properties depending on the pH value of the solutions and on the presence of active sites and the size of the surfaces.

Improvement of the mass transport, ion exchange capacity and surface characteristics account for the enhancement of the adsorptive materials prepared with oxidized xGnP. The reusability of the disks containing oxidized xGnP in comparison with plain ones was better in Na_2EDTA as an eluent. The sorption mechanism appears mainly attributable to chemical interaction between the metal ions and the surface functional groups. Surface acidity, pH and temperature are key parameters in determining the sorption rate of metal ions onto xGnP. Further research will be developed in order to use these new nanomaterials in preconcentration of heavy metals from large volumes of solutions.

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