Superparamagnetic nanosorbent for water purification: Assessment of the adsorptive removal of lead and methyl orange from aqueous solutions

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Abstract

The present study describes the preparation of 50.3 nm superparamagnetic nanosorbents with high surface area for the adsorptive removal of lead and methyl orange from water. This material is based on the surface modification of iron oxide superparamagnetic nanoparticles with a double-shell coating of mesoporous silica whose porosity was increased up to 570 m²/g by the addition of a porogenic material and its calcination. The adsorptive performance of the nanosorbent was evaluated as a function of several parameters (e.g. solution pH, pollutant initial concentration, and contact time), concluding that pHs around 5 are needed to avoid precipitation of Pb²⁺ as Pb(OH)₂ and the equilibrium adsorption capacity is reached after 2 h in all cases. The experimental data on the adsorption capacity of lead and methyl orange onto the nanosorbent were fit to a pseudo-second order kinetic model and Langmuir isotherm model. The maximum adsorption capacity value increases from 35 up to 50 mg/g_{NS} for lead removal with increasing nanosorbent surface area. Contrary, for methyl orange the maximum adsorption goes up to 240 mg/g_{NS}, indicating a larger nanosorbent surface affinity for the organic matter that is able to diffuse through the silica pores as probed by the intraparticle diffusion model. In addition, we found a good reusability (100% recovering after 4 sorption/desorption cycles for methyl orange removal), which makes of this magnetic nanosorbent suitable for remediation technologies.

Keywords

Water treatment; Iron oxide nanoparticles; Magnetic nanoparticles; Pollutant; Magnetic harvesting; Adsorption

1. Introduction

Nowadays, the deterioration of water quality coming from different sources and with different inorganic and organic pollutants is a subject of major environmental concern (Ihsanullah et al., 2016). First, heavy metals are considered persistent-contaminants that cannot be easily degraded into harmless products (Fu and Wang, 2011). Lead is one of the most common and hazardous that can be present not only in industrial wastewater but also in drinking water coming from corrosion of household plumbing and natural erosion (Ali et al., 2019; Fu and Wang, 2011). A second class of pollutant discharged to the environment is composed of organic dyes like methyl orange (MO) (molecular structure shown in Fig. S1). In fact, annually more than 10 % of the produced 700 kt dyes are effluents coming from textile, paint, paper, varnishes, ink, cosmetics, and plastic industries (Bilal et al., 2017; Crini, 2006). These highly colored wastes have harmful outcomes for the environment; apart of being aesthetically to sight, they cause obstructions of light distressing biological processes within a stream (Mohammadi et al., 2011).

Currently, there exist many methods for lead and methyl orange removal, which are already been used in wastewater treatment plants throughout chemical and physical treatments (Rasheed et al., 2019b). For lead removal, some of these processes are: chemical precipitation by the sulphide method, ion exchange with selective cation composites, adsorption by activated carbons or biosorbents, among others (Malik et al., 2019; Zare et al., 2018). On the other hand, methyl orange removal can be performed by adsorption using organic based sorbents and modified clays, electrochemical methods, membrane filtration, etc (Brillas and Martínez-Huitle, 2015; Kausar et al., 2018; Zare et al., 2018).

Solid phase extraction is a very effective and affordable technique for water purification, in which magnetic materials offer an advantage due to the easy separation by means of a magnet (Mazarío et

al., 2017). Moreover, magnetic interactions between particles can be minimized by reducing their size to the nanometer range, giving rise to a superparamagnetic behaviour diminishing aggregation while preserving the colloidal stability (Cali et al., 2018). Finally, these nanomaterials can present high surface area, good stability in a wide pH range, capability of being very selective, and reusability (Rajput et al., 2016). By developing these nanosorbents, a complex core/shell structure that combines a external porous matrix surrounding a magnetic core can be designed (Mehmood et al., 2017). The pollutant removal mechanism, either chemisorption or physisorption, will depend on the material functionalization (Rasheed et al., 2019a). In this context, here we have prepared a core-shell magnetic mesoporous silica nanosorbent (MNS) following a reproducible method described in Scheme 1 that will be tested for the removal of lead and methyl orange. The double-shell coating of silica consists of a first dense silica layer used to preserve the magnetic core from degradation and a second silica layer containing a porogenic agent to control the silica pore size. Two porogenic agents were used in this work, hexadecyltrimethoxysilane (C16TMS) and octadecyltrimethoxysilane (C18TMS) to analyze its effect on the generated porosity.

Scheme 1 Synthesis of superparamagnetic nanosorbent and lead (Pb^{2+}) and methyl orange (MO) extraction strategy. 1) External diffusion, 2) internal diffusion, 3) surface reaction.

2. Experimental

2.1. Chemical reagents and analysis

Iron chloride hexahydrate ($\geq 98\%$), lead chloride tetrahydrate ($\text{PbCl}_2 \cdot 4\text{H}_2\text{O}$, 98%), methyl orange (MO, 85%), tetraethyl orthosilicate (TEOS, $\geq 99\%$), polyoxyethylene(5)nonylphenyl ether (Igepal CO-520), ammonium hydroxide (30%), hexadecyltrimethoxysilane (C16TMS, $\geq 85\%$), octadecyltrimethoxysilane (C18TMS, 90%), oleic acid, sodium oleate ($\geq 82\%$), ethanol ($\geq 99.8\%$), cyclohexane ($\geq 99.5\%$), hexane (95%) and octadecene (90%) were purchased from Sigma-Aldrich. Two 500 mg/L stock solutions of Pb^{2+} and MO were prepared by dissolving a specific amount of lead chloride and MO in 500 mL of distilled water, respectively. Working standards of desired Pb^{2+} and MO concentrations were prepared by diluting different volumes of the stock solution. The Pb^{2+} concentration was estimated by inductively coupled plasma optical emission spectroscopy (ICP-OES) with an apparatus from Perkin Elmer, model OPTIME 2100DV, considering a wavelength of 220 nm . MO concentration was estimated by ultraviolet-visible spectroscopy carried out in a Perkin Elmer Lambda 35 UV/VIS Spectrometer. A calibration curve (absorbance vs concentration) for the analysis of MO concentration was obtained at a wavelength value of 464 nm , selected after evaluating the spectrum showed in Fig. S1 where the MO concentration was varied between $20 - 100\text{ mg/L}$ (values selected to facilitate quantitative measures of the adsorption process).

2.2. Magnetic nanoparticles synthesis (MNPs)

Thermal decomposition method was used to synthesize monodisperse iron oxide nanoparticles (Fe_3O_4) using iron oleate as precursor in an organic media (Bronstein et al., 2007).

Iron oleate was prepared by mixing 10.8 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ with 45 g of sodium oleate in 60 mL of distilled water, 80 mL of ethanol and 140 mL of hexane in a two-necked round-bottom flask. One of the flask necks was sealed and the other connected to a condenser. The flask was then magnetically stirred, heated in an oil bath at $70\text{ }^\circ\text{C}$ to boiling, and left for 4 h . Once the mixture was cooled, the condenser was turned off and the mixture was transferred to a separation funnel, so that the aqueous phase

could be separated and discarded. This last step was repeated 3 times after adding distilled water. The obtained solution was placed in a rotary evaporator (Buchi Rotavapor R-100) at 60 °C and 90 rpm for 1 hour until hexane and ethanol were evaporated. The final product was left in an inox-oven at 50 °C overnight.

Then, MNPs were prepared by mixing 4.5 g of liquid iron oleate with 1.4 g of oleic acid in 50 mL of octadecene in a 250 mL three-necked round-bottom flask. The flask was placed in a heating mantle where a nitrogen flow, a mechanical stirring, a temperature indicator and a condenser were located. The mixing was performed at 340 rpm until 65 °C were reached, and the nitrogen flux was turned off at 100 °C. Afterwards, the heating mantle was turned off one hour after octadecene boiling point was reached (320 °C). The sample was collected and washed several times with ethanol by centrifugation at 8000 RCF/g for 15 min. The washed sample was suspended in cyclohexane for further functionalization.

2.3. Silica-shell coating onto Fe₃O₄ particles (SiO₂@Fe₃O₄)

A first SiO₂ shell was grown onto the monodispersed MNPs through a scale up microemulsion process, using Igepal CO-520 as surfactant through a micellar-sol-gel-combined coating route (Cannas et al., 2010). Thus, 83 mg of MNPs were mechanically mixed using a shaker for 30 min with 300 mL of cyclohexane and 13.3 mL of polyoxyethylene(5)nonylphenyl ether (0.56 mmol, Igepal CO-520, containing 50 mol % hydrophilic group). Afterwards, 2.16 mL of NH₄OH 30 % were added and shaken for 15 min to form a transparent, brown solution. Subsequently, 2.5 mL of TEOS were added dropwise and shaken for another 24 h. After that, the mixture was washed 3 times with methanol, which causes the MNPs precipitation, and other 3 times with ethanol. After each wash, the SiO₂@Fe₃O₄ nanoparticles were collected by centrifugation at 8000 RCF/g for 15 min.

2.4. Mesoporous silica-shell coating onto SiO₂@Fe₃O₄ (MNS)

The final magnetic nanosorbent (MNS) was obtained by growing a second silica shell onto the already silica coated iron oxide nanoparticles with a mixture of TEOS and a porogenic agent (PA), C16TMS and

C18TMS. The molar ratio of TEOS:PA was varied (2.6:1 and 4.7:1) to analyse the influence of the amount of PA on the silica porosity and shell thickness. This second silica layer was deposited by stirring 15 mg of $\text{SiO}_2@\text{Fe}_3\text{O}_4$ particles in a mixture of 10 mL of distilled water, 132 mL of ethanol and 6 mL of aqueous 30 % NH_4OH solution at room temperature for 5 min. Afterwards, the specified volume of TEOS and PA were added, and shaken for 7 h. The product was then collected by centrifugation at 8000 RCF/g for 15 min, washed 3 times with ethanol, and calcined at 400 °C in air for 3 h to remove the porogenic agent and to allow the mesopore formation.

2.5. Magnetic nanosorbent characterization

Phase identification and crystal structure of the Fe_3O_4 nanopowder were analysed by X-Ray diffraction (XRD) performed in a Bruker D8 Advance diffractometer with a graphite monochromator using $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The patterns were collected within 20° and 70° in 2θ . Crystal size was calculated by the full width at half-maximum (FWHM) peak with the greatest intensity (311) by using the Scherrer's equation. Particle size and shape were studied by transmission electron microscopy (TEM) using a JEOL JEM 1010 microscope operated at 100 keV. The samples were prepared by placing one drop of a dilute particle suspension on an amorphous carbon-coated copper grid and evaporating the solvent at room temperature. The mean particle size and distributions were evaluated by measuring the largest internal dimension of at least 200 particles. Afterwards, the data were fitted to a lognormal distribution obtaining the mean size ($\bar{X}$) and the standard deviation (σ).

The magnetic properties of raw Fe_3O_4 particles, as well as MNS, before and after the mesoporous silica-shell formation, were carried out in a vibrating sample magnetometer MagLabVSM, Oxford Instrument. The samples were dried in an inox-coated oven at 50 °C overnight. Afterwards the samples were accurately weighted and pressed into the sample holder. The hysteresis loops of the powder samples were measured at 290 K up to 3000 kA/m and the values of saturation magnetization (M_s), remanent magnetization (M_r) in $\text{A.m}^2/\text{kg}_{\text{MNS}}$ and coercivity (H_c) in kA/m were obtained for each sample.

Thermal analyses (TGA/DSC) were performed on the MNS using a TA Instruments Q2000 differential scanning calorimeter; the samples were heated from room temperature to 800 °C at a rate of 10 °C/min in air. To confirm the presence of the silica and porogenic agent coating, the FTIR spectra of the samples were obtained by using a Bruker IFS 66VS in the range of 400 – 4000 cm⁻¹. The samples were prepared by diluting the dried powder in KBr at 2% w/w and pressed them into pellets.

Also, N₂ adsorption/desorption isotherms at 77 K were obtained for SiO₂@Fe₃O₄ and MNS before and after calcination by using a TriStar II 320 (Micrometrics) system. The samples were degasified for at least 12 h at 393 K and 0.1 mbar. The surface area was calculated using BET equation (Brunauer et al., 1938), while the pore size distribution by the BJH method (Villarroel-Rocha et al., 2014).

Finally, X-ray photoelectron spectroscopy (XPS) was used to characterize the surface chemistry of the samples after the sorption process. XPS spectra were acquired at normal emission in an ultrahigh vacuum (UHV) chamber with a base pressure of 10⁻¹⁰ mbar equipped with a hemispherical electron energy analyzer (SPECS Phoibos 150 spectrometer) and a 2D delay-line detector, using non-monochromatic Mg-Kα (1253.6 eV) and Al-Kα (1486.6 eV) x-ray sources. Survey and high resolution scans data were recorded with pass energy of 20 and 10 eV, and energy step of 0.1 and 0.05 eV, respectively (Redondo-Cubero et al., 2012). Data processing was performed using CasaXPS software (Casa Software Ltd., Cheshire, UK).

2.6. Sorption and desorption experimentation

Batch lead adsorption experiments were carried out at room temperature (20 ± 1 °C) in a plastic 15 mL conical vial containing 5 mg of MNS and 10 mL of Pb²⁺ or MO solutions with different initial concentrations (from 20 to 100 mg/L). The mixture was then shaken in a GFL 3015 mechanical shaker for 3 h and after equilibrium, the MNS was collected in less than 5 minutes by magnetic harvesting using a 60x30 mm magnet with a field at the surface of 0.4 kA/m. The residual pollutant concentration in the supernatant (C_e, mg/L) in the aqueous phase was determined.

The effect of the pH was analyzed just for Pb^{2+} assays in a pH range between 3 and 7 at a Pb^{2+} initial concentration of $100 \text{ mg}_{\text{Pb}}/\text{L}$. The effect of initial concentration was analyzed by using 0, 20, 40, 60, 80, 100 mg of pollutant/L in the experiments at pH 5.5. Data were fitted to three different isotherm models: Langmuir, Freundlich and Temkin. The models equations and linear plots are presented in Table S1. Langmuir adsorption isotherm is the most common model that assumes that the adsorbent surface is homogenous and has a monolayer coverage with a specific number of active sites where the molecules of the solute can be adsorbed. On the contrary, Freundlich isotherm model is given for systems with heterogeneous surfaces (n = heterogeneity factor) where adsorption limited levels does not exist, while the Temkin isotherm model consider that the possible adsorption heat reaction (b_T , J/mol) of the molecules in the surface layer decreases with the coverage in a linear way (Dadfarnia et al., 2015; Gallo-Cordova et al., 2017). In each model, the dependence of the equilibrium adsorption capacity, q_e ($\text{mg}/\text{g}_{\text{NS}}$) is established as a function of the pollutant equilibrium concentration, C_e (mg/L). Maximum adsorption capacity, q_m ($\text{mg}/\text{g}_{\text{NS}}$) was obtained by the Langmuir equilibrium model.

Reusability of MNS after MO and Pb^{2+} sorption process was performed by analyzing the adsorption capacity of 6 successive sorption/desorption cycles. For this, 0.02 g was mechanically mixed with the pollutant solutions (40 mL , C_0 : $100 \text{ mg}/\text{L}$) at optimal conditions (3 h, pH 5.5) at 20°C in an Erlenmeyer flask. The pollutant-loaded MNS was collected by magnetic harvesting after the sorption process and washed several times with distilled water and then mixed with a solution of HNO_3 0.03 M for 1 h at 20°C . Finally, the MNS was dried in an inox-coated oven at 50°C overnight. The same procedure was performed for each successive cycle and the MO and Pb^{2+} adsorption capacity was obtained.

2.7. Kinetic measurements

Kinetic studies of the adsorption process was performed using the MNS at pH of 5.5 and initial pollutant concentration of $40 \text{ mg}_{\text{Pb}}/\text{L}$ and $100 \text{ mg}_{\text{MO}}/\text{L}$ by varying the adsorption time (5, 25, 60, 180 and 1440 min). At the end of each lapsed time, magnetic harvesting was performed and the residual lead

concentration in the supernatant was measured by ICP-OES and MO concentration by UV-VIS spectrophotometry.

Sorption processes can be limited by different stages according to the adsorbent-adsorbate system. These stages are the boundary layer diffusion, the adsorption of ions onto the adsorbent sites and the intraparticle diffusion (Xu et al., 2012). In order to shed some light on the mechanism governing the adsorption process of our MNS, the obtained experimental data were fitted to the linear form of four different adsorption kinetic models: Pseudo-first order (PFO), Pseudo-second order (PSO) and Elovich. It has been argued that the PFO model is valid for long adsorption times, when the system is near equilibrium and only at the initial stage of adsorption, while the Elovich rate equation is known for neglecting desorption, describing chemisorption well (Tan and Hameed, 2017). On the other hand, the PSO model describes well most environmental kinetic adsorption processes where the rate-limiting step is the surface adsorption (chemisorption) (Robati, 2013). Finally, the intraparticle diffusion model was considered. In this case, if the plot of q_t vs $t^{1/2}$ is a straight line, the mechanisms will be limited by the intraparticle diffusion process, while if it shows a multi-linear plot there will be more steps influencing the process (Saleh, 2015). The equations of these kinetic models are presented in Table S2.

3. Results and Discussion

3.1. Characterization

3.1.1. Magnetite core.

TEM images of the magnetic cores are displayed in Fig. 1a, showing homogeneous monodispersed nanoparticles. The mean particle size and distribution were evaluated and adjusted to a log normal distribution resulting in a mean size of 13.0 nm and a standard deviation of 0.2 (Fig. 1d). The XRD pattern of the Fe_3O_4 particles is shown in Fig. 1b. No extra reflection related to other iron oxide phases such as hematite ($\alpha\text{-Fe}_2\text{O}_3$) or iron hydroxides are observed. The nanocrystallite size calculated by Scherrer's equation is 10.4 (0.2) nm.

3.1.2. SiO₂@Fe₃O₄ particles.

Silica-shell coated nanoparticles were obtained by a microemulsion process. The shell thickness was controlled by changing the reaction time and the amount of TEOS in the reaction (Ma et al., 2007). As it is shown in Fig. 1c, a silica shell is placed uniformly around the more electro-dense cores corresponding to the iron oxide, avoiding its agglomeration. It can be seen that most of the sample consists of uniform single core nanoparticles, and cores without coating or pure silica nanoparticles were not observed, suggesting that the amount of TEOS used for the coating was well-adjusted. Regarding the shell thickness, it is uniform and quite smooth with no distortions and the mean shell thickness was of 12.3 nm ($\sigma=0.1$). The final particle diameter was 30.4 nm ($\sigma=0.1$, Fig. 1d). It is worth to mention that the method is reproducible after performing the experiments in triplicate.

Fig. 1 Morphological and structural characterization of the MNPs and the SiO₂@Fe₃O₄: a) TEM image of Fe₃O₄, b) TEM image of SiO₂@Fe₃O₄, c) X-ray diffraction of the as-prepared MNPs, d) Fe₃O₄ and SiO₂@Fe₃O₄ particle size distribution.

3.1.3. Magnetic nanosorbent.

The second silica layer was deposited using TEOS and a porogenic agent (PA) that controls the silica pore size. Finally, the MNS were obtained by calcination of the PA doped nanocomposite to allow the formation of a mesoporous silica matrix. Four different MNS were prepared by tuning the PA nature and TEOS/PA proportion. MNS-1 and MNS-3 were prepared by using TEOS:C16TMS (molar ratio 4.7:1

and 2.6:1, respectively) while MNS-2 and MNS-4 were prepared with TEOS:C18TMS (molar ratio 4.7:1 and 2.6:1, respectively). TEM images for all MNS are shown in Fig. 2 showing clearly the increase in shell thickness due to the second silica layer containing PA and the rough surface. The final particle size has increased up to 50.3 nm ($\sigma=0.2$) for all the samples and differences in size as a function of the porogenic agent were not observed.

Fig. 2 Morphological and structural characterization of the MNS before and after calcination: a-d) TEM images of the MNS before calcination (a) MNS-1, b) MNS-2, c) MNS-3 and d) MNS-4, e) FTIR spectra for MNS before (dashed line) and after calcination (continuous line) and for the $\text{SiO}_2@\text{Fe}_3\text{O}_4$, and f) N_2 adsorption-desorption isotherms for MNS before calcination and $\text{SiO}_2@\text{Fe}_3\text{O}_4$. Pore size distribution figure inset.

The incorporation of the PA in the silica matrix is confirmed by TGA of the MNS before calcination. For all MNS the total weight loss is around 30 % (Fig. S2) mainly at 250 °C due the PA decomposition. Samples MNS-3 and MNS-4 present the highest weight loss percentages (33.5 and 37.6%, respectively) since in their preparation a greater amount of C16TMS (for MNS-3) and C18TMS (for MNS-4) was used. Also, MNS-4 presents a greater weight loss than MNS-3 in agreement with the larger molecular weight of C18TMS.

The effect of calcination in the silica and PA coating was followed by FTIR as shown in Fig. 2e. All the spectra for $\text{SiO}_2@\text{Fe}_3\text{O}_4$ and MNS, before and after calcination, show an absorption band at approximately 1080 cm^{-1} which corresponds to the Si-O bond on the nanoparticles surface due to the silica-shell (Arriortua et al., 2017). On the other hand, the spectra for the pre-calcined MNS (dashed line) show some differences. The small band at 1475 cm^{-1} is attributed to the C-H absorption, while the bands at 2931 and 2858 cm^{-1} assigned to $-\text{CH}_3$ and $-\text{CH}_2$ stretch vibrations, respectively, allow the identification of hexadecyl and octadecyl groups of the porogenic agents. The band at 3443 cm^{-1} was ascribed to $-\text{OH}$ groups on the surface of the particles (Lihui et al., 2015). All samples, before and after calcination, presented an adsorption band at $\approx 468\text{ cm}^{-1}$ due to the Fe-O bonds of magnetite or maghemite, which confirms that the core was not affected neither by the silica coating nor by the calcination (Medina et al., 2016).

The porosity of MNS was also studied due to its influence on the adsorption process. N_2 adsorption-desorption isotherms at 77 K were obtained for each sample and the results are shown in Fig. 2f. This kind of isotherms were described as an extension of the classical Langmuir adsorption isotherm from monolayer to ideal multilayer adsorption and where a limiting case of infinite many layers is considered (Keller and Staudt, 2005). The presented isotherms of MNS, pre-calcined MNS, and $\text{SiO}_2@\text{Fe}_3\text{O}_4$ could be described as type II, typically obtained in mesoporous materials, showing monolayer adsorption at low pressure and multilayer adsorption at high pressures (Shengxia et al., 2015).

All pre-calcined samples showed similar N_2 isotherms and the nitrogen volume adsorbed is quite low compared to the final MNS, which can be addressed to the presence of pores that rises after calcination. Also, the MNS presented a higher porosity than the uncoated $\text{SiO}_2@\text{Fe}_3\text{O}_4$, and the hysteresis between the adsorption and the desorption branch indicates the existence of mesopores (Qin et al., 2019), which volumes are summarized in Table 1. MNS-2 and MNS-4, prepared with C18TMS showed a higher porosity (greater values of BET surface area) than the MNS prepared with C16TMS, due to the greater size of C18TMS that generates greater porosity.

Table 1 Nanosorbents surface area and mesopore volume.

Sample	Porogenic agent	A_{BET} ($\text{m}^2/\text{g}_{\text{MNS}}$)	V_{mesopore} ($\text{cm}^3/\text{g}_{\text{MNS}}$)
$\text{SiO}_2@\text{Fe}_3\text{O}_4$	-	176	0.093
Pre-calcined MNS-1	C16TMS	37	0.109
MNS-1*	C16TMS	470	0.276
MNS-2*	C18TMS	522	0.340
MNS-3†	C16TMS	478	0.192
MNS-4†	C18TMS	568	0.266

TEOS:PA molar ratio: *4.7:1 and †2.6:1

275 The distribution of pore sizes of the MNS was obtained by BJH method and are shown in a inset in Fig.
276 2f. All samples presented micropore (less than 2 nm), mesopore (between 2 and 50 nm) and
277 macropore (> 50 nm) (Sangjin et al., 2003), being the area obtained for micropores and macropores
278 smaller than the one obtained for the mesopores. On the other hand, the pre-calcined samples
279 presented a quite lower pore volume and no micropore. This means that MNS present a higher volume
280 and adsorption capacity after calcination due to the elimination of the PA allowing the formation of
281 mesopores.

282 The magnetization curves for MNS at room temperature are shown in Fig. S3. The values of saturation
283 magnetization, remanence and coercivity were obtained from the magnetization loops and the results
284 are shown in Table S3. The remanence was nearly $0 \text{ A}\cdot\text{m}^2/\text{kg}_{\text{MNS}}$ for all MNP, while the values of M_s
285 were between 6 and $7 \text{ A}\cdot\text{m}^2/\text{kg}_{\text{MNS}}$. On the other hand, the MNS showed very low coercive fields (H_c),
286 being close to the superparamagnetic regime (Table S3). It should be mentioned that the saturation
287 magnetization values for these MNS ($>3 \text{ A}\cdot\text{m}^2/\text{kg}$) are enough to recuperate the adsorbent from the
288 media by magnetic harvesting after the sorption process (Gorria et al., 2009).

289 **3.2. Adsorptive measurements**

290 The organic and inorganic pollutant removal using the MNS is expected to take place by an adsorption
291 process, which is a superficial phenomenon where the molecules of the adsorbate (pollutant) are

bound to the solid surface of the MNS. In this process, mass transfer has a great significance were three steps are involved: external diffusion, pore diffusion and surface reaction as shown in Scheme 1. The first step consists in the transport of the adsorbate from the bulk phase to the external surface of the MNS. The pore diffusion consists in its transport through the MNS pores so that it can reach the internal surface and achieve the final step, the surface reaction, where the adsorbate is attached to the internal surface of the adsorbent (Tan and Hameed, 2017). To shed some light on this adsorption mechanism, we have analyzed the effect of the pH, the adsorption kinetics and isotherms and, finally, the desorption process and possible reusability.

3.2.1. Effect of pH.

Values between 3 and 7 were selected to perform the batch experimentation by using MNS-1. It can be seen from Fig. S4 that after the batch experimentation at different pH values, the obtained q_e values are very similar and the highest adsorption capacity was obtained at pHs 5 and 7. It is important to consider that according to lead speciation, at pH values higher than 7, species such as $Pb(OH)^+$ and $Pb(OH)_2$ are present in the media (Shengxia et al., 2015). Consequently, lead removal can be accomplished by simultaneous precipitation of $Pb(OH)_2$ and sorption of $Pb(OH)^+$. This has been proved by measuring the lead initial concentration of a suspension at different pH values. At pH 6 and 7 the concentration of lead of the as-prepared solutions decreased with time because of the precipitation of lead as $Pb(OH)_2$, while at pH values between 3 and 5.5, it remained constant. Therefore, a pH of 5.5 was chosen and the same value was used for MO experimentation for comparison purposes.

3.2.2. Adsorption kinetics.

The adsorption kinetics was investigated for the four different MNS for Pb^{2+} removal and the most efficient one was tested for MO removal (MNS-4). Fig. 3 shows the non-linear fitting of the different kinetic models with the equilibrium adsorption capacity for the removal of Pb^{2+} and MO using MNS-4 as a function of the contact time. Similar results were obtained for the rest of MNS for Pb^{2+} removal. It can be observed that during the first hour, the Pb^{2+} and MO sorption capacity increases rapidly

reaching a plateau after 2 h. In order to understand the mechanism of adsorption and the possible rate determining step, including mass transport and chemical reaction, different kinetic models were used to fit the experimental data: pseudo-first order (PFO), pseudo-second order (PSO) and Elovich. In the three models, the rate of change of the adsorption capacity, dq_t/dt , is settled as a function of the adsorption capacity during time, q_t , and the contact time, t . The non-linear equations have been linearized by integration, where the boundary conditions are $q_t = 0$ in $t = 0$ and $q_t = q_t$ in $t = t$. Also, for further analysis of the adsorption kinetics, the intraparticle diffusion model was considered to describe the pollutants diffusion mechanisms.

Fig. 3 Non-linear fit of the different kinetic models for: a) Pb^{2+} and b) MO removal using MNS-4 at room temperature.

As shown in Fig. 4, the plot for the intraparticle diffusion model q_t vs $t^{1/2}$ was considered as non-linear in the entire time range indicating that during the pollutant adsorption, several steps were influencing the process. In the case of Pb^{2+} removal, it could be seen that there exist two different stages: a very rapid surface adsorption with a curve that does not pass through the origin, implying that the process is controlled mainly by external diffusion. The adsorption equilibrium evidenced by the near zero value of the diffusion rate constant begins at what would be stage II (Guo et al., 2018). Oppositely, in the MO removal process, an intermediate linear proportion (stage II) can be noticed, indicating the presence of a slow intraparticle diffusion stage suggesting that organic pollutants are able to diffuse through MNS pores. Nevertheless, the linear plot does not pass through the origin indicating that intraparticle diffusion may not be the rate-determining step of the process (Saleh, 2015; Xu et al., 2012). The intraparticle diffusion constant values for the first (Pb^{2+}) and second (MO) linear portions are shown in Table S4.

Fig. 4 Intra particle diffusion kinetic model for the adsorption of lead and methyl orange.

Furthermore, the obtained kinetic parameters for the rest of the models are also shown in Table S4. The equilibrium adsorption capacity of all MNS was reached after 2 h. The experimental data best fitted the PSO model with a determination coefficient (R^2) of 1 in all four MNS and for both pollutants (Table S4). Therefore, it can be assumed that the rate-limiting step is the surface adsorption and the pollutants removal is due to the physicochemical interaction with the MNS. The fact that the best

experimental data correlation is obtained for the PSO model indicates that the process is limited by chemisorption in agreement with other studies of Pb^{2+} and MO removal with nanomaterials (Chang et al., 2016; Ge et al., 2012; Singh et al., 2018; Xin et al., 2012), but further experiments are needed to corroborate this result.

3.2.3. Adsorption Isotherms.

By considering the previously mentioned isotherm models, Table 2 shows the constants of each of them and the determination coefficients (R^2) obtained. From this information it can be concluded that Langmuir isotherm best describes the experimental data for the sorption process of Pb^{2+} and MO onto MNS. Therefore, it can be assumed that the adsorption takes place in monolayer and when the maximum adsorption capacity is reached, no further adsorption is accomplished because no more than one molecule can occupy a specific site. These results agree with many experiments of Pb^{2+} and MO adsorption using nanomaterials (Dadfarnia et al., 2015; Hua et al., 2012; Shen et al., 2018; Xu et al., 2012).

Table 2 Calculated isotherms coefficients for Langmuir, Freundlich and Temkin isotherms for lead (Pb^{2+}) adsorption using all MNS and $SiO_2@Fe_3O_4$ and for methyl orange (MO) adsorption on MNS-4 and $SiO_2@Fe_3O_4$.

		MNS-1	MNS-2	MNS-3	MNS-4	MNS-4	$SiO_2@Fe_3O_4$	
		Pb^{2+}	Pb^{2+}	Pb^{2+}	Pb^{2+}	MO	Pb^{2+}	MO
Langmuir								
b_0	L/mg	0.03	0.03	0.05	0.02	0.03	1.10	0.41
q_m	mg/g _{MNS}	37	45	43	50	240	4	40
R^2	-	0.98	0.97	0.97	0.96	0.98	0.97	0.99
Freundlich								
K_f	(mg/g)/(L/g) ^{1/n}	5.33	5.25	6.77	7.50	21.95	2.88	29.89
1/n	-	0.367	0.38	0.31	0.29	0.42	0.09	0.06
R^2	-	0.97	0.96	0.93	0.90	0.97	0.37	0.90
Temkin								
b_t	J/mol	357.76	333.12	383.82	404.81	54.38	6203.21	1208.87

K_t	L/g	0.58	0.51	0.84	1.02	0.31	860.77	2.24E+06
R^2	-	0.95	0.95	0.89	0.83	0.92	0.35	0.88

It can be observed that all MNS presented similar maximum adsorption capacity (q_m) values for the Pb^{2+} . Although the q_m of each MNS is lower than the expected for this kind of nanocomposites with high surface area, the obtained results agree with the external surface area values. Only small changes in surface are reflected in the adsorption capacities as it is the case for MNS-4 (568 m²/g) with the highest q_m value 50 mg_{Pb}/g_{MNS} and MNS-1 (470 m²/g) with the lowest q_m value, 32 mg_{Pb}/g_{MNS}. It should be mentioned that the fact that C16TMS and C18TMS porogenic agents lead to similar results, may help to reduce material cost preparation because the first is 20 times cheaper than the second one.

The theoretical and ideal estimation of the amount of Pb^{2+} that could be removed by MNS was calculated considering the total surface area and the external surface area of MNS, assuming that MNS are perfect spheres where Pb^{2+} occupies a spherical area on its surface. These calculations showed a q_{max} value of up to 1525 mg_{Pb}/g_{MNS}, suggesting that lead ions were not able to diffuse through the nanosorbent pores but they were adsorbed on the external surface. To increase the Pb^{2+} adsorption using these MNS it is necessary to potentiate the electrostatic forces between the MNS surface and the adsorbate molecules via further functionalization.

On the other hand, the maximum adsorption capacity when using MNS-4 was almost five times larger for MO sorption process (240 mg_{MO}/g_{MNS}) (see Table 2), which indicates that MNS have a better performance in the removal of organic pollutants. This difference between inorganic and organic compounds adsorption may be due to the different affinity of metals and organic matter for the silica surface. First, a change of surface charge is expected after the metal ions adsorption, which causes the decrease of the affinity between the sorbent surface and the adsorbate. In addition, PA doping and calcination may lead to some carbon rest at the pores surface, increasing the affinity to organic compounds and enabling its diffusion through the sorbent pores. For comparison, the maximum MO

and Pb^{2+} adsorption capacity of different magnetic adsorbents prepared by different methods have been collected in Table 3. In the case of Pb^{2+} , it can be observed that in order to obtain higher adsorption capacities, functionalization with specific compounds that increases the Pb^{2+} affinity is required. However, for MO removal, the maximum adsorption capacity values obtained in this work enable the MNS (with its modified surface) to become competitive against other uncoated magnetic materials for methyl orange remediation. It is important to consider that this values could be raised up by controlling the adsorption experimental conditions such as temperature, pressure, agitation, etc.

Table 3 Maximum adsorption capacities (q_m , mg/g) of lead and methyl orange on different adsorbents

Adsorbent	Pollutant	BET (m^2/g)	pH (-)	q_m (mg/g)	Reference
Fe_3O_4 nanospheres	Pb^{2+}	11.3	5	18.47	(Kumari et al., 2015)
Fe_3O_4 nanoparticles	Pb^{2+}	12.7	5	53.11	(Rajput et al., 2016)
Fe_3O_4 sulfonated magnetic nanoparticles	Pb^{2+}	18.32	7	108.93	(Chen et al., 2017)
CHT/ALG/ Fe_3O_4 @ SiO_2 composite	Pb^{2+}	-	4.2	245.28	(Facchi et al., 2018)
Needle-like nanocrystalline zeolites	Pb^{2+}	29.84	5	337.8	(Luo et al., 2018)
Superparamagnetic nanosorbent	Pb^{2+}	568	5.5	50	This work
Iron oxide/carbon nanocomposite	MO	394	4.8	71.02	(Istratie et al., 2016)
Activated carbon/ $NiFe_2O_4$	MO	157.1	3	182.82	(Jiang et al., 2015)
Chitosan/ Al_2O_3 /magnetite nanoparticles	MO	22.07	4-10	417	(Tanhaei et al., 2015)
Chitosan-coated Fe_3O_4 nanocomposites	MO	-	6-10	758	(Yang et al., 2016)
Superparamagnetic nanosorbent	MO	568	5.5	240	This work

When evaluating the maximum adsorption capacity of Pb^{2+} and MO with SiO_2 @ Fe_3O_4 particles, the q_m value for the MO removal was ten times higher (40 mg/g) than for Pb^{2+} removal (4 mg/g). However, the obtained values were quite smaller compared to the values obtained when using MNS. Adsorption data for SiO_2 @ Fe_3O_4 also fits best the Langmuir isotherm model, which means that the adsorption occurs in a monolayer. These results show that the adsorption capacity is significantly enhanced after the PA doping, in particular for MO removal. Fig. 5 shows the nonlinear isotherms for the sorption

process of Pb^{2+} by using all MNS, the sorption process of MO with MNS-4 and for both inorganic and organic pollutants with $\text{SiO}_2@\text{Fe}_3\text{O}_4$.

Fig. 5 Adsorption isotherms of a) MNS-1, b) MNS-2, c) MNS-3, d) MNS-4 for Pb^{2+} removal, e) MNS-4 for MO removal and f) $\text{SiO}_2@\text{Fe}_3\text{O}_4$ for Pb^{2+} and MO removal.

Finally, in order to ascertain the adsorption of pollutants onto the MNS external and internal surface, loaded samples were studied. In all cases, only emission from O1s, C1s and Si2p core levels is detected, with different peak intensities depending on each sample preparation process. On the contrary, Fe emission was not found in the XPS experiments for all the samples. This result confirms the conformal coating of the shell on the Fe_3O_4 core nanoparticle, and the perfect encapsulation of the samples. Also, this analysis concludes that MNS shell layer is mainly composed of SiO_2 . On the other hand, it should be expected the existence of Pb in the sample Pb^{2+} loaded MNS-4, or at least its presence on the outermost layers of the nanoparticles. However, Pb emission is not detected. This means that the quantity of Pb^{2+} in the MNS surface is very small and below the detection limit of the XPS technique or that during the MNS storage, desorption may have occurred.

A detailed comparison among the C1s spectra corresponding to all the samples displays a similar lineshape, which is related to the same chemical environment of the carbon atoms. However, it is readily observed that the relative height of C peaks is maximized for the MO loaded MNS-4. This is a clear indication of the MO molecules attached to the MNS external and internal surface, as it can be seen in the XPS spectra of the samples in Fig. S5

3.2.4. Desorption and Reusability.

Desorption tests showed that MO and Pb^{2+} loaded-MNS-4 needs just a small volume of an acidic solution to desorb efficiently the molecules of pollutant. The loaded samples underwent one hour of acidic treatment to achieve the pollutant desorption equilibrium. Adsorption and desorption cycles were repeated 6 times to analyse the regeneration capacity of the MNS-4 after the removal of MO and Pb^{2+} . Efficiency of the sorption experiments after desorption was calculated and the results are shown in Fig. 6. After 4 cycles there was no change in the efficiency values or the morphology of the MNS as demonstrated with TEM images after regeneration. Also, the magnetic saturation was analysed after the experimentation and there was no magnetic loss noticed. After 6 sorption/desorption cycles a $20 \pm 5\%$ efficiency loss was observed when using MNS-4 for MO removal while it remained constant for Pb^{2+} . The noticeable difference between the MNS reusability in these two adsorption processes may be due to the easiness of Pb^{2+} desorption from the surface of the material, while MO presented more difficulties to be desorbed from the MNS pores. Therefore, these materials can be used for pollutant removal at maximum activity during the first four cycles (MO) and first five cycles (Pb^{2+}) with a slightly activity decrease in the successive cycles.

Fig. 6 MNS-4 reusability tests for methyl orange and Pb²⁺ removal.

4. Conclusions

In this research, a 50.3 nm superparamagnetic nanosorbent was synthesized for the removal of organic and inorganic pollutants from water. The sorbent is based on a superparamagnetic core of iron oxide and a double silica shell whose surface area is tailored by introducing porogenic agents. The BET surface area indicated that the synthesized nanosorbents had a remarkable volume of mesopores that can be used for the adsorptive removal of methyl orange and lead in aqueous solutions. The pseudo-second order kinetic model was demonstrated to provide the best correlation for the adsorption processes, showing that the pollutants removal is due to the physicochemical interaction with the nanosorbents. Intraparticle diffusion model showed that only methyl orange was capable to diffuse among the nanosorbents pores. Organic matter showed larger affinity to the nanosorbents being the maximum adsorption capacity for methyl orange 240 mg/g_{MNSr}, much greater than the value obtained for lead adsorption (35-50 mg/g_{NS}). The main advantage of this material is that it can be separated from the aqueous media by magnetic harvesting with no need of an expensive and time-consuming process. The re-usability of the nanosorbent was tested, showing 100 % of efficiency until the fourth adsorption/desorption cycle for methyl orange removal and until the sixth cycle for lead removal. The use of very abundant inorganic materials such as iron and silica, and the possibilities of scaling up the

synthesis process are expecting to make these nanosorbents that are already competitive in adsorption capacity for organic mater, competitive in cost.

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6. Conflict of interest

There are no conflicts to declare.

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