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Magnetic water treatment in a wastewater treatment plant: Part II - Processing waters and kinetic study

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ABSTRACT

Magnetic sorption process is applied to real wastewater effluents from a Wastewater Treatment Plant. The complex media sorption is done by using different types of magnetic particles (resin and polymeric covered magnetite) giving good results for removing detergents, phosphates and COD and moderate results for the sorption of nitrogen and several heavy metals. Important kinetic parameters were obtained by data fitting for the pseudo first and second order, and for simplified Elovich models. Regeneration and reuse of the magnetic particles using a chemical-free method was also tested, as well as the effect of the concentration of the particles in the removal efficiency (which proved to be relevant).

1. Introduction

Waste generated by mankind is an unsolved problem that needs to be dealt with in behalf of mankind, nature and future generations. As water is the mostly used liquid effluent, the generation of wastewaters containing high loads of contaminants is an unavoidable consequence, that has been studied in order to minimize it through different techniques. For wastewater treatment, Science and Technology has provided, since several decades ago, the solution of the implementation of Wastewater Treatment Plants (WWTPs), where a conjugation of different techniques for contaminants degradation/removal, delivers an exit watery flow containing contaminants concentration within legally defined limits.

Nonetheless, much is still to be done, in order to face up with new, and more restrictive, contaminant emitting limits, emerging contaminants, reduction of generated wastes (at the end of the wastewater treatment process), decreasing costs and optimize processes. The search of techniques that may be applied locally is also a current goal, as the usual WWTPs are mainly central units that receive water from a large area (the only way cost is minimized), and thus always demand high throughputs. Among all the currently proposed novel processes, magnetic techniques stand as a low-cost, gentle process. Furthermore, by using sorption or reaction processes (Dhruv et al., 2015; Zhang et al., 2020; Zhanmeng et al., 2018; Vorontsov et al., 2019; Xu et al., 2020; Chen et al., 2020; Liu et al., 2019; Rai et al., 2018; Ravi et al., 2020; Usman et al., 2020; Augusto et al., 2020a, 2020b; Estévez et al., 2008; Augusto et al., 2019) when using particulate magnetic material, regeneration and reuse of particles is a possibility (Hernández et al., 2020), and thus no further wastes are created. Another important factor is that these techniques may be applied in small local wastewater treatment centers with low throughputs (by using nano or micromagnetic particles) as well as in usual regional wastewater treatment centers with high throughputs (micron and millimagnetic particles).

Although there is already a fair amount of research literature published concerning the applications of magnetic technologies to watery effluents treatment (Chibowski and Szczes, 2018; Zheng et al., 2019; Ali et al., 2019; Rai et al., 2018; Alvaro et al., 2007; Augusto et al., 2005, 2008, 2017; Castelo-Grande et al., 2015, 2021), its application to real samples and its integration in real wastewater treatment plants has been scarcely studied. Also, the large majority of published research is only centered on a specific contaminant - neglecting the influence of the multi-contaminant complex aspect of wastewaters (contaminants/nutrients competing for the same active center) - and also kinetic studies are rarely present. The reuse and regeneration of the magnetic particles are also an often neglected subject, as are the

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locations in the WWTP where these magnetic particles may be inserted.

In this paper, we present the research we have done concerning the application of magnetic particles for the sorption of contaminants. We have used two different particles (resin and polymeric covered magnetic particles) and compare the results with our previously published study (Castelo-Grande et al., 2021 a) using bare naked magnetite. The sorption was investigated for wastewater samples collected at three different locations of the WWTP (entrance, after the first settling tank, and at the exit of the centrifuge of the activated sludge). Results of the kinetics studies are also presented. The regeneration and reuse of the most promising particles was also researched, and the results detailed and compared with other published works (Augusto et al., 2019).

2. Materials and methods

2.1. Reagents

We have used in this work two different magnetic particles:

- Resin covered magnetite particles (Miex), obtained within the scope of MAGPRO2LIFE project, with sizes between 30 and 210 μm (depicted in Figure in Supplementary Material).

- Polymer covered magnetite particles, prepared by co-precipitation and alginate gelation, with sizes between 800 and 1600 μm (depicted in Supplementary Material).

Characterization of the used particles is detailed in (Augusto et al., 2019) and in Supplementary Material.

2.2. Experimental methodology

2.2.1. Sampling locations

We have used sampling from three extraction points located at different places of the the Salamanca's WWTP: 1 – Entrance (Sampling Point 1 – Sample 1 – Stream 1); 2 – Exit of the first settling tank (Sampling Point 2 – Sample 2 – Stream 2); 3 – Liquid flow exiting the activated sludge centrifuge (Sampling Point 3 – Sample 3 – Stream 3). These locations are shown in the Supplementary Material.

2.2.2. Methodology

For each trial (experiment) the experiments where repeated at least three times until coincident results were obtained between them.

2.2.2.1. Sample analysis. Samples were analyzed at the beginning and after predetermined times, measuring: COD, nitrates, nitrites, ammonium, total nitrogen, phosphates, chlorides and sulfates content by using Hach-Langue kits and their respective spectrophotometer, and using the analytical services of the University of Salamanca for analyzing their content on heavy metals. For several of the samples a pre-centrifugation and filtration procedure had to be made in order to remove possible solids interference.

2.2.2.2. Sorption experiments. For the sorption experiments we insert 1 g of the chosen magnetic particles in an erlenmeyer containing 50 mL of the sample, close the erlenmeyer and insert it in an orbital shaker (assuring a non-magnetic stirring that otherwise might affect the results). After the pre-selected time is reached, the bottle is taken out of the shaker and the liquid separated from the particulate media by using a magnetic separation/decantation procedure with the help of a strong magnetic field. The resulting liquid is processed for content analysis and the particles are directed towards regeneration and reuse procedures (see the schematic diagram presented in Supplementary Material).

2.2.2.3. – Kinetic experiments and analysis. For kinetic studies, different vessels are inserted at the same time in the shaker and then taken out separately after their specific set time is elapsed. The results are adjusted to the most commonly known kinetic models and the best fits determined.

Models:

We have applied the most common kinetic models to determine which would adjust better to each kinetic curve of each contaminant removal, namely: pseudo first-order, pseudo second-order, and simplified Elovich (Largitte and Pasquier, 2016).

In the following equations S are the adsorption sites, M is the adsorbate, C is the concentration of the adsorbate in solution, y is the order of reaction for the adsorbate, MS is the concentration of adsorbate bound to the sorbent, k_{ad} is the adsorption rate constant,k_d the desorption rate constant, Q is the amount of contaminant/nutrient sorbed in time t and $Qmax$ is the maximum sorbed quantity. The sorption rate is equal to dQ/dt.

<u>*Pseudo first-order model*</u> is defined based on the non-reversible equation:

$$\mathrm{S} + \mathrm{M} \rightarrow \mathrm{MS} \tag{1}$$

Then, the sorption rate can be written as

$$k_{ad} C^{y} \left(\frac{Q_{max} - Q}{Q_{max}} \right)^2 = k'_{ad} (Q_{max} - Q) \tag{2}$$

and the resulting equation, after integration

$$ln \left(1 - \frac{Q}{Q_{max}} \right) = -k'_{ad} t \tag{3}$$

<u>*Pseudo second-order model*</u> is defined based on the equation:

$2\,\mathrm{S} + \mathrm{M} \rightarrow \mathrm{M(S)_2}$ (4).

The assumptions are almost the same as for the pseudo first order model except that the ion uptake on the activated carbons is governed by a second-order rate equation. Then, the sorption rate can be written as

$$k_{ad} C^{y} \left(\frac{Q_{max} - Q}{Q_{max}} \right)^2 = k'_{ad} (Q_{max} - Q)^2 \tag{5}$$

and the resulting equation after integration

$$\frac{t}{Q} = \frac{t}{Q_{max}} + \frac{1}{k'_{ad} Q_{max}^2} \tag{6}$$

<u>The simplified Elovich model</u> is based on the equation

$$\mathrm{S} + \mathrm{M} \rightarrow \mathrm{MS} \tag{7}$$

The energy of adsorption increases linearly with the surface coverage according to the law:

$$Ea = Ea_0 + RT\beta Q \tag{8}$$

where E_a and E_{a0} are the energies of activation (*0* represents the standardized value), T is the temperature and R the perfect gas constant. Then, the adsorption rate constant k_{ad} can be written, using the Arrhenius equation, as:

$$k_{ad} = Cte \times e^{\left(-\frac{Ea}{RT} \right)} = \alpha' \times e^{(-\beta Q)} \tag{9}$$

with

$$\alpha' = Cte \times e^{\left(-\frac{Ea_0}{RT} \right)} \tag{10}$$

Then, the sorption rate can be written as:

$$\alpha \times e^{(-\beta Q)} \tag{11}$$

with

$$\alpha = C^{y} \alpha' \tag{12}$$

and the resulting integration gives:

$$Q = \frac{1}{\beta} ln(\alpha\beta) + \frac{1}{\beta} ln(t) \tag{13}$$

2.2.2.4. – Regeneration and reuse experiments. The regeneration of the particles has followed the footsteps of the procedure described in (Augusto et al., 2019), but with an adaptation considering the tested resin covered particles in order to not degrade the resin shell. Therefore, particles were inserted in a deionized water solution and then heated at 67 °C for 1 h, and then removed and inserted in another clean water solution heated during half an hour at 50 °C. This last procedure was repeated one more time. To remove the particles from solution a magnetic separation/decantation process was used. The final obtained particles were then cooled till 20 °C and inserted in an oven for 2 h at 80 °C, so they could be reused.

2.3. Instrumentation

For the sample analysis: Spectrophotometer (Hach-Lange DR3900), digestor (Hach-Lange LT200); fridge (TEKA Cl3 350).

For sorption and kinetics experiments: Oven (Argolab G-TCF-120); analytical balance (Sartorius Cubis MSE225S-100-DA); orbital shaker (ELMI Sky Line Shaker DOS-20 M); magnetic separation system (home-made).

For regeneration and reuse experiments: Oven (Argolab G-TCF-120); analytical balance (Sartorius Cubis MSE225S-100-DA); magnetic separation system (home-made); heating plate.

General instrumentation: Glass material (Erlenmeyers, beakers, burettes, vials, etc.); Buckner filter device (Nahita 300 mL), among other nonspecific instrumentation.

2.4. Initial conditions

Typical values obtained from the analysis made on the wastewater content at the three sampling sites are given in Table 1.

3. Results and discussion

The results are organized in four subsections. In the first subsection (3.1) we analyze the influence of an increase on the concentration (mass) of resin magnetic particles for the application in the most contaminated wastewater sampling point (sample 3 – exit of the centrifuge). Then the influence of the type of particles in the sorption results is tested (section 3.2) by using two different types of particles (resin and polymeric covered magnetic particles) and the results between them and the results obtained using bare magnetite (Castelo-Grande et al., 2021 a) are compared. The best kinetic models for the sorption curves for each particle and contaminant are then determined and presented (section 3.3), as well as the values of the associated kinetic parameters. Finally, the regeneration and reuse (section 3.4) of the best-behaved type of particles is tested and results presented.

3.1. Influence of magnetic particles concentration (mass of particles)

It was previously noticed (Castelo-Grande et al., 2021 a) that when the concentration of contaminants/nutrients is high, higher instabilities appear in the sorption graphics, and in many cases the removal efficiency is very low. It was then decided to increase the mass of the particles to its triple in the sorption experiments (from 1 g to 3 g) in order to determine if the simple effect of a concentration increase was enough to trigger higher removal efficiencies and stability. For this study we have used the resin-covered magnetite particles as they were the ones that have shown best behavior for several measured parameters.

In Figs. 1–6 we detail the results obtained for the experiments using higher concentration of particles (3 g experiments), and compare them with the results obtained for the experiments using the regular concentration of particles (1 g experiments). In some of the graphics (Fig. 1) only 3 g experiments are presented, because 1 g experiments were inconclusive considering the specific contaminant depicted. In Supplementary Material are presented the corresponding individual graphics, and the overall numerical results.

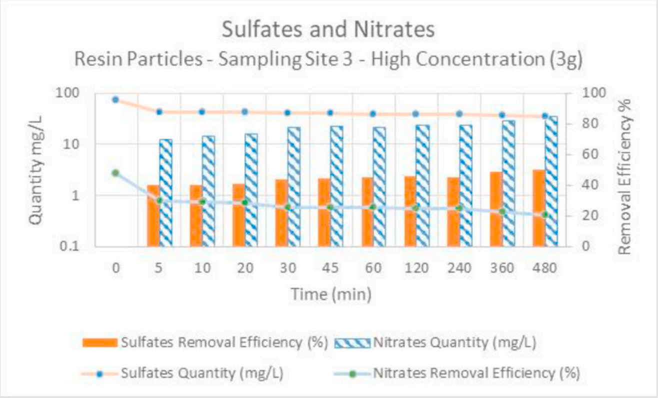

Fig. 1. Results (mass of particles 3 g) for Sulfates and Nitrates removal.

Table 1
Typical content of the wastewater samples collected at the three different sampling sites.

Contaminant	Wastewater origin						
	Sample 1 - Entrance		Sample 2 – Set. Tank		Sample 3 - Centrifuge		
	Resin	Polymer	Resin	Polymer	Polymer	Resin1g	Resin3g
Sulfate (mg/L)	–	–	–	–	–	–	71.9
Phosphates (mg/L)	6.83	6.26	6.23	6.00	157	109	75.3
Nitrates (mg/L)	0.599	–	0.563	–	5.62	–	2.64
Nitrites (mg/L)	0.076	–	0.053	–	2.44	2.53	0.69
Total Nitrogen (mg/L)	56.4	55.4	52.4	51.7	801	943	637
COD (mg O_2/L)	343	336	315	227	440	516	1030
Detergents (mg/L)	15.9	19.2	14.2	14.0	3.95	6.50	4.55
Cr (ppb)	6.00	6.8	7.6	9.9	–	–	–
Co (ppb)	0.9	1.1	0.1	0.1	–	–	–
Ni (ppb)	4.2	4.1	3.4	2.4	–	–	–
Cu (ppb)	1.6	–	0.7	–	–	–	–
Zn (ppb)	27.6	6.2	29.4	1.3	–	–	–
As (ppb)	3.6	2.6	3.9	2.5	–	–	–
Cd (ppb)	–	–	–	–	–	–	–
Hg (ppb)	–	–	–	–	–	–	–
Pb (ppb)	0.6	0.4	1.1	0.4	–	–	–

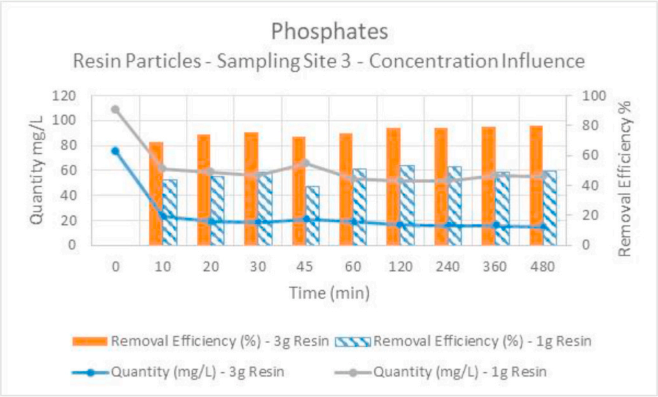

Fig. 2. Comparative results (mass of particles 1 g and 3 g) for phosphates removal.

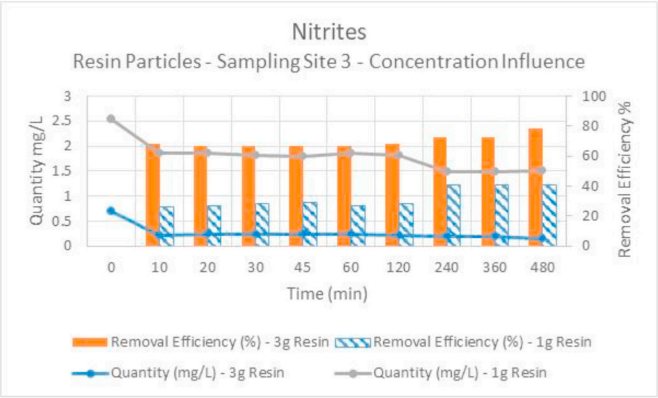

Fig. 3. Comparative results (mass of particles 1 g and 3 g) for nitrites removal.

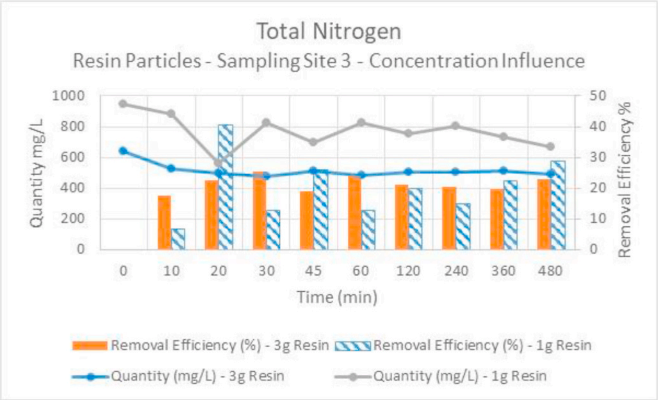

Fig. 4. Comparative results (mass of particles 1 g and 3 g) for total nitrogen removal.

3.1.1. *Discussion of results*

It is important to notice that for the 3 g case we have only followed the experiments until the 480 min, since this time is usually sufficient to achieve efficiencies at the desired level and to show already a clear improvement. Therefore, comparisons are only done until this time.

The large majority of the contaminants studied are clearly more sorbed when a higher concentration of particles is present. There are some fluctuations is some cases, which are caused by sorption-desorption phenomena as explained in (Castelo-Grande et al., 2021 a; Augusto et al., 2019). Also, the usual instabilities in some of the nitrogen compounds of the total-nitrogen-nitrates-nitrites cycle do appear, in some cases, caused by their constant transformation among these species and others (like ammonia, etc.) (Castelo-Grande et al., 2021 a; Augusto et al., 2019).

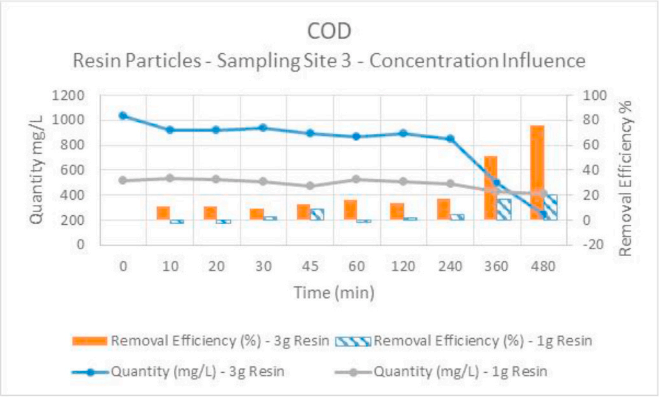

Fig. 5. Comparative results (mass of particles 1 g and 3 g) for COD removal.

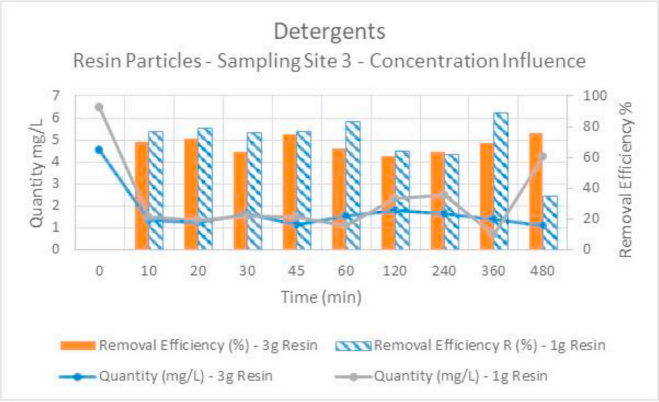

Fig. 6. Comparative results (mass of particles 1 g and 3 g) for detergents removal.

Individually we may conclude that: nitrates are highly removed by sorption in the magnetite particles for the high concentration case (84.6%). Sulfates are moderately removed by sorption for the high concentration case (50.4%); phosphates and organic matter (COD) present high efficiencies (80.2% and 76.2%, respectively) when sorbed by high concentration of particles, and moderate or low otherwise (49.5% and 19.8%, respectively); detergents present approximately the same efficiency behavior for both concentrations (around 80% for both), showing a high saturation level of the magnetite for this kind of compounds; for nitrates high concentrations of particles mean almost the double (around 80%) of efficiency as comparing to the low concentration values, while for total nitrogen, both concentrations are able to achieve a sufficient level of efficiency (more or less 30%).

3.2. *Influence of the type of magnetic particles*

In this section we analyze the influence of the type of magnetic particle used in the sorption results. It is important to notice that this is the major factor that may lead to the selection of one type of particles over the other. In fact, considering the final recovery and particle reuse, all types of particles tested have shown to be well recovered by the applied magnetic sedimentation method, thus this factor lacks relevance in this analysis.

In the supplementary material are shown the individual results obtained for each type of particle in each sample and for each contaminant/nutrient, in the graphical form as a function of time. In supplementary material are also presented the numerical results obtained for the different samples using the different types of magnetic particles tested in this part of the work (resin covered magnetite and polymeric cover magnetite).

In Figs. 7–9 are presented graphical comparisons between all these values and the values obtained previously for bare magnetite particles (Castelo-Grande et al., 2021 a) and for leachates (Augusto et al., 2019).

3.2.1. *Discussion of results*

A global analysis is very difficult to be done, given the huge amount of data. In fact, each type of particle behaves better for specific contaminants and for specific sampling points. Therefore, an individual analysis imposes.

Comparing the recovery efficiency for each type of particle we may notice that:

a) Sulfates are only able to be removed, with moderate efficiency, in the case of higher concentration of resin covered particles and for high contaminant concentration environments (leachates and activated sludge centrifuge exit).

b) Phosphates are very efficiently sorbed at moderate concentrations of contaminants and by resin or polymeric covered magnetite (with a slight upper head shown by resin particles), while performance in the other cases in moderate.

c) Nitrates are very well removed for high contaminant concentration environments (leachates and activated sludge centrifuge exit) and moderately to sufficient removed for the other tested cases.

d) Nitrites usually behave erratically with time, but we may stand out their high efficiency removal using magnetite at high contaminant concentration environments (leachates and activated sludge centrifuge exit); other cases exist (specially at entrance sampling point - magnetite and polymeric magnetite - at the exit centrifuge of activated sludge - resin and polymeric magnetite - and at the settling tank - polymeric magnetite) where this removal efficiency still achieves moderate levels.

e) For Total Nitrogen results are very similar, concerning the removal efficiency, for almost all cases and types of particles, presenting a moderate to sufficient sorption, except for the cases of leachates and exit of the centrifuge of the activated sludge (in the case of low concentration values of the resin magnetite) where these values reach slight higher levels, similarly to what is observed in the polymeric magnetite case for the exit of the centrifuge samples.

f) COD is highly reduced in the cases of low contaminant concentration environments (sampling points 1 and 2), and for the centrifuge sampling point when higher concentrations of resin are used. Usually resin covered particles behave slightly better than the other types of particles.

g) Detergents removal shows a behavior quite similar to the one described for COD with the difference that the general efficiency results are even better, and that resin covered particles efficiency stands-out into even higher values comparing to the other type of particles.

h) Heavy metals: Magnetite is the only one able to remove almost all heavy metals when applied to the samples from the 1st Settling Tank. Cr and Pb are well absorbed by all types of particles in almost every samples. Polymeric magnetite and magnetite are very, or moderately, efficient in removing As, Zn and Cu. Ni is sufficiently to low removed by almost all particles and samples. Hg is only moderately efficiently removed by magnetite in one of the samples (1st settling tank). We may conclude that for heavy metals the type of particle with lowest performance are the resin covered magnetite particles, while polymeric covered magnetite and bared magnetite provide about the same efficiency (although some particular cases are always present).

3.3. *Kinetics*

The behavior of the sorption of contaminants with time is always a relevant data. From the large-scale applications point-of-view, it is not only important to know the removal efficiency values, but also their behavior with time. In fact, for real wastewater treatment plants time is quite relevant, considering the water flow rates that must be handled, and therefore if full removal of contaminants is only achieved after a longtime, the process is simply discarded. Furthermore, usually a balance between time and efficiency is done, so that is quite common to see industries/large-scale applications using applications that do not work at their maximum efficiency, but that present enough efficiency for the maximum treatment time allowed.

We have applied the three most common kinetic models described in Materials and Methods section: pseudo first-order, pseudo second-order, and simplified Elovich.

The best fitting model (among these three most common fitting

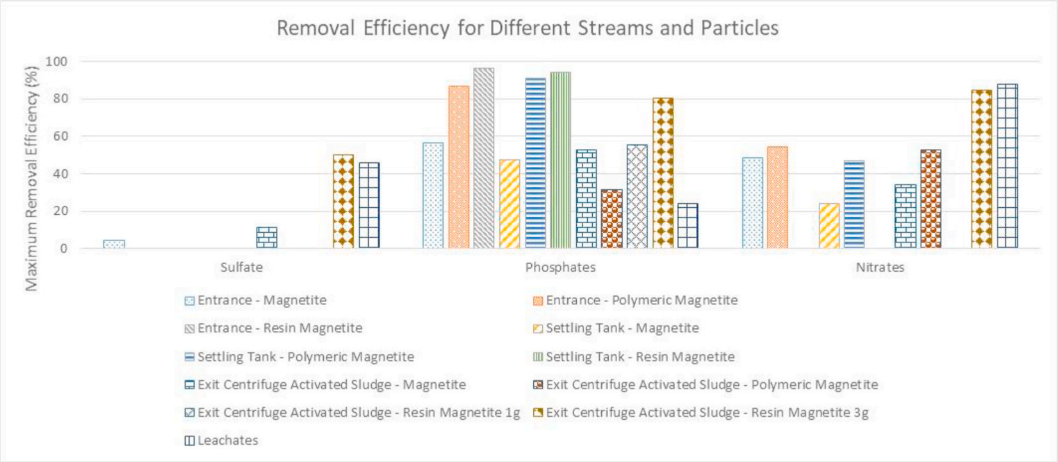

Fig. 7. Comparison between the maximum values of removal efficiency for sulfates, phosphates and nitrates, for the three wastewater samples, the leachate and the three types of particles used.

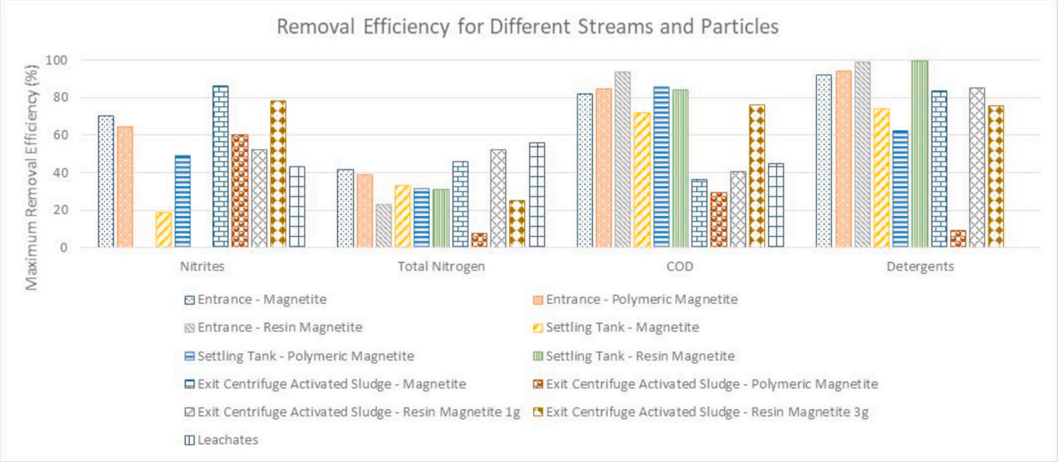

Fig. 8. Comparison between the maximum values of removal efficiency or nitrites, total nitrogen, COD and detergents, for the three wastewater samples, the leachate and the three types of particles used.

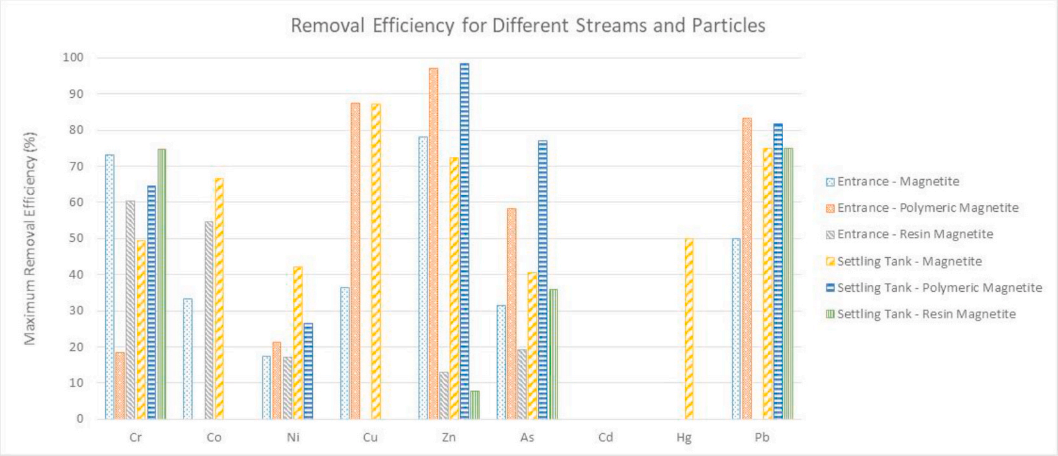

Fig. 9. Comparision between the maximum values of removal efficiency for heavy metals, for the three wastewater samples, the leachate and the three types of particles used.

models) was determined for each studied case, and the results are presented in Table 2, together with the values for the model parameters. In some cases, the fitting models either gave the same magnitude for the accuracy of fitting, or presented low accuracy of fitting, or even the parameters are not as expected; in these cases, other models, besides the best fitting model, are indicated together with the corresponding values for the model parameters. The non-expected values of the parameters are highlighted in yellow, and these are justified by the cycles of sorption-desorption that appear during the analysis (Castelo-Grande et al., 2021 a; Augusto et al., 2019), as previously described, and that may lead to the global process to be more desorptive than sorptive.

The graphics considering removal efficiency *versus* time, for all the cases studied in this work are presented in Supplementary Material, complemented with graphical depictions (Castelo-Grande et al., 2021 a).

3.3.1. Discussion of results

From the results it is clear that the pseudo-second order model is the model that best fits the large majority of sorption kinetics. This is in accordance with what is generally expected and found in scientific literature (Y.-S. Ho, 2006). The values detailed in Table 2 are very important for the design of a WWTP integrating the magnetic sorption process.

3.4. Reuse

For the tests concerning the reuse of the particles we have centered our analysis in the resin covered particles. Thus, we had to change our previous procedure (Augusto et al., 2019) to accommodate lower temperatures in order to prevent the degradation of the resin cover, as described in section 2.2.2.

In Supplementary Material are presented the results obtained using the resin particles after being regenerated and also the comparison, with time, of the results obtained by the regenerated particles with the ones obtained on the first application (original particles with no regeneration).

In Fig. 10 is shown a sum up of the best efficiency removal values obtained for all the sampling sites and for the contaminants studied in the reuse experiments.

3.4.1. Discussion of results

The particles regenerated and reused, in almost all studied cases, do not show the same efficiency as the original particles. This difference is only slight in the case of phosphates and total nitrogen. For the case of COD, the efficiency drops considerably when regenerated particles are reused. On the opposite, nitrites have more affinity with the regenerated particles (especially for the sample taken from the exit of the Activated

Table 2
Best fitting sorption models for the contaminants/nutrients removed. Values highlighted in yellow represent desorption processes/values. (*) → fitting accuracy $0.4 < r^2 < 0.6$, (**) → fitting accuracy $0.1 < r^2 < 0.3$, (***) → fitting accuracy $r^2 < 0.05$, no indication → fitting accuracy $0.8 < r^2 < 1.0$. P2O stands for the pseudo 2nd order model, P1O stands for the pseudo 1st order model, and SE stands for the simplified Elovich model. The letters refer to the parameters of each model.

Contaminant/Nutrient	Sample 1 – Entrance of the WWTP						Sample 2 – Exit 1st Settling Tank						Sample 3 – Exit Centrifuge Activated Sludge					
	Magnetite		Resin		Polymeric		Magnetite		Resin		Polymeric		Magnetite		Resin		Polymeric	
Sulfates	P2O(*)						P2O						P2O (*)					
	Q_{max}	k'_{ad}					Q_{max}	k'_{ad}					Q_{max}	k'_{ad}				
	−0.312	0.030					−4.19	−0.023					0.157	−0.056				
	SE (**)						SE (**)						SE (**)					
	β	α					β	A					β	α				
	−2.93	−271.5					4.70	4.8E-16					1.25	0.016				
	P1O (**)						P1O (*)						P1O (**)					
	k'_{ad}						k'_{ad}						k'_{ad}					
	−0.343						0.0008						0.0032					
Phosphates	P2O		P2O		P2O		P2O		P2O				P2O		P2O		P2O	
	Q_{max}	k'_{ad}	Q_{max}	k'_{ad}	Q_{max}	k'_{ad}	Q_{max}	k'_{ad}	Q_{max}	k'_{ad}			Q_{max}	k'_{ad}	Q_{max}	k'_{ad}	Q_{max}	k'_{ad}
	4.36	0.016	6.22	0.00047	6.04	0.016	2.77	0.011	13.87	0.020			40.65	0.0012	55.25	0.0035	37.74	0.0014
	SE		SE				SE				SE							
	β	α	β	α			β	α			β	α						
	−3.15	−4.3E-4	1.08	0.057			2.96	1.00			1.45	0.043						
	P1O		P1O								P1O							
	k'_{ad}		k'_{ad}								k'_{ad}							
	0.0041		0.001								0.0016							
Nitrates	P2O		P2O				P2O (*)				P2O		P2O (**)				P2O	
	Q_{max}	k'_{ad}	Q_{max}	k'_{ad}			Q_{max}	k'_{ad}			Q_{max}	k'_{ad}	Q_{max}	k'_{ad}			Q_{max}	k'_{ad}
	0.320	0.163	0.323	0.042			0.347	0.024			0.224	7.35	0.030	1.83			1.93	0.012
Nitrites	P2O(*)		P2O				P2O				P2O		P2O		P2O		P2O (**)	
	Q_{max}	k'_{ad}	Q_{max}	k'_{ad}			Q_{max}	k'_{ad}			Q_{max}	k'_{ad}	Q_{max}	k'_{ad}	Q_{max}	k'_{ad}	Q_{max}	k'_{ad}
	-2E-3	5.05	0.051	0.074			−0.043	2.28			0.027	0.522	6.46	−0.061	1.33	0.015	0.726	0.0010
	SE (**)						SE						SE (**)		SE		SE (**)	
	β	α					β	α					β	α	β	α	β	α
	−1000	-1E-10					−100	−0.0028					−9.79	-3E-32	8.04	1.23	15.31	1.83
	P1O (**)												P1O(***)				P1O (**)	
	k'_{ad}												k'_{ad}				k'_{ad}	
	0.0006												−0.0015				−0.0002	
Total Nitrogen	P2O		P2O		P2O		P2O		P2O		P2O		P2O(*)		P2O		P2O	
	Q_{max}	k'_{ad}	Q_{max}	k'_{ad}	Q_{max}	k'_{ad}	Q_{max}	k'_{ad}	Q_{max}	k'_{ad}	Q_{max}	k'_{ad}	Q_{max}	k'_{ad}	Q_{max}	k'_{ad}	Q_{max}	k'_{ad}
	24.63	0.0023	21.55	0.0057	12.92	0.00056	16.39	0.00096	17.67	6.9E-05	16.95	0.00034	333.3	2.97E-05	312.5	4.32E-05	−67.57	0.00014
	SE				SE		SE										SE (**)	
	β	α			B	A	β	α									β	α
	0.296	4.61			0.589	0.467	0.436	1.90									0.026	0.0050
	P1O				P1O		P1O				P1O						P1O (**)	
	k'_{ad}				k'_{ad}		k'_{ad}				k'_{ad}						k'_{ad}	
	0.0033				0.0017		0.0028				1.8981						−0.0003	
COD	P2O		P2O		P2O		P2O		P2O		P2O		P2O		P2O			
	Q_{max}	k'_{ad}	Q_{max}	k'_{ad}	Q_{max}	k'_{ad}	Q_{max}	k'_{ad}	Q_{max}	k'_{ad}	Q_{max}	k'_{ad}	Q_{max}	k'_{ad}	Q_{max}	k'_{ad}		
	476.2	0.00030	312.5	6.58E-6	312.5	4.66E-05	263.2	0.00018	4.81	−0.0069	277.8	7.17E-06	175.4	0.0051	476.2	1.7E-6		
	SE		SE		SE		SE		SE								SE (**)	
	β	α	β	α	B	A	B	A	B	α							β	α
	0.040	6.67E6	0.0242	3.35	0.035	247	−0.048	-1E-04	0.032	5.77							0.042	0.0041
			P1O				P1O		P1O		P1O				P1O			
			k'_{ad}				k'_{ad}		k'_{ad}		k'_{ad}				k'_{ad}			
			0.0008				0.0032		0.0005		34.5				0.0003			
Detergents	P2O		P2O		P2O		P2O		P2O		P2O(**)		P2O		P2O		P2O	
	Q_{max}	k'_{ad}	Q_{max}	k'_{ad}	Q_{max}	k'_{ad}	Q_{max}	k'_{ad}	Q_{max}	k'_{ad}	Q_{max}	k'_{ad}	Q_{max}	k'_{ad}	Q_{max}	k'_{ad}	Q_{max}	k'_{ad}

(*continued on next page*)

Table 2 (*continued*)

Contaminant/Nutrient	Sample 1 – Entrance of the WWTP			Sample 2 – Exit 1st Settling Tank			Sample 3 – Exit Centrifuge Activated Sludge		
	Magnetite	Resin	Polymeric	Magnetite	Resin	Polymeric	Magnetite	Resin	Polymeric
	27.9 0.0022 SE β A 0.286 13.04 P1O k'_{ad} 0.005	14.7 0.00065	19.01 0.012 SE B A 1.73 7.99 E+10 P1O k'_{ad} 0.0042	11.38 0.0016 SE β α 0.454 0.433 P1O k'_{ad} 0.0043	192.3 0.00022	5.55 0.00058 SE(***) β α −4.65 −0.011 P1O (**) k'_{ad} −0.0011	2.72 −0.024 SE (**) β α 1.92 1.62 P1O(**) k'_{ad} −0.0002	3.78 −0.028 SE (**) β α −4.25 -6E-12 P1O(**) k'_{ad} 0.0001	0.366 −0.0068 SE (**) β α 38.91 4E-16 P1O(**) k'_{ad} −0.0002

Contaminant/ Nutrient	Magnetite	Resin	Polymeric	Contaminant/ Nutrient	Magnetite	Resin	Polymeric	Contaminant/ Nutrient	Magnetite	Resin	Polymeric
Cr	P2O Q_{max} k'_{ad} −1.48 0.0037 P1O (**) k'_{ad} −0.001	P2O Q_{max} k'_{ad} 0.244 −0.0304 SE(*) β A 2.07 0.00191 P1O(**) k'_{ad} 0.001	P2O Q_{max} k'_{ad} 4.08 0.00295	Cu	P2O(**) Q_{max} k'_{ad} −26.81 1.99E-05 SE (**) B A −0.873 −0.00403 P1O(**) k'_{ad} 1.15	P2O (**) Q_{max} k'_{ad} −1.00 0.0258 SE(***) B A 28.57 1.02E-12 P1O(***) k'_{ad} 0.0252		Hg	P2O Q_{max} k'_{ad} 0.0360 −0.186 SE(**) B A −47.85 −0.00799 P1O (*) k'_{ad} −0.0209		
Co	P2O (*) Q_{max} k'_{ad} 0.178 0.0293	P2O Q_{max} k'_{ad} −0.805 −0.00561 SE B A −5.41 −0.00938 P1O(**) k'_{ad} 0.0004	P2O Q_{max} k'_{ad} 0.567 0.0230	Zn	P2O Q_{max} k'_{ad} 28.99 0.00239	P2O Q_{max} k'_{ad} 18.12 −0.00164 SE(**) B A 3.04 3.06 E+23 P1O(**) k'_{ad} −0.0006	P2O (**) Q_{max} k'_{ad} −2.1132713 0.003246 SE(**) B α −2.1110407 −3.65114 P1O(**) k'_{ad} −0.0005	Pb	P1O k'_{ad} 0.0147	P2O Q_{max} k'_{ad} 0.0705 −0.804 SE (**) B A −13.44 −0.00029 P1O (***) k'_{ad} −0.0022	
Ni	P2O(**) Q_{max} k'_{ad} −0.641 0.00390 SE (*) B A −8.58 −3.47E-05 P1O(**) k'_{ad} 0.0002	P2O Q_{max} k'_{ad} −10.37 0.000834 SE B A −0.548 −0.119 P1O(**) k'_{ad} 3.00E-05	P2O Q_{max} k'_{ad} −3.80 0.00767 SE(**) B A 1.12 6.61 P1O(***) k'_{ad} 2.00E-05	As	P2O Q_{max} k'_{ad} 0.424 −0.0611 P1O k'_{ad} 0.0011	P2O Q_{max} k'_{ad} 2.06 0.0141	P1O k'_{ad} 0.0024				

(continuation) - Best fitting sorption models for the contaminants/nutrients removed. Values highlighted in yellow represent desorption processes/values. (*) → fitting accuracy $0.4 < r^2 < 0.6$, (**) → fitting accuracy $0.1 < r^2 < 0.3$, (***) → fitting accuracy $r^2 < 0.05$, no indication → fitting accuracy $0.8 < r^2 < 1.0$. P2O stands for the pseudo 2nd order model, P1O stands for the pseudo 1st order model, and SE stands for the modified elovich model. The letters refer to the parameters of each model.

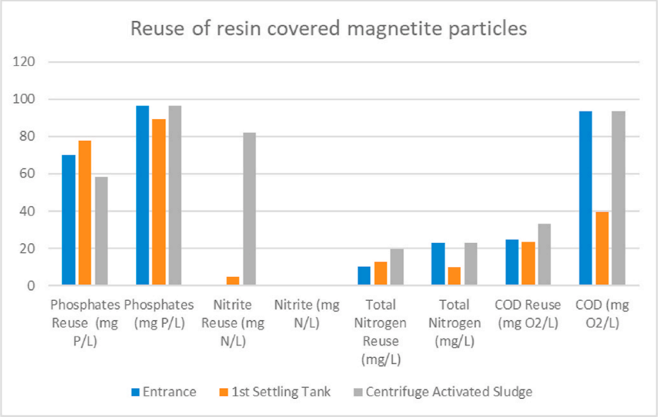

Fig. 10. Best efficiency removal values obtained for the sorption process of samples obtained at the three sampling sites by regenerated resin covered particles - reuse.

Sludge Centrifuge). It is also important to notice that the source of the sample (and thus contaminant content) has only a slight influence on the removal efficiency. Regenerated particles seem to improve the similarity of behavior between samples from the different sampling points. Probably a most aggressive regeneration method, or using higher temperatures in the applied regenerated method, would improve the efficiency results.

4. Conclusions

Magnetic sorption of contaminants proved to represent a good option as a process unit to be inserted in the flow process diagram of a Wastewater Treatment Plant. In fact, the results presented in this work show global good results for the treatment of contaminants present in wastewaters entering the WWTP under analysis and even at different points inside the internal flow process. In the case of low removal efficiencies, one option may be an increase in the concentration of magnetic particles, in order to reach higher level of efficiency, as proved by the experiments detailed in this article. The capability of sorption is present not only in bare magnetite particles (the cheapest ones) but also in composed particles (resin or polymeric covered magnetite particles) where results may be even better, depending on the contaminants under analysis and the sampling site. From the kinetics experiments and model fitting we may use the important results detailed in this paper to extrapolate the sorption behavior of each contaminant from each sampling point, which allow to better control the process and residence times in the pilot-scale adaptation. Particles may also be regenerated and reused, although a stronger regeneration method than the one used in this paper is advised.

Credit author statement

Teresa Castelo-Grande: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing – original draft, Writing – review & editing, Supervision, Project administration, Funding acquisition; Paulo A Augusto: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing – original draft, Writing – review & editing, Supervision, Project administration, Funding acquisition; Javier Rico: Investigation; Jorge Marcos: Investigation; Roberto Iglesias: Investigation; Lorenzo Hernández: Formal analysis, Investigation; Domingos Barbosa: Conceptualization, Methodology, Writing – original draft, Writing – review & editing, Project administration, Funding acquisition

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2021.112177.

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