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Magnetic coagulant based on *Moringa oleifera* seeds extract and super paramagnetic nanoparticles: optimization of operational conditions and reuse evaluation

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ABSTRACT

The aim of this study was the development of a new magnetic coagulant based on nano structured iron oxide functionalized by *Moringa oleifera* (MO) compounds present in aqueous saline extract, for water treatment, with removal of the physical-chemical indicatives parameters, turbidity, apparent color, and compounds with absorption at UV_{254nm}(UV_{254nm}). The nano structured iron oxide(maghemite, γ-Fe_2O_3) was synthesized without organic solvents use. These nanoparticles were functionalized by the compounds present in aqueous saline MO (without oil, extracted by ethanol and hexane) extract. Tests of coagulation and flocculation were performed by using a *Jar Test* equipment with medium to high turbidity water (80 NTU). The magnetic coagulant achieved removals of 94.4% for turbidity, 87.5% for apparent color and 63.4% for UV_{254nm}, with surface waters using applied magnetic field within 30 min of settling. The treatment of coagulation followed by flocculation with magnetic functionalized MO coagulant could lessen physico-chemical properties assessed with diminished sedimentation time. The coagulant used in the study can be reused without significant loss of efficiency due to possibility of magnetic separation, showing an economically viable method and low environmental impact.

Keywords: Coagulation/flocculation; *Moringa oleifera*; Nanoparticles; Maghemite; Magnetic coagulant

1. Introduction

Considering the importance of drinking water in the world, and bearing in mind the concerns about the viability of recent practices to meet the growing demands for water, there is an urgent need to develop new technologies and materials, which, associated with natural coagulants, may replace or reduce the use of inorganic products that result in toxic residual, as the Al in drinking water management [1].

The emergence of nano technology has been identified as a promising proposal that can play an important role in the supply of drinking water. The use of coagulants derived from plants, such as coagulants based on *Moringa oleifera* (MO) associated with nano materials is an innovative way to improve the performance of the coagulant activity. This combination can offer several advantages, such as greater efficiency in coagulation/flocculation (C/F) and speed in sedimentation step, significant reduction in the volume of generated sludge and reusability of nano materials, constituting this way an excellent alternative to be used in water coagulation/flocculation/settling (C/F/S) processes [2–4].

MO seeds have been used as primary coagulant for potable water clarification and residual water treatment due to the presence of a cationic coagulant water soluble protein, capable of reducing the turbidity of the water treated. The seeds can be used in powder form or as aqueous extract

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[5,6]. Poumaye et al. [7] demonstrated in his study that this natural coagulant can be used in the cleaning of water with high efficiency.

However, the presence of the oil derived from the seeds and many other organic compounds in the crude extract of MO, favors increasing the amount of organic matter in the treated water [8] preventing storage and consumption for more than 24 h [9]. This fact represents a disadvantage for their large-scale application in water treatment, being highly recommended the treatment of crude extract [10]. Oil extraction from the seeds before the preparation of the crude extract can be a proper purification option, allowing the recovery of oil for industrial and food processes and the extract for water clarification.

With regard to this coagulant, it is known that in its use, the flakes formed in C/F steps are light and difficult to settling, usually requiring 90 min for sedimentation of particles in suspension [11], but this necessary time is considered a very long time to be used in a treatment plant [12]. Therefore, the demand for more efficient coagulants that form flakes quickly settle able has increases in scientific research.

Nano materials have been suggested as an efficient and cost-effective environmentally correct alternative for water treatment, from the point of view of conservation of resources and environmental conservation [1,13–15]. Nano structured iron oxide use for clean-up water has been deeply studied due to the advantages of this material present compared to other materials in nano-scale. Its low cost, ease of separation through the application of magnetic field (due to ferromagnetic property), high surface area, adsorption capacity of pollutants and efficient action as photo catalyst on organic pollutants degradation reactions and metallic pollutants reduction,as well as on inactivation of viruses in aquatic media, show the potential of this material use for residual water decontamination [14,16–18].

Considering the aspects above mentioned, the aim of this study is to develop a new coagulant with magnetic properties composed of nano structured iron oxide functionalized with MO coagulant extract, for water treatment, based on removals of turbidity, apparent color and organic matter removals, as well to optimize coagulant concentration and operational parameters, in addition to study the reuse of generated sludge.

2. Methodology

Surface raw water was collected at Companhia de Saneamento do Paraná – Sanitation Company of Paraná State - (SANEPAR), located in Maringá, PR, Brazil, whose origin is the Pirapó River basin and its characteristics were evaluated for turbidity; apparent color and UV_{254nm} absorption compounds [19] are shown in Table 1. This water was used in coagulation/flocculation assays, using iron oxide nanoparticles functionalized with MO as coagulant. The medium to high turbidity values were chosen because this is the average turbidity for water in this source.

2.1. Magnetic nanoparticles synthesis

The nanoparticles composed by maghemite phase of iron oxide were synthesized by sol-gel method by using water as solvent [20]. Nitrate iron aqueous solutions were mixed with polyvinyl alcohol (PVA) aqueous solution in a suitable ratio in order to obtain the highest amount of maghemite phase. The mixture was heated until thermal degradation and calcined at 400°C for 4 h in muffle.

Table 1
Raw water characterization

Parameters	Values	Analysis method
Apparent color (uH)[(a)]	280	Spectrophotometer Hach model DR/2000
Turbidity (NTU)[(b)]	80	Policontrol turbidimeter model AP2000
UV_{254nm} (cm^{-1})	0.175	Spectrophotometer Hach model DR/2000

Analysis method performed according to Standard Methods [19].
(a) Hazen init = (mg Pt-Co.L^{-1}); (b) (turbidity unit)

2.2. MO seeds preparation

Mature seeds from MO provided from Universidade Federal de Sergipe (UFS),Aracajú- SE, Brazil,were removed from the pods, dried, peeled and grounded in home blender (Fig. 1).

2.2.1. MO seeds oil extraction using hexane as solvent - MO(hex) obtaining

For the oil extraction with (hexane) by the Soxhlet method, 10 g of grounded MO seeds, they were placed in cellulose cartridges extractors, and these were placed in Soxhlet extractors for 8 h. The grinding was used to facilitate the extraction process to ensure greater surface contact with the solvent. The de-fatted seeds were used to prepare a saline extract [21–23].

2.2.2. MO seeds oil extraction using ethanol as solvent - MO(et) obtaining

Grounded MO seeds were mixed to 95% of ethanol aqueous solution (5% w/v) for 30 min under stirring and room temperature [24]. De-fatted seeds were separated by centrifugation and dried in room temperature for 24 h before to be used to prepare the saline extract [23].

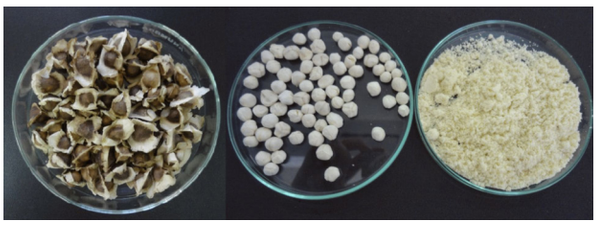

Fig. 1. MO seeds, pelled MO seeds and grounded MO seeds.

2.3. Preparation of MO(et) and MO(hex) saline extract

0.5 g, 1.0 g and 2.0 g of seed powder without oil was mixed with 100 mL of NaCl aqueous solution (1 mol/L) under magnetic stirring for 30 min. Afterwards, this mixture was vacuum filtered on a qualitative membrane, obtaining a 0.5%, 1% and 2% (considering initial mass) of saline extract [25]. The obtaining of extracts by saline solution was used due to be an efficient method in which the extraction occurs by a salting-out mechanism, which increases the ionic strength and the solubility of the active constituents, improving the coagulant capacity of MO seeds [26]. The coagulants were prepared and use as soon as possible, due to the short lifetime of MO extract [27,28].

2.4. Obtaining MOFe(et) and MOFe(hex) magnetic coagulants

10 mL of saline extracts, MO(et) or MO(hex) were added to 1 mL of γ-Fe_2O_3 aqueous dispersion (prepared mixture 5 mg, 10 mg or 20 mg of γ-Fe_2O_3 in 2.5 mL of distilled water) and stirred by ultrasound for 15 min. The mixtures (MO extract + iron oxide aqueous dispersion) called MOFe(et) (if used MO defatted with ethanol) and MOFe(hex) (if used hexane for MO oil extraction) were stirred at room temperature for 1 h (Fig. 2).

Different concentrations of MO(et) or MO(hex) and γ-Fe_2O_3 aqueous dispersion were combined and letters were used for their designation as shown in Table 2.

2.5. Magnetic coagulant characterization

The magnetic coagulants were characterized by zeta potential, FTIR spectroscopy and magnetic measurements. Zeta potential was evaluated in function of media pH (2–12) by electro phoretic light dispersion using a Beckman Coulter Delsa (TM) Nano Zeta Potential Analyzer, adjusting pH with HCl 0.01 M and NaOH 0.01 M. For FTIR spectroscopy, the samples were compacted in 1% KBr pellets and it was used a FTIR-BOMEN 100 equipment with 21 scan/

Table 2
Combined concentrations of MO(et) or MO(hex) and γ-Fe_2O_3 aqueous dispersion and their designations

	γ-Fe_2O_3 (mg)[a]	MO(hex) or MO(et) (%)[b]
A	0	0
B	0	0.5
C	0	1
D	0	2
E	5	0
F	5	0.5
G	5	1
H	5	2
I	10	0
J	10	0.5
K	10	1
L	10	2
M	20	0
N	20	0.5
O	20	1
P	20	2

[a]Inital mass of γ-Fe_2O_3 in 2.5 mL of water (initial dispersion);
[b]MO initial concentration in saline extract

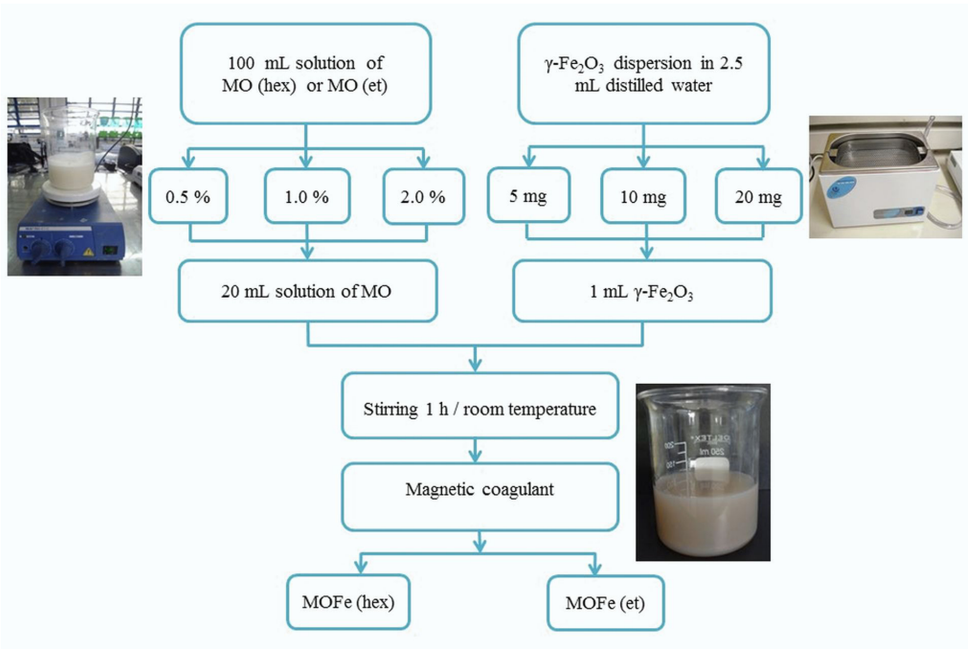

Fig. 2. Fluxogram of MOFe (hex) and MOFe (et) magnetic coagulants prepare.

min and 4 cm^{-1} of resolution. In order to characterize the fraction of MO soluble in saline extract and the magnetic coagulants, the samples were centrifugated and the sediments were dried and used for KBr pellets production. The magnetic behavior of the coagulants was investigated from the magnetic measurements obtained by a VSM magnetometer (Lake shore) through the magnetization curves (M) as a function of the applied magnetic field (H).

2.6. C/F essays for selecting the optimal coagulant mixture

C/F assays were carried out in a six-paddle stirrer *jar test* (Nova Ética), using 500 mL of raw water. The operational conditions used (rapid mixing rate; coagulation time; slow mixing rate; flocculation time) were optimized by Madrona et al. [25] (Table 3). Sedimentation was performed under applied magnetic field of 260 $A{\cdot}m^{-1}$ measured by using a Tools application, obtained using a ring magnet composed by barium ferrite (availability as a residue, extracted from automotive speakers) and also in the absence of magnetic field, in order to evaluate magnetic settling, for 15 and 30 min [29] . After raw water mixture, the final concentrations of MO were 200 $mg{\cdot}L^{-1}$ (initial 0.5%), 400 $mg{\cdot}L^{-1}$ (initial 1%) and 800 $mg{\cdot}L^{-1}$ (initial 2%). For γ-Fe_2O_3, the final concentrations were 10 $mg{\cdot}L^{-1}$ (initial 5 mg), 20 $mg{\cdot}L^{-1}$ (initial 10 mg) and 40 $mg{\cdot}L^{-1}$ (initial 20 mg) [29]. The used pH was the result of coagulant mixture with raw water without no subsequently adjustment.

2.7. Essays for selecting optimal operation conditions for C/F step

In order to reduce time and energy expended in *Jar Test* essays, in addition to optimize efficiency of C/F step, the operational conditions of these steps were evaluated by using the studied coagulants MOFe(et) and MOFe(hex). This evaluation was performed in terms of efficiency removal of apparent color, turbidity and UV_{254nm}, with the modification of mixture rates (RMR and SMR) and mixture times (CT and FT), in order to obtain suitable operational conditions for removal impurities of the raw water provided from Maringá, Brazil (apparent color 280 uH, turbidity 80 NTU, UV_{254nm} 0.175 cm^{-1}). All essays were performed in duplicate.

Table 4 presents the combinations of operational conditions (selected by variation of initial adopted operational conditions presented in Table 3) for *Jar Test* essays in C/F steps. All possible combinations in terms of RMR, CF, SMR and FT were performed and a letter was designed for each combination. The results were obtained for 15 and 30 min of settling time.

2.8. Settling kinetics

Jar test essays were performed in order to verify the required time of settling. The used operational conditions were the optimal conditions selected in the previous essays (essays for selecting optimal operation conditions for C/F step), been RMR 120 rpm, CT 5 min, SMR 15 rpm and FT 20 min. The settling time variated from 0 to 90 min; the required time to achieve expected parameters (apparent color, turbidity and UV_{254nm}) removal was evaluated.

Table 3
Jar Test operational conditions

Operational conditions	
RMR (rapid mixing rate) (rpm)	100
CT (coagulation time) (min)	3
SMR (slow mixing rate) (rpm)	15
FT (flocculation time) (min)	15
ST (settling time) (min)	15–30

[25]

Table 4
Combinations of operational conditions for C/F step adopted from Madrona et al. [25] and letter designation

Essay	RMR (rpm)	CT (min)	SMR (rpm)	FT (min)
L	120	1.0	35	10
M	80	5.0	35	10
N	120	1.0	35	20
O	120	5.0	15	20
P	120	5.0	35	10
Q	80	5.0	35	20
R	80	1.0	35	20
S	80	1.0	15	20
T	120	1.0	15	10
U	80	5.0	15	10
V	80	1.0	15	10

After C/F steps, *jar test* was turned-off and the first water sample was collected at zero time, following by rest for settling of flocculated material. Afterwards, samples were collected at times 3, 6, 9, 12, 15, 30, 45, 60, 75 and 90 min, being evaluated for each settling time the parameters apparent color, turbidity and UV_{254nm}.

2.9. Super paramagnetic nanoparticles regeneration

For the regeneration of iron oxide nanoparticles present at the resulting sludge of the C/F/S process, this sludge was rinsed by mixing in a solution of 20% ethanol in water, stirred for 10 min at room temperature and the supernatant (washed nanoparticles) was then removed by magnetic separation.

The washed nanoparticles were again functionalized by compounds present in saline extract of MO, obtaining a new coagulant. This coagulant was used for new tests of C/F/S. The evaluation of parameters removal was performed by using the combination K of MOFe(hex) coagulant and C/F optimized parameters (O essay). The coagulant regeneration potential was studied in two successive reuses.

2.9.1. Regenerated nanoparticles characterization

The regenerated nanoparticles were characterized by attenuated total reflectance – Fourier transform infrared spectroscopy (ATR-FTIR) and magnetic measurements.

The ATR-FTIR technique allows the direct sample analysis, without any previous preparation, at room temperature. This analysis were performed with a Bruker Vertex 70 v equipment by using the crystal platinum ATR diamond, range of 128, aperture of 6 mm and scanner velocity of 10 kHz.

The magnetic behavior of the regenerated nanoparticles was investigated from the magnetic measurements obtained by a VSM magnetometer (Lake shore) through the magnetization curves (M) as a function of the applied magnetic field (H).

3. Results and discussion

The iron oxide nanoparticles used in this study presented crystalline phase maghemite (γ-Fe_2O_3), crystallites with average diameter of 15 nm and preferably cubic shapes. These nanoparticles presented super paramagnetic properties, with saturation magnetization of 43 emu g^{-1} as previously obtained characterization [29].

3.1. Magnetic coagulant characterization

In order to evaluate the changes caused by functionalization of MO on the iron oxide, magnetic coagulants were characterized by zeta potential and FTIR spectroscopy, whose data are presented below.

The non-functionalized iron oxide, the soluble fractions of saline extract of MO(hex) and MO(et) and the magnetic coagulants MOFe(et) and MOFe(hex) (MO functionalized iron oxide) were characterized by FTIR spectroscopy (Fig. 3).

It could be observed that iron oxide FTIR spectrum presents two broad bands in range 400–700 cm^{-1}, related to Fe-O bonds and two bands in the range 1400–1600 cm^{-1} due to nitrate and carbonate residual from the synthesis process [30,31].

The soluble fractions of saline extract of MO(hex) and MO(et) spectra presents groups of peaks related to C-H bonds (such as 2900 cm^{-1}), carbonyl groups bands, such as 1670 cm^{-1} and 1540 cm^{-1} (bands characteristic of protein amide I and II) and poly saccharides bands (nearly to 1100 cm^{-1}) [32]. These bands are characteristics of biomass source materials. It could be observed that the process of oil removal from seeds does not alter significantly the soluble fraction of saline extract of MO(et) and MO(hex), since both spectra are so similar.

The magnetic coagulants MOFe(hex) and MOFe(et) spectra present overlapped bands of iron oxide nanoparticles and soluble fraction of saline extract of MO(et) and MO(hex) (respectively). The increase of 1650 cm^{-1} peak intensity possibly occurs due to formation of COOFe bonds [33] between iron atoms from maghemite surface and carbonyl groups present in proteins from MO, indicating that obtained coagulants are formed by iron oxide nanoparticles functionalized by the compounds of MO saline extract, showing that the used method of functionalization was efficient.

Zeta potential analyses were performed with pH variation from 2 to 12 (Fig. 4). It could be observed that iron oxide curve presents wide variation of zeta potential with pH change. The presence of the hydroxyl group on the synthesized iron oxide nano particle surfaces was confirmed by infrared measurement as described later. In a basic environment, the surface shows negative charge potential due to the dissociation of Fe–OH followed by the formation of $Fe–O^-$ [34,35]. The zero potential charge of iron oxide is found at pH 4.35. Above this pH, the material surface is negatively charged. This behavior is similar to the reported by Silva et al. [36].

The zeta potential curves versus pH for saline extract of MO(hex) and magnetic coagulant MOFe(hex) present similar behavior, with mild variation of zeta potential with pH change, presenting positive charge below pH 5 and negative charge above pH 6. It is also observed that for all evaluated pH range, the zeta potentials of MO(hex) and MOFe(hex) coagulant present more positive values than non-functionalized iron oxide. It could be explained by the presence of cationic protein responsible from coagulant characteristic of MO [37]. When MO(hex) was introduced into maghemite

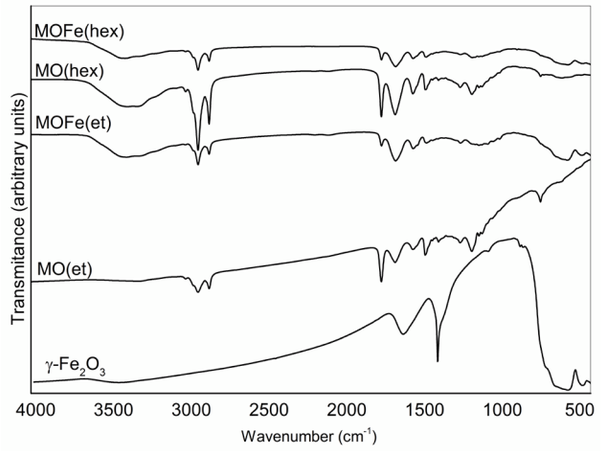

Fig. 3. FTIR spectra of iron oxide nanoparticles (γ-Fe_2O_3), magnetic coagulants MOFe(hex) and MOFe(et) and soluble fraction of saline extract of MO(hex) and MO(et).

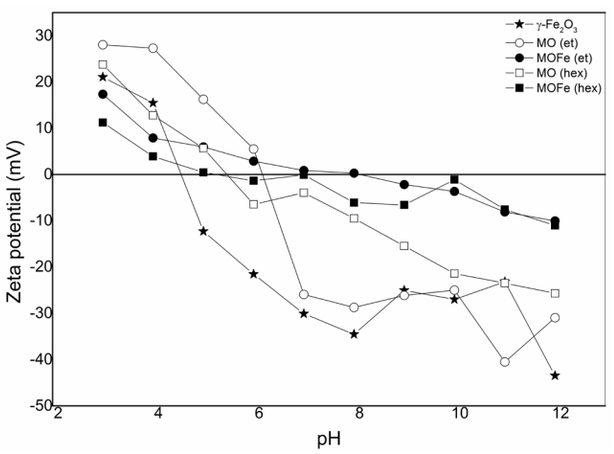

Fig. 4. Zeta potential of iron oxide nanoparticles (γ-Fe_2O_3), saline extract of MO(hex) and MO(et) and magnetic coagulants MOFe(et) and MOFe(hex).

colloid solution, MO soluble molecules (as proteins) preferred to attach to the surface of the nanoparticles because carboxylic acids have a high affinity for metallic oxides. In this system, the Fe–OH bond at the surface of iron oxide nanoparticles reacted with the carboxylic acid group of the MO proteins molecules via an acid–base reaction, giving Fe–O–C species with the elimination of H_2O [35]. This similar behavior indicates that iron oxide surfaces were effectively covered by MO(hex) saline extract compounds [38].

Related to zeta potential versus pH curves for MO(et) saline extract and magnetic coagulant MOFe(et), these present positive charges for pH below 6 and negative charges for pH above 7. The MO(et) saline extract present more evident variation of zeta potential with pH compared to MO(hex) saline extract. This possibly occurs due to the highest content of OH functional groups arising out of the use of ethanol in the oil extraction process. In other way, comparing MO(et) saline extract with its respective coagulant, MOFe(et), it could be supposed that the lower zeta potential variation with pH occurs due to the fact that OH groups present in MO(et) saline extract could be attached to iron oxide in the coagulant mixture. Therefore, these groups are less available to dissociation, so, leading to lower variation of surface charge.

The magnetic properties of the coagulants were determined by the behavior of the magnetization hysteresis circuit (M) as a function of the applied magnetic field (H) at 25°C by field cyclization between –15 and 15 kOe. The results show that MOFe(hex) and MOFe(et) coagulants exhibited typical super paramagnetic properties due to the negligible values of remanence and coercivity in the magnetization curve as a function of the applied magnetic field [39] and saturation magnetization of 1.87 emu g^{-1} for MOFe(hex) and 2.93 emu g^{-1} for MOFe(et) (Figs. 5 and 6). The fact that they exhibit super paramagnetic behavior is crucial for the application of magnetic coagulants, since it allows magnetic sedimentation using a conventional magnet, but still allows a wide dispersibility when in the absence of such a field, avoiding the characteristic aggregation of ferromagnetic materials, enabling better coagulant activity.

Considering the results of the characterization of coagulants, it can be observed that the method of functionalization of iron oxide with compounds present in saline extracts of MO(et) and MO(hex) was conducted with efficiency, corroborating the results obtained by FTIR.

3.2. *Evaluation of quality parameters removal by C/F/S process by using MOFe(et) and MOFe(hex) magnetic coagulants*

The magnetic coagulants MOFe(et) e MOFe(hex) were tested in order to evaluate which coagulant combination present better efficiency for quality parameters removal (Figs. 7 and Fig. 8, respectively). All coagulant combinations were tested under magnetic field influence and without the same, at the times of 15 and 30 min, related to apparent color, turbidity and UV_{254nm} removal.

For all evaluated parameters (apparent color, turbidity and UV_{254nm} removal), using MOFe(et) coagulant, the largest removals were achieved by using coagulant combination O (40 mg·L^{-1} of γ-Fe_2O_3 and 400 mg·L^{-1} of MO(et)) under applied magnetic field and using 30 min of sedimentation. Related to apparent color removal (Figs. 7a and b), it achieved 83.8% of removal (45.5 uH of residual apparent color). For turbidity parameter (Figs. 7c, d), it was achieved 89% of removal (8.8 NTU of residual turbidity). Related to UV_{254nm} removal (Figs. 7e, f), it was achieved 53.4% of removal (0.082 cm^{-1} of residual UV_{254nm}).

For MOFe(hex) coagulants (Fig. 8), the highest removals were achieved by using coagulant combination K (20 mg·L^{-1} of γ-Fe_2O_3 and 400 mg·L^{-1} of MO(hex)) under magnetic field and at 30 min of sedimentation. Related to apparent color removal (Figs. 8a, b), it was achieved 85.5% of removal (40.5 uH of residual apparent color). For turbidity parameter (Figs. 8c, d), it was obtained 90.6% of removal (7.5 NTU of residual turbidity), value near the same parameter for MOFe(et). Related to UV_{254nm} removal (Figs. 8e, f), it was achieved 60.6% of removal (0.069 cm^{-1} of residual UV_{254nm}), highlighting in relation to coagulant MOFe(et) for the same parameter.

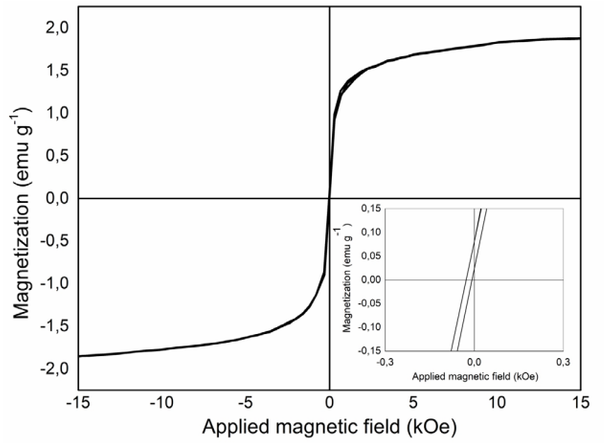

Fig. 5. Magnetization curve as a function of the magnetic field applied at room temperature of the coagulant MOFe(hex) obtained.

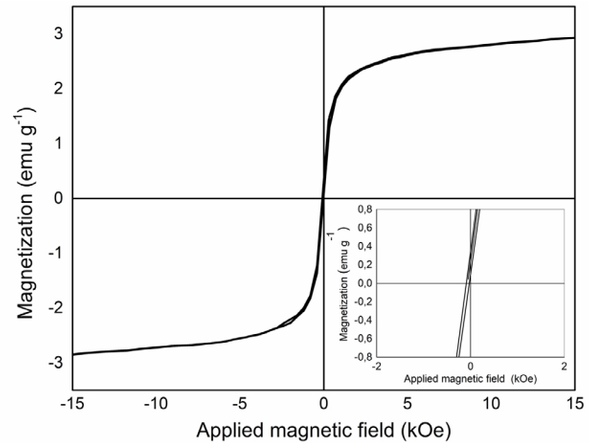

Fig. 6. Magnetization curve as a function of the magnetic field applied at room temperature of the coagulant MOFe(et) obtained.

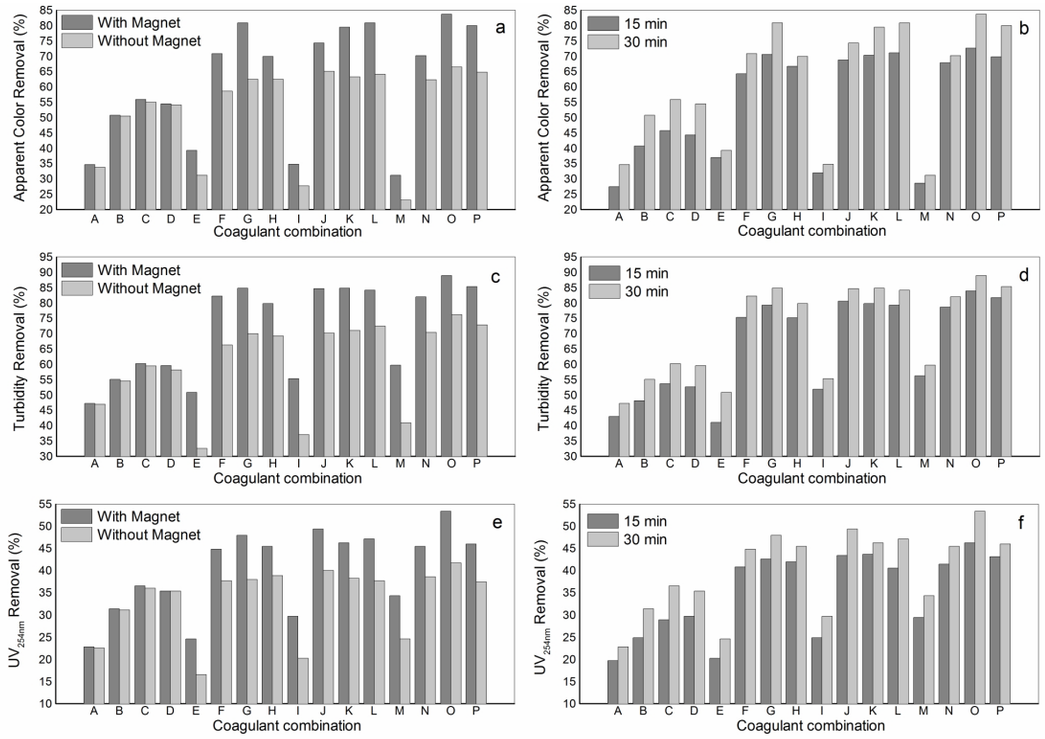

Fig. 7. Quality parameters removal of (a, b) apparent color, (c, d), and (e, f) UV_{254nm} using MOFe(et) coagulant under magnetic field and without the same, at 15 and 30 min of settling.

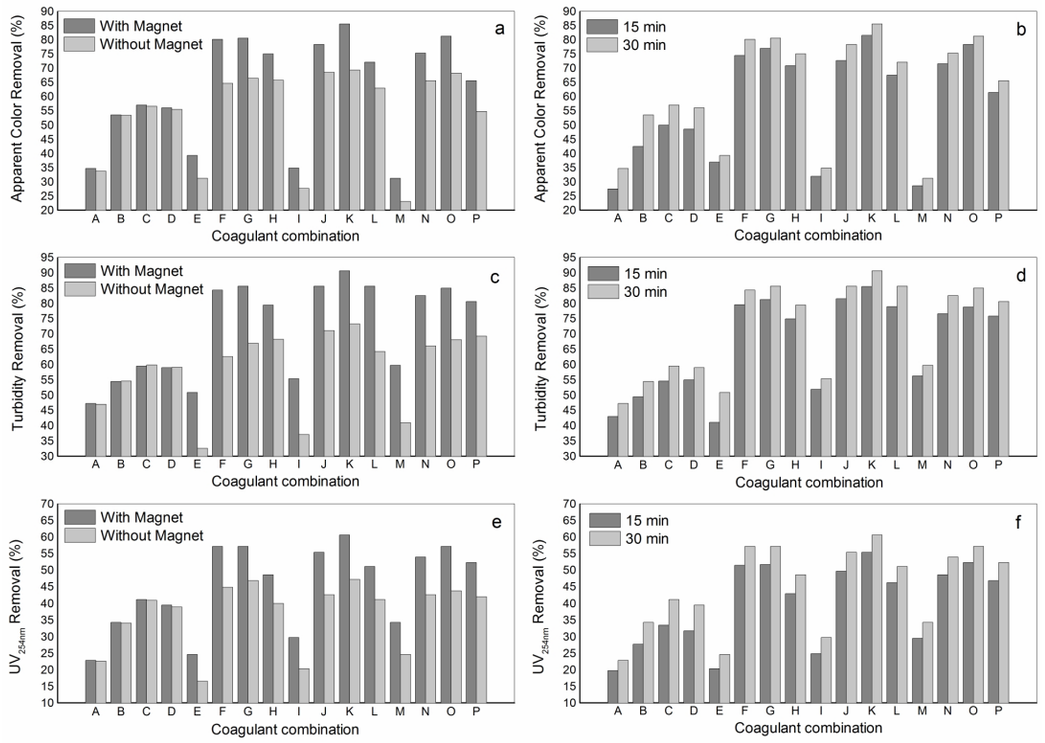

Fig. 8. Quality parameters removal of (a, b) apparent color, (c, d) turbidity, and (e, f) UV_{254nm} using MOFe(hex) coagulant under magnetic field and without the same, at 15 and 30 min of settling.

Apparent color and turbidity results could be explained mainly to the content of γ-Fe_2O_3, which due to its magnetic properties promotes sedimentation, increasing the removal efficiency parameters. The same behavior related to magnetic field application was reported by Alabdraba et al. [40], this can be explained by super paramagnetic properties of coagulant, which tends to be attracted to the magnetic field, and this way present highest efficiency compared to gravity sedimentation [41,42].

The presence of magnetic coagulant promotes the formation of magnetic flakes, which could be attracted to the applied magnetic field, increasing the removal of physical-chemical parameters. It could be explained according to the magnetization curves theory, which reported that when nanoparticles were under magnetic field action, the internal magnetic moment spins to the same direction of magnetic field. This fact increases the magnetic properties of nanoparticles, so, the combination of iron oxide nanoparticles with saline extract of MO and magnetic field allows the water impurities aggregation, improving C/F process [4].

It was observed that using magnetic coagulants, the C/F efficiency process could be improved with 30 min of sedimentation under applied magnetic field. Therefore, in this study, 30 min of settling was established as optimal time for highest parameters removal. Also, the positive zeta potential of MO suggest that the main mechanism of flakes formation can be adsorption and charge neutralization. However, there are studies describing inter facial properties of a coagulating protein extracted from MO seeds and its interaction with other compounds like surfactants and inorganic materials, which has the same mechanism behavior of organic matter present in natural waters [22].

Related to MO content, the highest removal parameters were achieved with 1% of concentration (400 mg·L^{-1}). These results corroborate with previous studies, which reported that using 400 mg·$L^{-1}$of MO solution as coagulant, it could be obtained water turbidity removals from water supply and total coliforms removal from waste water [43,44].

In study of Valverde et al. [45], similar behavior was observed using 400 mg·L^{-1} of MO and 15 mg·$L^{-1}$of aluminum sulphate (with 90 min of sedimentation), in which could be achieved respectively 90% and 80% for apparent color and turbidity removal. These results indicate that the obtained coagulant combination of MO and an inorganic compound could be a good option to water treatment, as reported in the present study.

The results presented in this study show that the proposed coagulant, obtained from a combination of a natural coagulant (MO) (without oil, extracted by ethanol or hexane) with a magnetic compound (iron oxide nanoparticles in maghemite phase) could be an excellent alternative for water treatment, mainly due to the shorter time of sedimentation needed to achieve good physical-chemical parameters removal using magnetic settling.

However, between the two evaluated coagulants, MOFe(hex) presents highest removal parameters with K combination (20 mg·L^{-1} of γ-Fe_2O_3 and 400 mg·L^{-1} of MO(hex)), thus, this combination coagulant was selected to realize the subsequent studies: *jar test* operation conditions optimization, sedimentation kinetics and regeneration of nanoparticles used in C/F/S process, which are presented subsequently.

3.3. Essays for Jar Test operation conditions optimization at C/F step

Cardoso et al. [11] reported that the required times of fast and slow mixtures influences in physical-chemical parameters removals during C/F process. Heller and de Pádua [46] reported that times and rates of mixing should, preferably, be determined based on experimental evaluations.

Based on these affirmations and considering MOFe(hex) combination K (20 mg·L^{-1} of γ-Fe_2O_3 and 400 mg·L^{-1} of MO) as the optimal coagulant combination, it was chosen to study the operational conditions of C/F using this coagulant in order to further increase the efficiency of this step. It was adopted 30 min of sedimentation under magnetic field, as established previously.

Table 5 presents the results of parameters removal efficiency using MOFe(hex) combination K with the variations of conditions for C/F process. All essays were performed in duplicate and the presented value is the average of these values.

It could be observed that using combination O of operational parameters (RMR 120 rpm, CT 5 min, SRM 15 rpm, and FT 20 min) (Table 5), the efficiency of magnetic coagulant was increased to 94.4% of turbidity removal (4.5 NTU of residual turbidity), 87.5% of apparent color (35 uH of residual apparent color) and 63.4% of UV_{254nm} (0.064 cm^{-1} of residual UV_{254nm}).

Based on these results, it could be proposed that coagulant combination K of MOFe(hex) (20 mg·L^{-1} of γ-Fe_2O_3 and 400 mg·L^{-1} de MO(hex)) and operational conditions O (RMR 120 rpm, CT 5 min, SRM 15 rpm and FT 20 min) present the best conditions to be a very interesting alternative, with low cost and lower inorganic content than traditional coagulant for water treatment.

3.4. Sedimentation kinetics

After established the optimal coagulant (combination K of MOFe(hex)) and optimal operational conditions O (RMR 120 rpm, CT 5 min, SMR 15 rpm and FT 20 min), the C/F essays were repeated with variation of settling time and the removal parameters were evaluated, as presented in Fig. 9.

It could be observed in Fig. 9 that in a general way, increasing settling time increases the removal of evaluated parameters. This behavior is because the higher settling time is, the higher the amount of flocculated particles decanted. However, based on sedimentation kinetics, it could be observed that at 30 min of settling, it was achieved higher efficiency removal(87% for apparent color, 93.7% for turbidity, and 62.6% for UV_{254nm}). Although the threefold increase (90 min) does not result in considerably higher removals (89.6% for apparent color, 95% for turbidity, and 64.6% UV_{254nm}), it indicates that for 30 min the results were very interesting considering the raw water characteristics.

In previous studies using only MO as coagulant, 60 min and 90 min of gravitational settling were the needed time to achieve the same parameters removal that were obtained with 30 min under magnetic field in the present study [11,25,47].

Table 5
Removals of apparent color, turbidity and UV_{254nm} in C/F step with operational conditions variation using coagulant combination K of MOFe(hex) (20 mg. L^{-1} of γ-Fe_2O_3 e 400 mg. L^{-1} de MO(hex))

Essay	Apparent color		Turbidity		UV_{254nm}	
	Residual	% Removal	Residual	% Removal	Residual	% Removal
L	64	77.1	11	86.9	0.087	50.3
M	54	80.9	9.0	88.8	0.079	55.1
N	48	82.9	8.0	90.0	0.078	55.4
O	35	87.5	4.5	94.4	0.064	63.4
P	62	78.0	10.5	86.9	0.082	53.1
Q	40	85.7	7.0	91.3	0.072	59.1
R	41	85.4	6.5	91.9	0.073	58.3
S	59	78.9	9.0	88.8	0.093	47.1
T	116	58.6	18.0	77.5	0.150	14.3
U	50	82.3	8.5	89.4	0.087	50.6
V	120	57.3	18.0	77.5	0.158	10.0

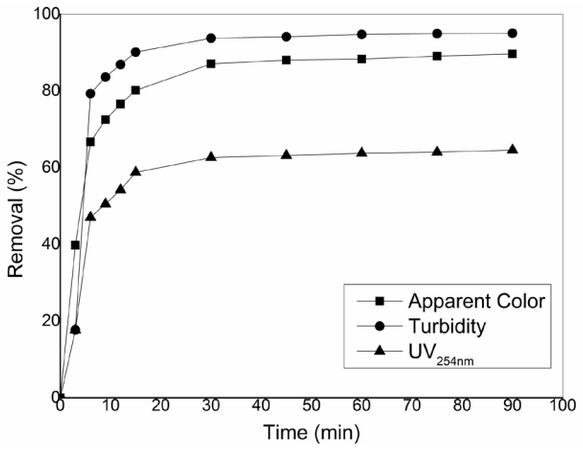

Fig. 9. Removal parameters of apparent color, turbidity and UV_{254nm} using coagulant combination K of MOFe(hex) and optimal operational conditions O (RMR 120 rpm, CT 5 min, SMR 15 rpm and FT 20 min) for different settling times.

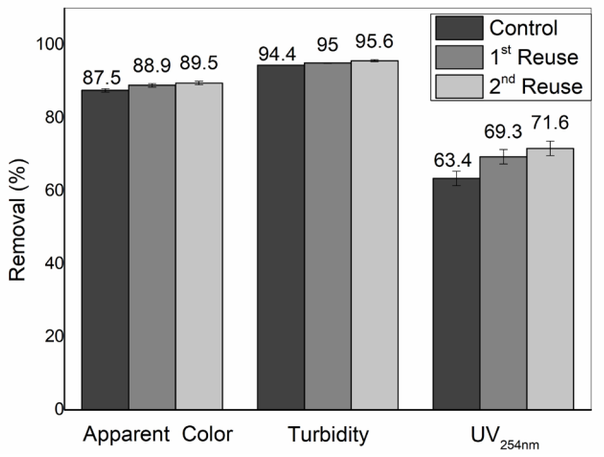

Fig. 10. Removal parameters of apparent color, turbidity and UV_{254nm} in C/F/S process using regenerated nanoparticles at operational conditions O (RMR 120 rpm, CT 5 min, SMR 15 rpm, and FT 20 min) and coagulant combination K (20 mg·L^{-1} of γ-Fe_2O_3 and 400 mg·L^{-1} of MO(hex)). Control is the coagulant MOFe(hex) prepared with nanoparticles as obtained.

3.5. Super paramagnetic nanoparticles regeneration

C/F/S essays were realized using the magnetic coagulant containing regenerated nanoparticles obtained from residual sludge and re-functionalized by the compounds present in saline extract of MO(hex). It was used the coagulant combination K (20 mg·L^{-1} of γ-Fe_2O_3 and 400 mg·L^{-1} de MO) and optimal operational conditions D (RMR 120 rpm, CT 5 min, SMR 15 rpm and FT 20 min) as previously established. The settling time was 30 min under magnetic field, as previously defined.

Fig. 10 presents efficiency results of removal of apparent color, turbidity and UV_{254nm} using the regenerate coagulant in two successive reuses. The essays were performed in duplicates and only the average values are presented.

It could be observed that removals efficiency remained practically unchanged, with a slight increase for apparent color and turbidity removals, and a significant increase for UV_{254nm} removal for 1st and 2nd reuses, after nanoparticles washing with ethanol. In order to verify the changes occurred with nanoparticles used in coagulant during the ethanol washing, it was obtained FTIR-ATR spectra (Fig. 11) to evaluate possible functional groups that lead to better efficiency in quality parameters removal.

It could be observed that after ethanol washing, nanoparticles do not present bands present in nanoparticles as obtained spectrum, as nitrate and carbonate impurities (1400–1700 cm^{-1}) and C-H groups (2900–2800 cm^{-1}) residual from synthesis. This behavior shows that ethanol washing could remove residual synthesis impurities from iron oxide nanoparticles. Consequently, it leads to higher available γ-Fe_2O_3 surface area, allowing greater functionalization with compounds present in MO(hex) saline extract, leading to higher parameters removal.

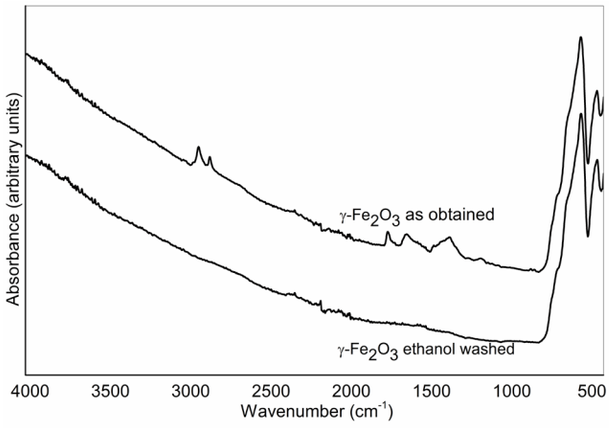

Fig. 11. FTIR-ATR spectra for γ-Fe_2O_3 as obtained and γ-Fe_2O_3 ethanol washed.

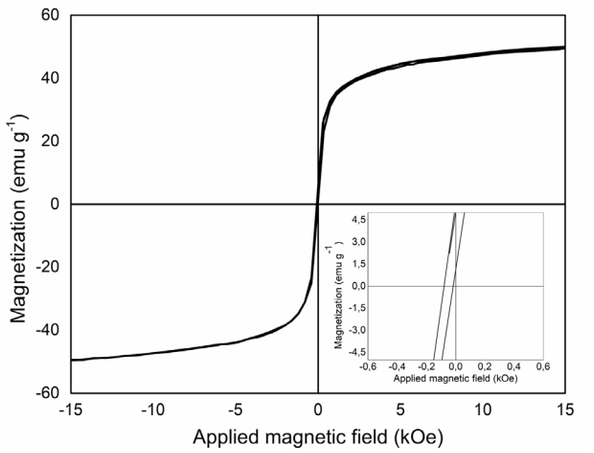

Fig. 12. Magnetization curve as a function of the magnetic field applied at room temperature of the iron oxide nanoparticles washed with ethanol.

The washed nanoparticles were further characterized by magnetic measurements to verify possible changes in their magnetization after ethanol washing (Fig. 12)

From the result shown in Fig. 12 we can observe that after washing of the nanoparticles with ethanol they continued to present typical super paramagnetic properties due to the negligible values of remanence and coercivity in the magnetization curve (M) as a function of the applied magnetic field (H)[39], with magnetization of saturation of 49.5 emu·g^{-1}. This demonstrates once again that the ethanol washing was able to remove possible impurities from the synthesis, improving the magnetic properties of the nano particulate material, corroborating with the results presented by FTIR-ATR, this being the possible factor that favored the increase of the removal capacity of the quality parameters when the regenerated nanoparticles, with higher saturation magnetization, were used in a new functionalization and applied in new C/F/S tests.

Unlike reported in this study where there was an increase in removal of physical chemical parameters after re-functionalization and reuse of nanoparticles, Okoli et al. [4] in their study, evaluating iron oxide nanoparticles obtained by water-in-oil and oil-in-water micro emulsions associated with MO protein for turbidity removal, and the reuse of the obtained coagulant, observed that after the 3rd reuse, it was possible to achieve 60% of removal (the removal using as obtained nanoparticles was nearly to 68%). In the present study, it was possible to reuse the nanoparticles in C/F/S process without loss of efficiency (removals increase of 87.5–89.5% for apparent color, 94.4–95.6% for turbidity, and 63.4–71.6% for UV_{254nm}), indicating regeneration possibility and potential material saving and cost reduction. Due to the reuse of iron oxide nanoparticles in coagulants combination, the volume of produced sludge related to inorganic compounds was extremely reduced. In addition, the sludge produced by MO is composed of bio degradable by products, so that the sludge can be reused as, for example, organic fertilizer, as it does not contain heavy metals, only a few content of iron oxide, that is present naturally in the soil.

4. Conclusions

This work demonstrates advancement in the development of eco friendly water treatment strategy using magnetic iron oxide nanoparticles and their functionalization with MO compounds soluble in saline extract as well as the preparation of MOFe(hex) and MOFe(et) magnetic coagulants systems for water treatment.

The MOFe(hex) and MOFe(et) magnetic coagulants were evaluated in order to find the optimal concentration of MO and iron oxide nanoparticles in the studied systems. Since, for the optimal magnetic coagulant combination, the operational parameters for C/F/S essays were evaluated, with the objective to achieve the higher efficiency removal of apparent color, turbidity, and compounds with UV_{254nm} absorption. Developed magnetic coagulants could effectively remove more than 87% of apparent color, 94% of turbidity, and 63% of UV_{254nm} in river waters under the influence of an applied magnetic field for 30 min, whereas conventional water treatment processes require several hours. The present investigation also suggests the possibility of regenerating the iron oxide nanoparticles and their reuse for C/F/S with no damage on efficiency.

The combination of natural coagulant MO plus magnetic nanoparticles and magnetic field enhanced the effectiveness of the system in coagulating/flocculating impurities in water samples. The data shown in this work represent water treatment approaches (with safe materials) that are simple to use, low cost, robust and environmentally friendly.

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References

[1] T.E. Cloete, M. Kwaadsteniet, M. Botes, M. López-Romero, Nano technology in water treatment applications, Caister Academic Press, Norfolk, 2010.

[2] M. Mikhaylova, D.K. Kim, N. Bobrysheva, M. Osmolowsky, V. Semenov, T. Tsakalakos, M. Muhammed, Super paramagnetism of magnetite nanoparticles: dependence on surface modification, Langmuir, 20 (2004) 2472–2477.

[3] Q. Li, S. Mahendra, D.Y. Lyon, L. Brunet, M.V. Liga, D. Li, P.J.J. Alvarez, Antimicrobial nano materials for water disinfection and microbial control: Potential applications and implications, Water Res., 42 (2008) 4591–4602.

[4] C. Okoli, M. Boutonnet, S. Järås, G. Rajarao-Kuttuva, Protein-functionalized magnetic iron oxide nanoparticles: time efficient potential-water treatment, J. Nanopart. Res., 14 (2012) 1–9.

[5] B. Bina, M. Mehdinejad, G. Dalhammer, G. Rajarao, M. Nikaeen, H.M. Attar, Effectiveness of *Moringa oleifera* coagulant protein as natural coagulant aid in removal of turbidity and bacteria from turbid waters, World Acad. Sci. Eng. Technol., 4 (2010) 261–263.

[6] C.-Y. Yin, Emerging usage of plant-based coagulants for water and wastewater treatment, Process Biochem., 45 (2010) 1437–1444.

[7] N. Poumaye, J. Mabingui, P. Lutgen, M. Bigan, Contribution to the clarification of surface water from the *Moringa oleifera*: Case M'Poko River to Bangui, Central African Republic, Chem. Eng. Res. Des., 90 (2012) 2346–2352.

[8] A. Ndabigengesere, K.S. Narasiah, Quality of water treated by coagulation using *Moringa oleifera* seeds, Water Res., 32 (1998) 781–791.

[9] S.A.A. Jahn, Using *Moringa* seeds as coagulants in developing countries (PDF), J. AWWA, 80 (1988) 43–50.

[10] K.A. Ghebremichael, K.R. Gunaratna, H. Henriksson, H. Brumer, G. Dalhammar, A simple purification and activity assay of the coagulant protein from *Moringa oleifera* seed, Water Res., 39 (2005) 2338–2344.

[11] K.C. Cardoso, R. Bergamasco, E.S. Cossich, L.C.K. Moraes, Otimizing mixture and decantation times in the process of coagulation/flocculation of raw water using *Moringa oleifera* Lam, Acta Sci-Technol., 30 (2008) 193–198.

[12] M.N. Alo, C. Anyim, M. Elom, Coagulation and antimicrobial activities of *Moringa oleifera* seed storage at 3°C temperature in turbid water, Adv. Appl. Sci. Res., 3 (2012) 887–894.

[13] J.-Y. Bottero, J. Rose, M.R. Wiesner, Nano technologies: Tools for sustainability in a new wave of water treatment processes, Integr. Environ. Assess. Manage., 2 (2006) 391–395.

[14] N. Savage, M. Diallo, Nano materials and water purification: opportunities and challenges, J. Nanopart. Res., 7 (2005) 331–342.

[15] J. Theron, J.A. Walker, T.E. Cloete, Nano technology and water treatment: applications and emerging opportunities, Crit. Rev. Microbiol., 34 (2008) 43–69.

[16] R.D. Ambashta, M. Sillanpää, Water purification using magnetic assistance: A review, J. Hazard. Mater., 180 (2010) 38–49.

[17] H. Guo, F. Ma, X. Feng, X. Lou, M.O. Tade, Application of iron oxide based nano materials (NMs) in magnetic assisted chemical separation (MACS) processes for water/wastewater treatment, Adv. Mater. Res., 610–613 (2013) 1242–1251.

[18] M.F. Silva, E.A.G. Pineda, R. Bergamasco, Aplicação de Óxidos de Ferro Nanoestruturados como Adsorventes e Fotocatalizadores na Remoção de Poluentes de Águas Residuais, Quim. Nova, 38 (2015) 393–398.

[19] APHA, Standard methods for the examination of water and wastewater, American Public Health Association (APHA): Washington, DC, USA, 2005.

[20] M.F. Silva, L.A.S. de Oliveira, M.A. Ciciliati, L.T. Silva, B.S. Pereira, A.A.W. Hechenleitner, D.M.F. Oliveira, K.R. Pirota, F.F. Ivashita, J.A. Paesano, J.M. Pastor, J.I. Perez-Landazabal, E.A.G. Pineda, Nano metric particle size and phase controlled synthesis and characterization of g-Fe_2O_3 or (a+ g)-Fe_2O_3 by a modified sol-gel method, J. Appl. Phys., 114 (2013) 104311–104317.

[21] S.A. Muyibi, S.A. Abbas, M.J.M.M. Noor, F.R. Ahmadun, Enhanced coagulation efficiency of *Moringa oleifera* seeds through selective oil extraction, IIUM Eng. J., 4 (2003) 1–11.

[22] M.C. Bongiovani, F.P. Camacho, L. Nishi, P. Ferri Coldebella, K. Cardoso Valverde, A.M.S. Vieira, R. Bergamasco, Improvement of the coagulation/flocculation process using a combination of *Moringa oleifera* Lam with anionic polymer in water treatment, Environ. Technol., 35 (2014) 2227–2236.

[23] T.R.T. dos Santos, M.C. Bongiovani, M.F. Silva, L. Nishi, P.F. Coldebella, M.F. Vieira, R. Bergamasco, Trihalomethanes minimization in drinking water by coagulation/flocculation/sedimentation with natural coagulant *Moringa oleifera* Lam and activated carbon filtration, Can. J. Chem. Eng., 94 (2016) 1277–1284.

[24] J. Sánchez-Martín, K. Ghebremichael, J. Beltrán-Heredia, Comparison of single-step and two-step purified coagulants from *Moringa oleifera* seed for turbidity and DOC removal, Bioresour. Technol., 101 (2010) 6259–6261.

[25] G.S. Madrona, G.B. Serpelloni, A.M.S. Vieira, L. Nishi, K.C. Cardoso, R. Bergamasco, Study of the effect of saline solution on the extraction of the *Moringa oleifera* seed's active component for water treatment, Water Air Soil Pollut., 211 (2010) 409–415.

[26] T. Okuda, A.U. Baes, W. Nishijima, M. Okada, Isolation and characterization of coagulant extracted from *Moringa oleifera* seed by salt solution, Water Res., 35 (2001) 405–410.

[27] S. Katayon, S.C. Ng, M.M.N.M. Johari, L.A.A. Ghani, Preservation of coagulation efficiency of *Moringa oleifera*, a natural coagulant, Biotechnol. Bioprocess Eng., 11 (2006) 489–495.

[28] S. Katayon, M.J. Megat Mohd Noor, M. Asma, A.M. Thamer, A.G. Liew Abdullah, A. Idris, A.M. Suleyman, M.B. Aminuddin, B.C. Khor, Effects of storage duration and temperature of *Moringa oleifera* stock solution on its performance in coagulation, Int. J. Eng. Technol., 1 (2004) 146–151.

[29] T.R.T. Santos, M.F. Silva, L. Nishi, A.M.S. Vieira, M.R. Fagundes-Klen, M.B. Andrade, M.F. Vieira, R. Bergamasco, Development of a magnetic coagulant based on *Moringa oleifera* seed extract for water treatment, Environ. Sci. Pollut. Res., 23 (2016) 7692–7700.

[30] M. Gotic, S. Music, Mössbauer, FT-IR and FE SEM investigation of iron oxides precipitated from $FeSO_4$ solutions, J. Mol. Struct., 834–836 (2007) 445–453.

[31] D. Predoi, A study on iron oxide nanoparticles coated with dextrin obtained by coprecipitation, Dig. J. Nanomater. Bios., 2 (2007) 169–173.

[32] H.M. Kwaambwa, R. Maikokera, Infrared and circular dichroism spectroscopic characterisation of secondary structure components of a water treatment coagulant protein extracted from *Moringa oleifera* seeds, Colloids Surf. B., 64 (2008) 118–125.

[33] N. Ghaemi, S.S. Madaeni, P. Daraei, H. Rajabi, S. Zinadini, A. Alizadeh, R. Heydari, M. Beygzadeh, S. Ghouzivand, Polyether sulfone membrane enhanced with iron oxide nanoparticles for copper removal from water: Application of new functionalized Fe_3O_4 nanoparticles, Chem. Eng. J., 263 (2015) 101–112.

[34] U. Schwertmann, R.M. Cornell, Iron oxides in the laboratory: Preparation and Characterization, Wiley-VCH Verlag GmbH, Weinheim, 2007.

[35] S. Yu, G.M. Chow, Carboxyl group (-CO_2H) functionalized ferrimagnetic iron oxide nanoparticles for potential bio-applications, J. Mater. Chem., 14 (2004) 2781–2786.

[36] M.F. Silva, A.A.W. Hechenleitner, D.M.F. de Oliveira, M. Agüeros, R. Peñalva, J.M. Irache, E.A.G. Pineda, Optimization of maghemite-loaded PLGA nano spheres for biomedical applications, Eur. J. Pharm. Sci., 49 (2013) 343–351.

[37] A.T.A. Baptista, P.F. Coldebella, P.H.F. Cardines, R.G. Gomes, M.F. Vieira, R. Bergamasco, A.M.S. Vieira, Coagulation–flocculation process with ultra filtered saline extract of *Moringa oleifera* for the treatment of surface water, Chem. Eng. J., 276 (2015) 166–173.

[38] L.N. Okassa, H. Marchais, L. Douziech-Eyrolles, K. Herve, S. Cohen-Jonathan, E. Munnier, M. Souce, C. Linassier, P. Dubois, I. Chourpa, Optimization of iron oxide nanoparticles encapsulation within poly (D,L-lactide-co-glycolide) sub-micron particles, Eur. J. Pharm. Biopharm., 67 (2007) 31–38.

[39] M.F. Silva, M.A. Ciciliatti, A.A.W. Hechenleitner, R. Penãlva, M. Agüeros, J.M. Irache, A.J.A.. de Oliveira, A.A. Farooqi,

E.A.G. Pineda, Super paramagnetic maghemite loaded poly (μ- caprolactone) nano capsules: characterization and synthesis optimization, Matéria (Rio de Janeiro), 19 (2014) 40–52.
[40] W.M.S. Alabdraba, M.B. Albayati, A.Y. Radeef, M.M. Rejab, Influence of magnetic field on the efficiency of the coagulation process to remove turbidity from water, Int. Rev. Chem. Eng., 5(2013) 1–8.
[41] A.-H. Lu, E.L. Salabas, F. Schüth, Magnetic nanoparticles: synthesis, protection, functionalization, and application, Angew. Chem. Int. Ed., 46 (2007) 1222–1244.
[42] M. Faraji, Y. Yamini, M. Rezaee, Magnetic nanoparticles: Synthesis, stabilization, functionalization, characterization, and applications, J. Iran. Chem., 7 (2010) 1–37.
[43] P.A.V.L. Monaco, A.T. Matos, I.C.A. Ribeiro, F.S. Nascimento, A.P. Sarmento, Utilização de extrato de sementes de moringa como agente coagulante no tratamento de água para abastecimento e águas residuárias, Rev. Ambiente Água, 5 (2010) 222–231.
[44] E.N. Ali, S.A. Muyibi, H.M. Salleh, M.Z. Alam, M.R.M. Salleh, Production of natural coagulant from *Moringa oleifera* seed for application in treatment of low turbidity water, J. Water Resour. Prot., 2 (2010) 1–8.
[45] K.C. Valverde, L. Nishi, A.M. Salcedo Vieira, M.C. Bongiovani, P.F. Coldebella, G.S. Madrona, O.A.A. dos Santos, R. Bergamasco, Optimization of process conditions in water treatment through coagulation diagrams, using *Moringa oleifera* Lam and aluminium sulphate, Desal. Water Treat., 56 (2015) 1787–1792.
[46] L. Heller, V.L. de Pádua, Abastecimento de água para consumo humano, UFMG, Belo Horizonte, 2006.
[47] G.S. Madrona, I.G. Branco, V.J. Seolin, B.D. Alves, M.R. Fagundes-Klen, R. Bergamasco, Evaluation of extracts of *Moringa oleifera* Lam seeds obtained with NaCl and their effects on water treatment, Acta Sci-Technol., 34 (2012) 289–293.