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Treatment the effluents by adsorption-coagulation with compounds of iron and aluminum prepared by indirect electrocoagulation

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Abstract
In Morocco, the demand for water is growing continuously in conjunction with demographic change and water consuming activities. In the textile sector, there is a need for recycling of wastewater containing dying compounds. The present study aims to removing pollutants in the case of a colorful effluent at neutral pH, and the optimization of various experimental parameters influencing them. The first step was devoted to the synthesis of adsorbent-coagulant structures by indirect electrocoagulation process using iron or aluminum electrodes in an electrolytic solution of sodium chloride (10^{-2} mol L^{-1}), at neutral pH. In a second step, different mix compounds have been prepared (100% Al, 75% Al and 25% Fe, 50% Al and 50% Fe, 25% Al and 75% Fe, 100% Fe). These mixtures were then used for the treatment of solutions polluted by a textile dye (blue trypan), phenol, oxalic acid and cadmium sulfate. The XRD analysis of these structures showed that the dominant presence of aluminum hydroxides and oxides ($Al(OH)_3$ and $Al_2O_3.3H_2O$) and iron oxides ($MgFe_2O_4$ and Fe_3O_4) and as a mixed product ($MgAl_{0.2}Fe_{1.8}O_4$). The study of zeta potential and behavior of colloidal particles showed that they are mainly positively charged at neutral pH. The removal efficiencies of cadmium, oxalic acid, and phenol in the polluted solutions were specific to the produced structures. Finally, all the prepared compounds were efficient for the removal of the dye (blue trypan).

Keywords: electrocoagulation, coagulation, adsorption, dye, iron, aluminum.

Résumé
Au Maroc, la demande en eau connaît une croissance continue en liaison avec l'évolution démographique et les activités consommatrices de cette ressource essentielle. Dans le domaine du textile, plus particulièrement, il existe un besoin de recycler les eaux chargées en colorants. Cette étude visait l'élimination des matières polluantes dans le cas d'un rejet coloré de pH neutre et l'optimisation des différents paramètres expérimentaux influençant celles-ci. La première étape de cette étude a été consacrée à la synthèse de structures adsorbantes et coagulantes par un procédé d'électrocoagulation indirecte en utilisant des électrodes de fer ou d'aluminium, dans une solution électrolytique de chlorure de sodium (10^{-2} mol L^{-1}), à pH neutre. Dans une deuxième étape, différents mélanges de composés (100% Al, 75% Al et 25% Fe, 50% Al et 50% Fe, 25% Al et 75% Fe et 100% Fe) ont ensuite été utilisés pour le traitement de solutions polluées par un colorant (trypan bleu), du phénol, de l'acide oxalique et du sulfate de cadmium. L'analyse par DRX de ces structures a révélé qu'elles contiennent des formes cristallines à base d'oxydes et d'hydroxydes d'aluminium lorsque l'aluminium est seul dans le mélange, ou à base d'oxydes et d'hydroxydes de fer lorsque le fer est seul dans le mélange. Dans le cas de mélanges, la présence d'autres structures telles que la magnétite (Fe_3O_4), $Al(OH)_3$ et $MgAl_{0.2}Fe_{1.8}O_4$ a été observée. L'étude des structures a aussi révélé que celles-ci se présentent en proportion élevée sous formes de colloïdes chargés positivement expliquant le caractère attractif de ces composés. L'élimination du cadmium, de l'acide oxalique et du phénol en solution varie d'un composé à l'autre selon le type du coagulant utilisé. D'un autre côté, tous les composés préparés se sont montrés très efficaces pour l'élimination du colorant trypan bleu.

Mots-clés: électrocoagulation, coagulation, adsorption, colorant, fer, aluminium.

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1. Introduction

Wastewater from the textile industry contains high concentrations of dyes, often over-used to reach a certain degree of dyeing. Most of the time, those dyes are not easily biodegradable, which makes biological treatments hard to apply [1]. Several other techniques have thus been proposed to treat colorful effluents [2-3]. These techniques include, among others, electrocoagulation [4-9] and either clay [10], aluminum synthetic compound [11] or activated carbon adsorption [12-13].

Among the most efficient techniques for effluent discoloration, electrocoagulation is an electrochemical technique during which sacrificial anodes (iron or aluminum electrodes) are progressively solubilized in the water to treat and act as coagulant formation precursors. [14-16]. Released iron and aluminum produce metallic hydroxide flocs, which can in turn eliminate pollutants through surface complexing or electrostatic attraction [17-18]. However, the technico-economical performance of this electrocoagulation process is highly conditioned by the nature of the effluent to treat.

A new approach called indirect electrocoagulation has been developed recently; it aims at producing adsorbent and coagulant structures from aluminum or iron separately in a well-characterized environment and under optimized operational conditions, then using these structures to treat wastewater [19-21].In some cases, this process is less expensive and more efficient to treat polluted wastewater than the usual electrocoagulation process.

Considering this context, the present study concerns the treatment of solutions polluted by an organic azoic dye called trypan blue [19], phenol, oxalic acid and cadmium, using several combinations of different proportions of structures previously produced using indirect electrocoagulation.

2. Material and methods

2.1 Synthesis of the adsorbents-coagulants compounds

Aluminum and iron adsorbents-coagulants compounds were derived from electrocoagulation using a pyrex electrolytic cell, in which 15 L volumes of NaCl (10^{-2} mol L^{-1}) solution prepared with tap water. The synthesis of these adsorbents-coagulants was carried out at neutral pH. The cell contained four aluminum or iron electrodes measuring 25 cm × 25 cm × 0.1 cm (thickness). Two electrodes were connected to the negative terminal of a direct current generator (DC, AL, 823 ELC) and acted as anodes, while the two others were connected to the positive terminal, acting as cathodes. The electric potential was kept constant at 12 V during the reaction carried out at room temperature [11]. The distance between electrodes was 4 cm. After a 24 h reaction time, solutions were decanted and filtered. The residues retained by filters were dried at a temperature below 50°C. Two types of adsorbent-coagulants were produced: the first was produced from the iron electrodes (Fe), and the second, by the aluminum electrodes (Al). The synthesized structures were shredded manually and screened using a 450 µm screen, then used to prepare compounds in different proportions of iron- and/or aluminum-based adsorbents-coagulants. Those compounds were hydrated, dried, shredded and screened to be used as adsorbents-coagulants to decontaminate certain solutions. The iron- or aluminum-based compounds thus prepared are named as follows:

- (N1) : 100% Al and 0% Fe.
- (N2) : 75% Al and 25% Fe.
- (N3) : 50% Al and 50% Fe.
- (N4) : 25% Al and 75% Fe.
- (N5) : 0% Al and 100% Fe.

2.2 Characterization of the adsorbents-coagulants

The X-ray diffraction analysis (XRD) of the different crystalline phases of the compounds was carried out using a Philips X'Pert PRO device equipped with a vertical goniometer with a θ-θ configuration which allows for the direct reading of the angular position on the arms of the goniometer with a good absolute angular accuracy of 0.0025° and a repeatability of less than 0.0001°.

Each compound's zeta potential was studied by solubilizing 0.2 g of each compound in a 100 mL volume of distilled water. The pH of these solutions was adjusted to pH = 7 using a sodium hydroxide solution (0.1 mol NaOH L^{-1}). The zeta potential was measured with a zetaphoremeter IV, model Z400.

2.3 Pollutants removal

In order to study the pollutants removal capacity of the compounds produced using indirect electrocoagulation, six different distilled water solutions were prepared:

- **Solution 1:** Organic azoic dye, trypan blue ($C_{34}H_{28}N_6Na_4O_{14}S_4$) with a mass corresponding to an 8.73 mg L^{-1} concentration.
- **Solution 2:** Phenol (C_6H_6) with a mass corresponding to a 20 mg L^{-1} concentration.

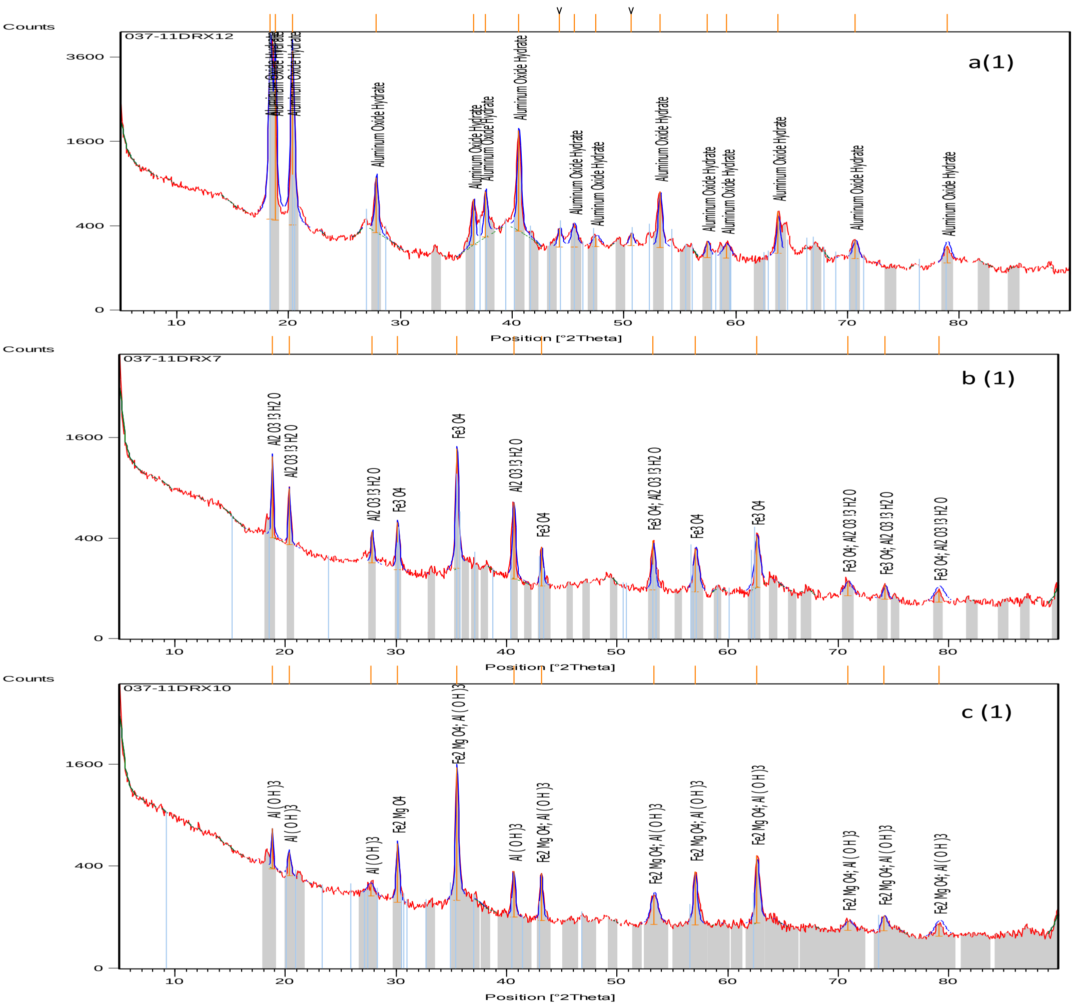
- **Solution 3:** Dye (trypan blue) and phenol with masses respectively corresponding to 8.73 and 20 mg L^{-1} concentrations.
- **Solution 4:** Phenol and oxalic acid ($C_2H_2O_4$, H_2O) each with a mass corresponding to a 20 mg L^{-1} concentration.
- **Solution 5:** Cadmium sulfate ($3CdSO_4.8H_2O$) with a mass corresponding to a 50 mg L^{-1} concentration.
- **Solution 6:** A mixture of Cadmium sulfate, trypan blue, phenol and oxalic acid with masses respectively corresponding to 50, 8.73, 20 and 20 mg L^{-1} concentrations.

The pH of these solutions was adjusted to pH = 7 using a sodium hydroxide solution (0.1 mol NaOH L^{-1}). The pH was measured with an Accumet Research pH-meter model AR 25 dual channel pH/ion meter from Fisher Scientific (Nepean, Ontario, Canada) equipped with a Cole-Parmer double junction along with an Ag/AgCl pH electrode.
Volumes of 1 L of these solutions to treat were put in contact, at room temperature, with 2 g masses of each of the adsorbents-coagulants (N1 to N5). These experiments were carried out using a Jar tester (Philipps and Bird Inc., model PB-700, Richmond, VA, USA). Contact time was set at 120 min with a shaking speed of 250 rotations per minute (rpm). After a 24h decanting period, the absorbency at 596 nm was measured using a UV-visible spectrometer (Varian, model Cary 50, Mississauga, ON, Canada).
The chemical oxygen demand (COD) in the solutions was measured according to the 5220D method with a standard curve (0-1000 mg L^{-1}) [20]. Absorbency measuring was carried out using a UV-visible spectrometer.

3. Results and discussion

3.1 Chemical characterization of the adsorbents-coagulants

The X-ray diffraction (XRD) determination of the different crystalline phases was carried out for all five prepared compounds with different aluminum and iron proportions, at neutral pH. Results are shown in Figure 1. On the other hand, Table 1 identifies the dominant crystalline structures found in the prepared compounds.



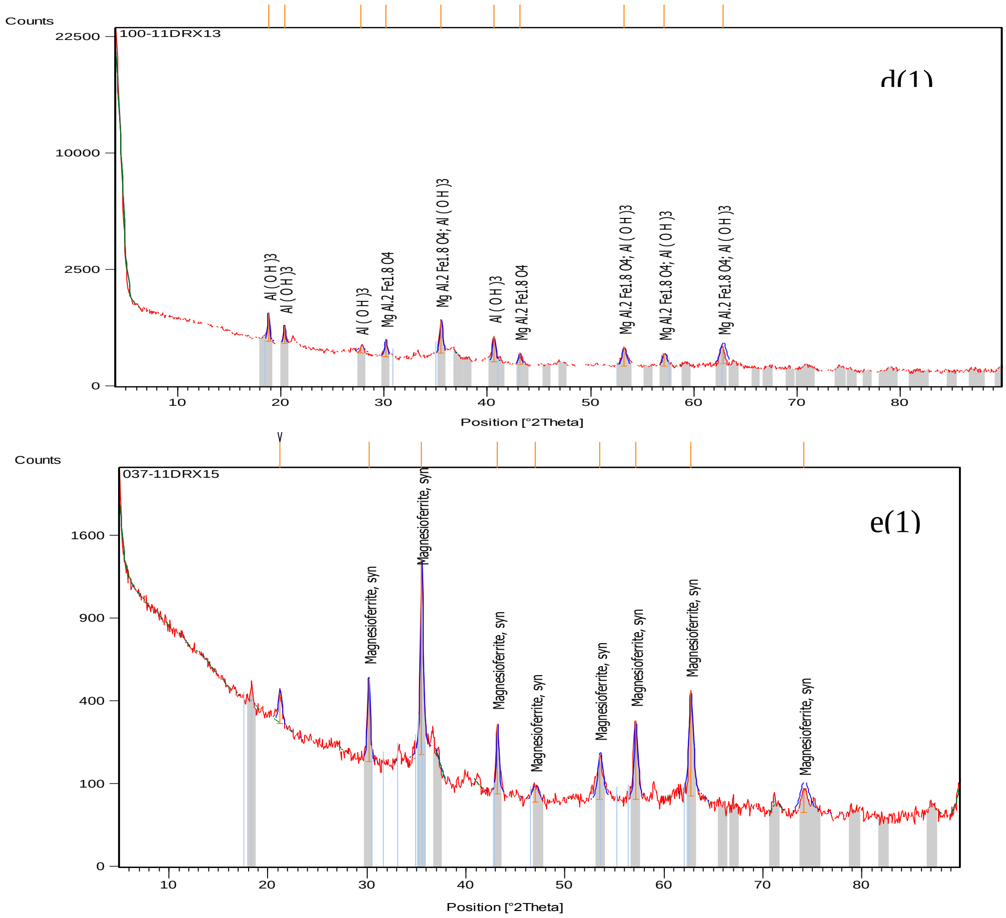


Figure 1: Chemical composition of the adsorbents-coagulants prepared in neutral medium. a(1): 100%Al/0%Fe (N1); b(1): 75%Al/25%Fe (N2); c(1): 50%Al/50%Fe (N3); d(1): 25%Al/75%Fe (N4); e(1): 0%Al/100%Fe (N5).

According to the XRD results, compound N1, prepared with only aluminum (100%Al/0%Fe), is mostly composed of aluminum oxide hydrate ($Al_2O_3.3H_2O$). Concerning N2 (75%Al/25%Fe) and N3 (50%Al/50%Fe), the dominant components were $Al_2O_3.3H_2O$ and magnesium ferrite ($MgFe_2O_4$). In the case of N4 where iron was dominant (25%Al/75%Fe), the formation of $Al(OH)_3$ and $MgAl_{0.2}Fe_{1.8}O_4$ was observed. Concerning compound N5, prepared with iron only (0%Al/100%Fe), the dominant presence of magnesium ferrite ($MgFe_2O_4$) was observed. When one of the components is dominant or when components appear in equal proportions, the presence of structures such as magnetite (Fe_3O_4), $Al(OH)_3$ and $Mg\ Al_{0.2}\ Fe_{1.8}\ O_4$ in addition to the abovementioned oxides and hydroxides, previously reported by other authors [22].
It is important to mention that iron [23] and aluminum [24-25] hydroxides are known for their adsorption properties towards dyes.

Table 1: Major crystalline phases of the adsorbents-coagulants prepared in neutral medium revealed by XRD

Compounds	Cristalline phases	
N1	$Al_2O_3.3H_2O$	(a1)
N2	$Al_2O_3.3H_2O$ Fe_3O_4	(b1)
N3	$Al(OH)_3$ $MgFe_2O_4$	(c1)
N4	$Al(OH)_3$ $MgAl_{0.2}\ Fe_{1.8}\ O_4$	(d1)
N5	$MgFe_2O_4$	(e1)

3.2 Zeta potential

Figure 2 presents the distribution of the percentages of the colloidal particles in compounds N1 to N5, prepared using indirect electrocoagulation.

According to this figure, the compounds prepared exist in high proportion in the form of electro-positive colloids, which explains the attractive properties of these structures.

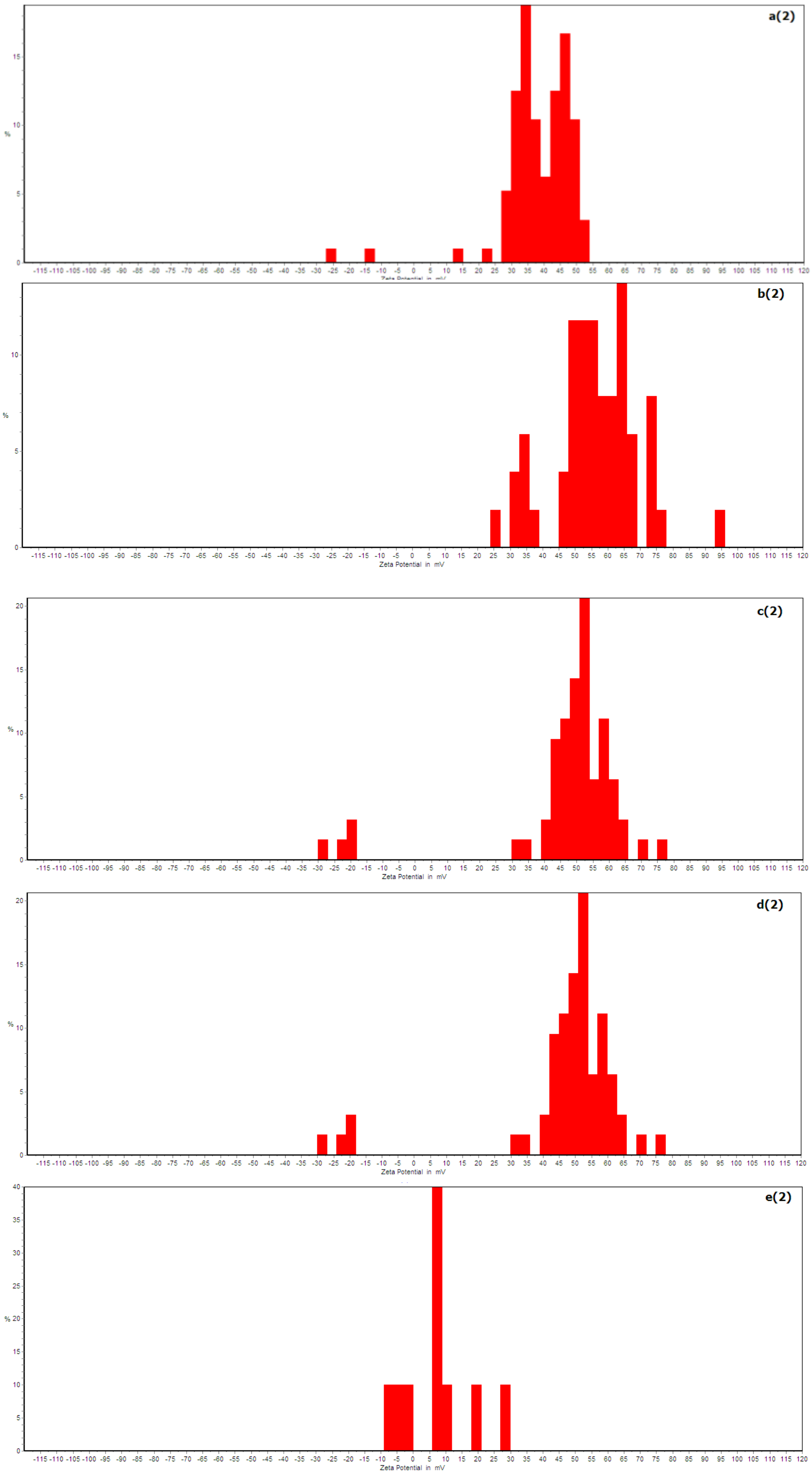


Figure 2: Zeta potential of colloids particles of the adsorbents-coagulants prepared in neutral medium. a(2): 100%Al/0%Fe (N1); b(2): 75%Al/25%Fe (N2); c(2): 50%Al/50%Fe (N3); d(2): 25%Al/75%Fe (N4); e(2): 0%Al/100%Fe (N5).

3.3 Blue trypan removal

Dye removal efficiencies ([trypan blue]$_i$ = 8.73 mg L^{-1}) contained in solutions 1, 3 and 6 obtained after adding a 2 g L^{-1} concentration of adsorbent-coagulant compounds are presented in Table 2.

Table 2: Dye removal from blue trypan solution (8.73 mg L^{-1}) at neutral pH using 2 g L^{-1} of the adsorbents-coagulantsrepared by indirect electrocoagulation with iron and aluminum electrodes

Compounds	**Blue trypan removal (%)**		
	Solution 1	**Solution 3**	**Solution 6**
N1	99.0	98.4	90.5
N2	99.3	98.7	89.8
N3	98.5	97.5	88.8
N4	98.4	97.3	88.4
N5	96.6	95.8	88.0

Results revealed a great retention capacity for this dye (solution 1), from 97 to 99%, by all prepared compounds using either aluminum only, iron only or a mix of both in different proportions. It is important to note that for solution 1, the highest removal efficiency for trypan blue (99.3%) was observed in the case of compound N2 (75%Al/25%Fe) mainly composed of aluminum oxide hydrate and iron oxide ($Al_2O_3.3H_2O$ et Fe_3O_4), while the lowest efficiency (96.6%) was found for compound N5 (0%Al/100%Fe).
Concerning the presence of phenol along with the dye, efficiency varies from 9.8 to 98.4%. The simultaneous presence of several pollutants along with the trypan blue (solution 6) was also observed, leading to a slight decrease in the removal efficiency for this dye (88.0 to 90.5%). There is a competition between anionic dye and pollutants in solutions 3 and 6 in regard to the retention sites of the prepared compounds.
The high elimination of trypan blue can mostly be explained by the fact that it is an anionic dye which can easily adsorb on positively charged coagulants-adsorbents produced through indirect electrocoagulation. Dye removal could also be associated with high concentrations in elements such as magnesium (Mg) and silicon (Si) in the compounds produced, which also enhance the removal of anionic dyes [26].
The removal of trypan blue is mainly associated with processes of co-precipitation or electrostatic attraction on the surface of metallic hydroxides (or oxides). Actually, the pollutant may act as a ligand (L) and bind to iron or aluminum hydroxides according to the following reactions [27-28]:

$$L-H_{(aq)} + (HO)OFe_{(s)} \rightarrow L-OFe_{(s)} + H_2O$$

$$L-H_{(aq)} + (HO)(OH)_2Al_{(s)} \rightarrow L-(OH)_2Al_{(s)} + H_2O$$

3.4 Cadmium removal

Table 3 shows removal efficiencies for the cadmium present in solutions 5 and 6 by compounds N1 to N5 adjusted to 2 g L^{-1}.

Table 3: Cadmium removal at neutral pH using 2 g L^{-1} of the adsorbents-coagulants prepared by indirect electrocoagulationwith iron and aluminum electrodes

Compounds	**Cadmium removal (%)**	
	Solution 5	**Solution 6**
N1	67.8	55.3
N2	75.6	70.3
N3	68.1	62.6
N4	72.2	67.4
N5	80.9	75.9

Removal efficiencies for cadmium vary depending on the compound used (N1 à N5) and the solution treated (solutions 5 and 6). When cadmium is the only element in solution, efficiency varies from 67.8% to 80.9%, while when pollutants are mixed (solution 6), removal efficiency is lower and varies from 55.3 to 75.9% depending on the compound used.
It is possible to assert that cadmium removal efficiency is higher for the iron-based compound (N5) compared with the aluminum-based (N1). However, the trend is not as clear for mixed compounds N2, N3 and N4.
The lowest removal efficiency when cadmium is the only element in solution (67.8%) was found for N1 for which the zeta potential is positive, and positively charged cadmium may be slightly attracted by the surface of

the positively charged coagulant. However, it was found that the highest efficiency (80.9%) was for coagulant N5 for which almost 20% of the colloidal particles were negatively charged, according to the zeta potential (Figure 2), thus attracting the positively charged cadmium. It was also assumed that magnesium (Mg) is replaced by cadmium (Cd) in compound $MgFe_2O_4$, thus enhancing the removal of the latter.
The decrease (5 to 12%) in removal efficiencies for cadmium in solution 6 compared with that of solution 5 can be explained by the competition that exists between cadmium and other pollutants present in the mixed solution to treat.
Typically, the cadmium present in the solution is probably eliminated through adsorption, as well as through complexation and electrostatic attraction on the surface of the compounds that have negatively or positively charged sites, which can attract opposed charge dissolved species [7, 29].

3.5 Organic matter removal

Table 4 shows removal efficiency results for COD and thus the organic matter found in solutions 2, 3, 4 and 6 with the compounds prepared and adjusted to a 2 g L^{-1} concentration.

Table 4: Chemical oxygen demand (COD) removal from the solutions 2, 3, 4 and 6 using 2 g L^{-1} of the adsorbents-coagulants prepared by indirect electrocoagulation with iron and aluminum electrodes

Compounds	**COD removal (%)**			
	Solution 2	**Solution 3**	**Solution 4**	**Solution 6**
N1	68.8	65.3	67.0	59.4
N2	64.4	60.2	58.8	54.0
N3	65.9	58.8	57.9	53.7
N4	65.6	58.3	57.5	53.0
N5	64.5	56.7	55.7	51.9

According to these results, removal efficiency for COD does not vary much depending on the solutions and compounds tested, from 51.9 to 68.8%. The highest removal values for COD were obtained with the aluminum-based compound (N1), which can be explained by the dominant presence of smaller particles, thus leading to a larger specific surface area. Results show as well that the more organic matter (solution 6) the solution to treat contains, the more the removal efficiency decreases. This decrease is linked to the competition between the different pollutants for adsorbent-coagulant structures retention sites.

Conclusion

Over the course of the present study, adsorbent-coagulant structures were synthetized through indirect electrocoagulation using iron and aluminum electrodes in a sodium chloride solution (10^{-2} mol L^{-1}) as base electrolyte at neutral pH. Different mixtures of these structures were then used to treat solutions polluted by a dye (trypan blue), phenol, oxalic acid and cadmium sulfate.
The compounds produced contain aluminum oxide- and hydroxide-based crystalline forms when only aluminum is used in the mixture, or iron oxide- and hydroxide-based crystalline forms when only iron is used. When one of the components is dominant or components are present in equal proportions, other structures such as magnetite (Fe_3O_4), $Al(OH)_3$ and $Mg\ Al_{0.2}\ Fe_{1.8}\ O_4$.are found in addition to the abovementioned oxides and hydroxides.
The analysis of these structures also revealed that they are present in high proportions in the form of positively charged colloids, thus explaining the attraction properties of the compounds.
The removal of cadmium, oxalic acid and phenol in solution varies from one compound to the other depending on the type of coagulant used. On the other hand, all coagulants prepared performed well to eliminate trypan blue dye.

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