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Immobilization of heavy metals by modified bentonite coupled coagulation/flocculation process in the presence of a biological flocculant

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ABSTRACT

Nanometer sized and sheet-like bentonites play an important role in the removal of metal ions from contaminated water. They exist everywhere in nature and can develop a good and less expensive alternative in wastewater cleanup containing heavy metals. However, their use may generate turbid suspensions difficult to settle. Therefore, a coupling of adsorption on natural material was chosen. A modified Algerian bentonite in coagulation/flocculation processes was used with a biological flocculant obtained from waste recovery of fishery products. The results demonstrate that the modified bentonite has a very high adsorption capacity. The treatment efficiency was evaluated by measuring turbidity. The removal rate was observed around 99%.

Keywords: Bioflocculant; Heavy metals; Multiple adsorptions; Modified bentonite; Turbidity

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1. Introduction

Historically, water quality has been an important factor for securing human well-being. Currently, one of the most serious environmental problems is the pollution of the hydrosphere, which is being threatened by human activity. Its quality has been deteriorated in developed and developing countries because of the chemical waste released in to the global environment. In Algeria, water scarcity increases due to aquifers over exploitation which is considered as the main reason as well as the quality degradation of water resources. Indeed, the water sector is also weakened by various forms of pollutions, especially by heavy metals. Several techniques are used for the removal of metal cations namely: electrodeposition, electrocoagulation, reverse osmosis, lime precipitation, ion exchange, cementation, adsorption on activated carbon, etc. Nowadays, natural products are increasingly

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used substitutes to clays [1–3], polysaccharides chitin and chitosan, which have been the subject for a large number of applications such as adsorption and coagulation/flocculation [4]. Clays are the most notable nanoparticles due to their ubiquity and reactivity [5]. Their nanometer size and sheet-like structure provide them with large surface areas [6] for adsorption as well as a crucial role on natural and anthropogenic pollutants removal [7,8]. In addition to their wide availability in nature (over 99% of the soil composition) [9], the manifested interest to these materials is justified by the importance of their developed surface area [10], the presence of ionic charges on the surface as well as their ability to exchange cations. On the other hand, their use as polluted effluents, treatment generates considerable turbid suspensions that require dozens of days to settle. For this reason, several researchers focused on the use of chitosan as a flocculant for removing the cloudiness [11–16]. In this work, we first focus our study on the adsorptive properties of modified Algerian clay on the adsorption of three metal cations, namely, Co^{2+}, Ni^{2+}, and Zn^{2+}, on single and multicomponent mixtures, and then evaluate the effectiveness of chitosan taken from waste shrimp on the flocculation of turbid suspensions.

2. Materials and methods

2.1. Material

2.1.1. Modified bentonite

The raw clay used was taken from Roussel deposit of Hammam Boughrara, located 25 km northeast of Maghnia (Algeria). Only white and grayish-white colored clays with diameters between 1 and 15 cm were selected in our study. The samples have crispy characteristics under dry conditions, while they tend to burgeon and inflate under humid conditions. All clay samples were submitted to different treatments [17–19] (mechanical, successive sedimentations, washing with hydrochloric acid, and saturation with sodium chloride). X-ray diffraction (XRD) analysis, Fig. 1, shows the presence of montmorillonite with feldspar and quartz in smaller proportions. The chemical composition of the clay is given in Table 1.

2.1.2. Chitosan

The chitosan used as a flocculant was prepared in laboratory by alkaline hydrolysis of chitin (taken from shrimp shells). The hydrolysis was carried out over an incubation period of one week at 35°C in sodium hydroxide solution (40%). The deacetylation degree (DD) of chitosan was determined by conductometric assay [20], while the molecular weight (MW) was measured using viscosimetric method [21] (Table 2).

2.2. Solution preparation

2.2.1. Metal solutions

Nitrate salts of each metal ion [$Ni\ (NO_3)_2{\cdot}6H_2O$], [$Co\ (NO_3)_2{\cdot}6H_2O$], and [$Zn\ (NO_3)_2{\cdot}6H_2O$] and distilled water were used to prepare our metal solutions (1 g L^{-1}).

2.2.2. Chitosan solution

Chitosan is a glucosamine polymer whose flocculating effect is well noticed under solution conditions. About 100 mg of chitosan powder is dissolved under slow agitation in dilute acetic acid (1 mL acetic acid (99%) in 100 mL of distilled water).

2.3. Experimental procedure

In order to study the efficiency of the adsorption and coagulation/flocculation processes in the removal of metal ions as well as minimizing turbidity, a combination between coagulation/flocculation and adsorption procedure was setup. The settling time was maintained over 30 min. First, equimolar solutions of metal ions (80 mg L^{-1}) were prepared at fixed pH 7, by addition of either hydrochloric acid (0.1 N) or sodium hydroxide (0.1 N) in the presence of pH-meter HANNA (pH*211*). About 3 g of bentonite powder was added under stirring (200 rpm) over the course of 30 min.

Following optimization of chitosan's concentration/dose (C_F) using jar-test HANNA(PF4 portable jar-test), the amount of chitosan was added over the period of 5 min under agitation (200 rpm) (coagulation step), then we reduced stirring to 40 rpm for 20 min (flocculation step). Finally, the stirring was stopped and the progression of turbidity was followed using turbidimeter HANNA(LP2000) (Fig. 2). After 30 min, the samples were filtrated and analyzed by atomic absorption spectroscopy.

The removal efficiency was calculated according to the following equation:

$$E(\%) = \left(\frac{C_0 - C_r}{C_0}\right) \times 100 \qquad (1)$$

where C_0 is the initial metal ion concentration (mg L^{-1}) and C_r is the residual metal ion concentration (mg L^{-1}).

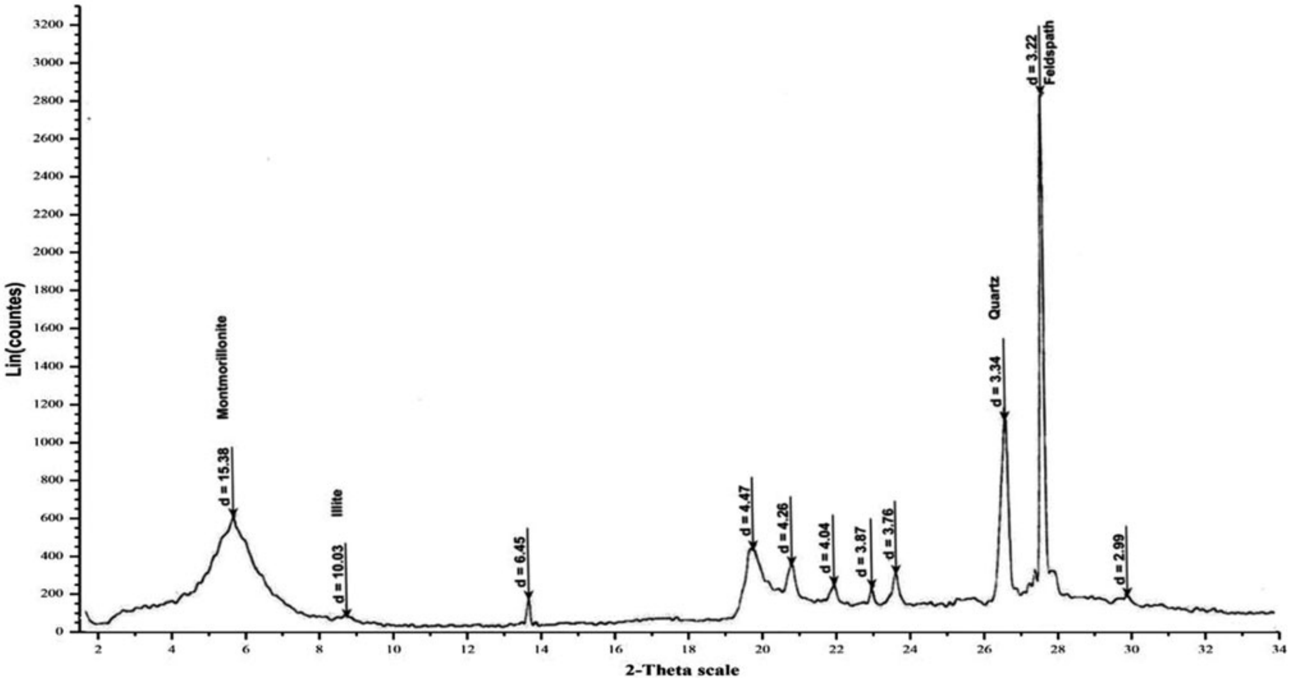

Fig. 1. X-ray diffraction (XRD) Spectrum of modified bentonite.

Table 1
Chemical composition of the modified bentonite

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O
60–70	17–20	1–3	0.5–1	2.5–4	0–0.75	1–2

Table 2
DD (%) and MW of the used chitosan

DD (%)	MW (KDa)
89	387

The adsorption capacity was calculated as follows:

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{2}$$

where C_0 is the initial metal concentration (mg L^{-1}), C_e is the final or equilibrium concentration (mg L^{-1}), V is the volume of the metal solution (mL), and W is the weight of bentonite (g).

2.4. Adsorption mechanism

The sorption of heavy metal cations on bentonite has been extensively studied. The conceptual proposed mechanism is the cationic exchange process between metal cations present in water and cations residing on the surface of the bentonite frame work [22–24]. It is suggested that the adsorption of heavy metal cations was due to the surface reaction between terminal hydroxyl groups on bentonite and the metal cations in the solution [25,26]. The surface reaction can be described as:

$$n \equiv \mathrm{S-OH} + \mathrm{M}^{n+} \leftrightarrow (\mathrm{S-O})n - \mathrm{M} + n\mathrm{H}^+ \tag{3}$$

$$\equiv \mathrm{SO}^- + \mathrm{MOH}^+ \rightarrow \mathrm{SOMOH} \tag{4}$$

$$n \equiv \mathrm{SO}^- + \mathrm{M}^{n+} \leftrightarrow (\mathrm{S-O})n - \mathrm{M} \tag{5}$$

$$n\mathrm{MOH}^+ + \mathrm{M}'(z) \leftrightarrow \mathrm{Mn}(z)^+\mathrm{M}^{n+} + n\mathrm{OH}^- \tag{6}$$

Eqs. (3)–(5) represent the surface reaction and charge combination mechanism, and Eq. (6) represents the ion-exchange mechanism. M´(z) is the metal cation (mostly Na^+ or Ca^{2+}) in the bentonite frame work. MOH^+ is the hydrolyzed divalent metal cation (M^{2+}) in aqueous solution. According to Eqs. (3)–(5), a pH decrease would be observed if the adsorption follows the surface reaction mechanism, while a preserved pH should be observed once the exchange ion mechanism is dominated [27].

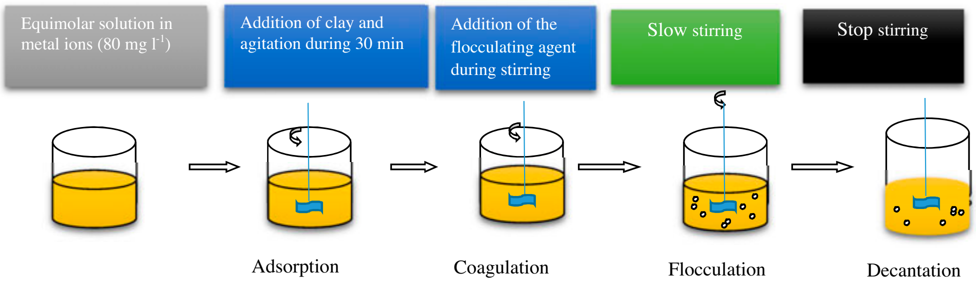

Fig. 2. Schematic diagram of the treatment protocol.

3. Results and discussion

3.1. *Adsorption*

The percentage of elimination of metal ions (Ni^{2+}, Co^{2+} and Zn^{2+}) after 30 min of treatment with mono and multi-adsorption on the modified bentonite are shown in Fig. 3.

3.2. *The changes in pH values of modified bentonite suspension over time on different metal-containing solutions*

The pH variation of different metal solution during adsorption (Fig. 4) provides an idea about the implied mechanism of these metals either separately or together.

According to Fig. 4, adsorption of the studied ionic metals in a mono-component system on bentonite, generally, introduces a progressive increase of the solution's pH throughout the adsorption period, until a stable pH is reached. This stability reflects the establishment of an equilibrium system where no changes are produced [28].

However, we conclude a fluctuation in the trend of pH in multicomponent solutions, which reflects the implication of two mechanisms, i.e. ionic exchange and external surface complexation [27].

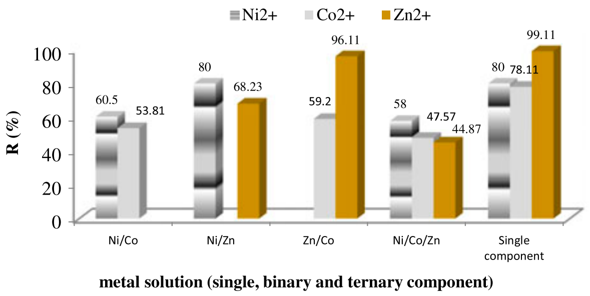

Fig. 3. Percentage of Ni^{2+}, Co^{2+}, and Zn^{2+} on modified bentonite in different solutions (single, binary, and ternary component): $t = 30$ min; $C_0 = 80$ mg L^{-1}; $C_A = 3$ g L^{-1}; and pH 7.

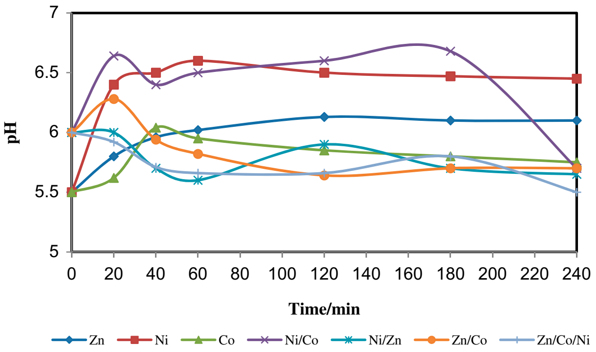

Fig. 4. The variation in the pH values of modified bentonite suspensions as a function of time.

Fig. 3 and Table 3 show that the modified bentonite has a very interesting adsorption capacity for all metals in different solutions (single, binary, and ternary component). The order of affinity of these metals in solutions is given in Table 4.

The total elimination of zinc in mono adsorption systems (Table 3) is probably due to its precipitation on the surface of bentonite (see Table 5).

Generally, the order of affinity of those metal cations, in binary and ternary solutions, follows the reverse order of the hydrated cations' radii, except for Zn^{2+} and Co^{2+}. This discrepancy may be ascribed to the different solubility of $Co(NO_3)_2$ and $Zn(NO_3)_2$. At 25°C, both latter metal ions have solubilities of 103 g and 120 g in 100 g water, respectively [29]**.** It was suggested that the solubility was an influencing factor on the adsorption capacity, since a higher solubility of sorbate in water would enable a higher affinity to the adsorbent [25]**.**

3.3. *Coagulation/flocculation of clay suspensions*

3.3.1. *Unassisted settling clay suspensions*

The follow up of the natural settling of clay suspensions is shown in Fig. 5, which represents the

Table 3
Adsorption capacity of modified bentonite in different solutions

Metal ion	Solution	Removal (%)	Adsorption capacity (mg g^{-1})
Zn^{2+}	Only	99.11	26.43
	In the presence of nickel	68.23	17.10
	In the presence of cobalt	96.11	25.63
	In the presence of nickel and cobalt	44.87	11.96
Co^{2+}	Only	78.11	22.90
	In the presence of zinc	59.20	16.95
	In the presence of nickel	53.81	16.75
	In the presence of zinc and nickel	47.57	12.68
Ni^{2+}	Only	80.00	21.32
	In the presence of zinc	80.00	21.32
	In the presence of cobalt	60.50	18.18
	In the presence of zinc and cobalt	58.00	15.45

Table 4
Order of affinity of Ni, Co, and Zn in single, binary, and ternary systems

Solution	Range affinity
Single component	Zn > Ni > Co
Ni/Co	Ni > Co
Ni/Zn	Ni > Zn
Zn/Co	Zn > Co
Ni/Co/Zn	Ni > Co > Zn

Table 5
Cation sizes and precipitation pH

Cation	Ionic radius in crystals[a] (nm)	Hydrated cation radius[b] (nm)	Precipitation pH[c]
Ni^{2+}	0.049	0.404	8–14
Co^{2+}	0.065	0.423	8–14
Zn^{2+}	0.074	0.430	7–8

[a] Lide [29]. Data are for ions with coordination number of six.

[b] Nightingale [30]. The hydrated cation radii were determined at 25°C.

[c] Qie and Zheng [27]. Precipitation pH.

evolution of elimination rate of turbidity as function of time. The elimination rates were calculated using the equation:

$$A(\%) = \left(\frac{T_0 - T}{T_0}\right) \times 100 \tag{7}$$

where T_0 represents the initial turbidity of the suspension in NTU and T is the residual turbidity of the suspension in NTU.

According to Fig. 5, turbidity removal of unassisted clay suspensions after 17 d of settling does not exceed 80%. This result reveals the slow natural settling of the suspensions.

3.3.2. Effect of the flocculant dose

The effect of the flocculant dose was carried out for each one of the suspensions at pH 7. The results are shown in Fig. 6. It can be noted that for each suspension, the residual turbidity varies with the added chitosan amount. Thus, the effectiveness of chitosan can reduce turbidity either at very small or very high doses. In fact, at higher doses, the surface of bentonite particles will be loaded with the same charge because they are coated with chitosan which leads to the destabilization (repulsion) of the suspensions [31]. The optimal dose of chitosan (C_F) is observed between 0.25 and 0.50 mg, while all surface charges can be considered as neutral (Fig. 7).

The results of the effect of pH on turbidity removal of clay suspension are presented in Fig. 8. A slight reduction is observed at acidic and basic pH. Significant percentages are recorded at pH 7 (Fig. 9).

3.4. Chemical coupling of adsorption and flocculation of Ni^{2+}, Co^{2+}, and Zn^{2+} cations

The results illustrated in Figs. 10 and 11 show that the presence of metal ions with clay suspension does not affect the flocculation efficiency of chitosan. However, lower values of turbidity are recorded in the presence of all metals except Zn.

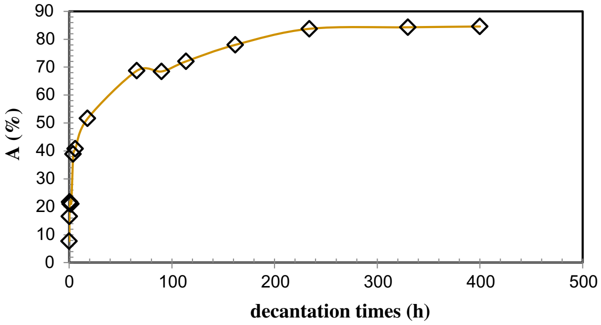

Fig. 5. Turbidity removal vs. settling time: $C_A = 3$ g L^{-1}, $C_F = 2$ mg L^{-1}, and $T_0 = 1{,}100$ NTU.

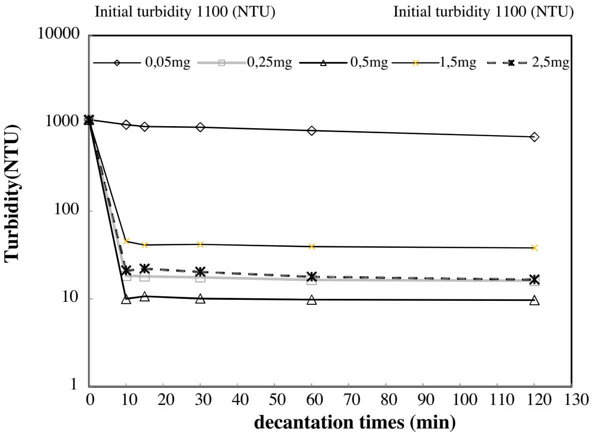

Fig. 6. Decantation of the argillaceous suspensions after coagulation/flocculation with different chitosan concentrations: $T_0 = 1{,}100$ NTU, $C_A = 3$ g L^{-1}, and $V = 250$ mL.

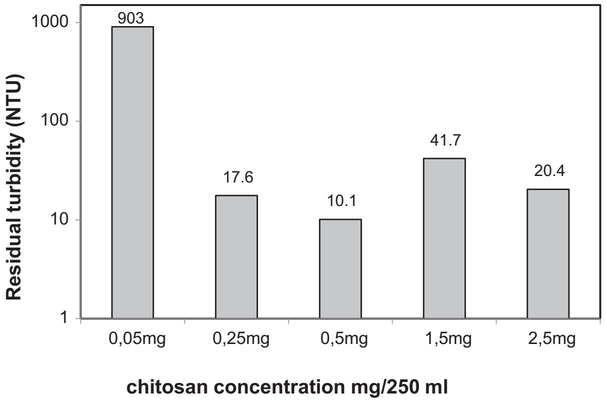

Fig. 7. Residual turbidity of the argillaceous suspensions after 30 min of coagulation/flocculation with different chitosan concentrations: $T_0 = 1{,}100$ NTU, $C_A = 3$ g L^{-1}.

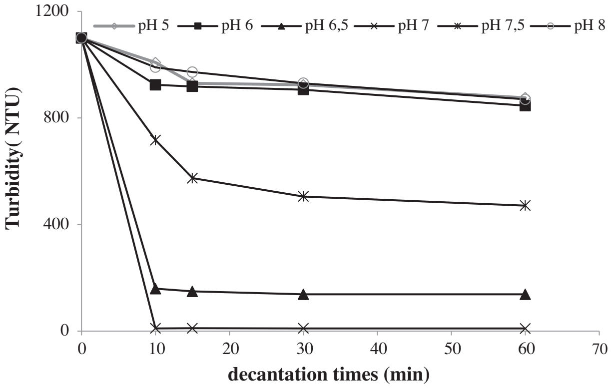

Fig. 8. Decantation of the argillaceous suspensions after coagulation/flocculation: $T_0 = 1{,}100$ NTU, $C_A = 3$ g L^{-1}, and $C_F = 2$ mg L^{-1}.

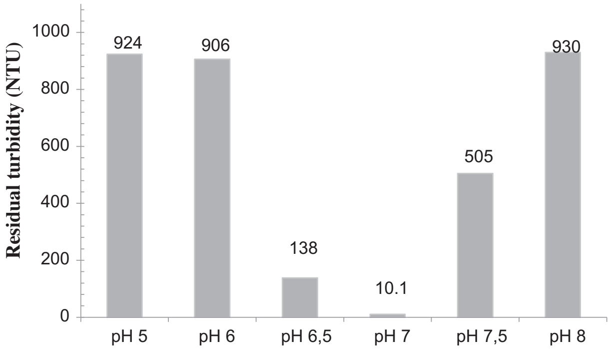

Fig. 9. Residual turbidity of the argillaceous suspensions at the end of 30 min of decantation after coagulation/flocculation with different pH values: $T_0 = 1{,}100$ NTU, CF = 2 mg L^{-1}.

3.4.1. Effect of flocculant on the removal of metal cations

In order to evaluate the effectiveness of bentonite on the metal adsorption, after 30 min of treatment in the presence of chitosan, the measurement of residual concentrations of each metal is carried out in different mixture systems (single, binary, and ternary component), prior to and following the addition of chitosan. The percentage of metal removal of each metal before and after the addition of flocculant is plotted in Fig. 12 and Table 6.

Co and Ni metal removal is broadly unaffected by the presence of chitosan, with the exception of Ni in the presence of Zn or in the presence of Zn and Co. However, the elimination of Co in the presence of Ni, after adsorption/flocculation, is 99.30% against 56.73% after adsorption. Therefore, it can be assumed that free

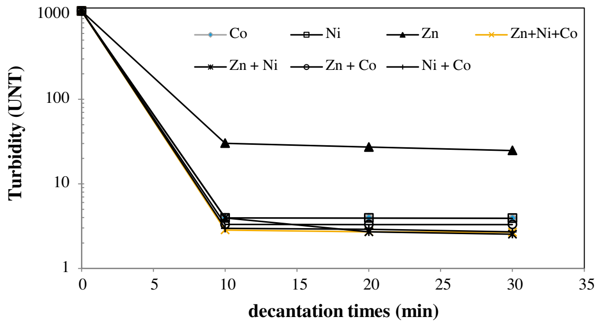

Fig. 10. Decantation of the argillaceous suspensions after coupling process (adsorption and coagulation/flocculation).

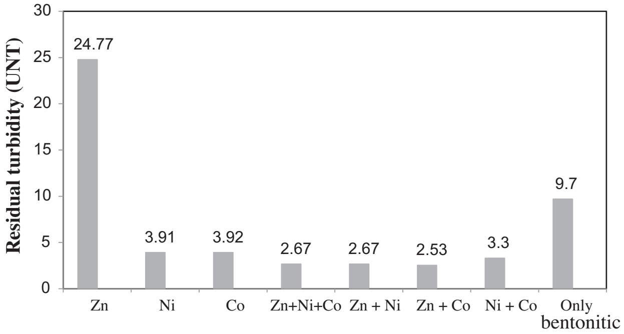

Fig. 11. Residual turbidity of the argillaceous suspensions at the end of 30 min of decantation after coupling process (adsorption and coagulation/flocculation).

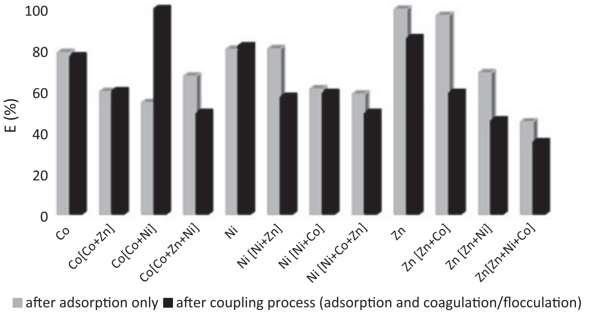

Fig. 12. Elimination rate of metal cations after adsorption only and after adsorption/flocculation: $C_0 = 80$ mg L^{-1}, $C_A = 3$ g L^{-1}, $C_F = 2$ mg L^{-1}, and pH 7.

ions of unabsorbed Co on bentonite are removed by chitosan.

Table 6
Removal ions after coupling of both processes (adsorption and coagulation/flocculation)

		Removal (%)	
Metal ion	Solution	After adsorption only	After coupling process (adsorption and coagulation/flocculation)
Zn^{2+}	Only	99.11	85.27
	In the presence of nickel	68.23	45.68
	In the presence of cobalt	96.11	58.78
	In the presence of nickel and cobalt	44.87	35.18
Co^{2+}	Only	78.11	76.43
	In the presence of zinc	59.20	59.52
	In the presence of nickel	53.81	99.30
	In the presence of zinc and nickel	47.57	49.06
Ni^{2+}	Only	80.00	81.37
	In the presence of zinc	80.00	56.78
	In the presence of cobalt	60.50	58.71
	In the presence of zinc and cobalt	58.00	49.12

On the other hand, it is worth noting that Zn adsorption in mono and multicomponent systems is usually affected by the presence of chitosan. In all cases, the elimination of flocculation/adsorption is lower than that of adsorption. Decrease of this latter is probably due to the fact that Zn^{2+} ions form weak bonds with bentonite adsorption sites (outer complexation). Once in contact, these ions can be exchanged with chitosan groups ($Ch–NH_3^+$) as described in (Eq. (8)).

$$\equiv SO^{-}MOH^{+} + Ch–NH_3^{+} \leftrightarrow \equiv SO^{-}{}^{+}H_3N–Ch + MOH^{+} \tag{8}$$

$$(\equiv SO)_2–M + Ch–NH_2 \leftrightarrow \equiv SO–M–NH–Ch + \equiv SOH \tag{9}$$

Thus, the implied mechanism during coagulation/flocculation of bentonite-chitosan process in the presence of metal cations can either include a mechanism implying a cationic exchange system between chitosan ($Ch–NH_3^+$) groups and metal cations adsorbed on bentonite surface (Eq. (8)). Equally, the complexation between chitosan ($Ch–NH_2$) groups and metal cations adsorbed on bentonite surface is also plausible [32] (Eq. (9)).

4. Conclusion

(1) The current study had two main objectives. First, the performance of modified sodium bentonite obtained from Maghnia (Algeria) in the removal of metal cations, i.e. Co^{2+}, Ni^{2+}, and Zn^{2+} from synthetic aqueous solutions containing different bentonite mixtures (single, binary, and ternary components). Secondly, the performance of chitosan as well as the effect of the combination of bentonite and chitosan on the removal of turbid suspensions in mixtures. The elimination of three metal cations showed the effectiveness of the modified Algerian bentonite in the removal of heavy metals; elimination of metals varied between 80 and 99% for mono-compound systems, from 54 to 96% for binary systems, and 44 to 58% for ternary ones.

(2) Also, the affinity of bentonite toward the three cations is in the order Zn > Ni > Co, while a solution containing a mixture of all studied cations, has an order of affinity Ni > Co > Zn

(3) The effect of pH and adsorbent quantity showed an optimal value of pH 7 and 3 g $L^{-1,}$ respectively. The use of prepared chitosan as coagulant and flocculant agent has shown a very good efficiency for the removal of turbid suspensions in mixtures containing clay. The removal percentage after 10 min of settling exceeds 99% compared to best rate obtained in the case of unassisted settling (80% after 17 d). The presence of metal cations improves the coagulation/flocculation of the clay suspension by chitosan.

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