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EVALUATION OF A NEW BIO-BASED-FLOCULANT EXTRACTED FROM WATER-MELON, ON THE REMOVAL OF LEAD IONS FROM WATER

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Abstract:

The current study, aims to eliminate lead ions in drinking water or industrial waste, by the coagulation and flocculation process, adopting a coupling of NaOH with a new bioflocculant "BFM" extracted from the crust and fruit of a variety of melon named "Pineapple". The removal process was tested on 100mg / l samples of pb^{2+} ions, as a function of pH, NaOH and "BFM" doses. the experimental results gave an elimination efficiency which reaches about 99% for a pH 11, and a dose of "BFM" of 1 mg / l. A comparative study of the sedimentation rate between our bio-flocculant and a commercial flocculant "sodium alginate" showed a very competitive performance of "BFM".

Keywords: Bio-Flocculant; Heavy Metals; P^{b2+}; Coagulation; Flocculation; Water Treatment; Polymers; Turbidity.

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1. Introduction

Anthropogenic activities, especially those that generate heavy metals such as metallurgical industries, hydrocarbon refineries, pigments ..., are the source of serious pollution [1,2]. The accumulation of these metals in nature has a major influence on water resources as well as human and animal health [3,4].

The future of life on our planet is closely linked to the legal and technical measures taken to reduce these contaminants in nature. However, these measures sometimes remain limited because of their yields, technical complicity or their costs that exceed the limits of economic feasibility [5]. The usual techniques used for the treatment of industrial discharges or water destined for potabilization, such as reverse osmosis, electrocoagulation, precipitation, ion exchange resin, adsorption on activated carbon, remain out of reach of the developing and underdeveloped countries [6].

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Adsorption on other substrates such as kaolinite or bentonite have in turn given promising results but they generate large volumes of sludge which must be disposed of later [7].

The process of coagulation and flocculation by synthetic polymers remains the simplest, cheapest and most adopted in the treatment plants, of industrial discharges or those of drinking water, except that it generates sludge loaded with organic matter that is hardly biodegradable [8,9].

In this work, we adopted a technique based on the coupling of a classical method which is metallic precipitation by NaOH, in parallel with the floculation using a new bio-flocculant extracted from melon "BFM", to improve on the one hand the yield of elimination and on the other hand reduce the intakes of the reagents used in the treatment.

2. Materials and Methods

The extraction of the bio-based polymer " BFM " used in the flocculation, has been done by soaking small pieces of 0.1 cm of melon fruit named "Pineapple" with its flesh in 2% formaldehyde for 2 H to eliminate pigment, than washed massively with distilled water and added to 0.2 M HCl solution for 24 H at room temperature to eliminate the mono-sugars [10]. The pretreated fruit was again washed with distilled water and returned to heating at 60°C in distilled water for two cycles of two hours each. After cooling, the filtrate undergoes a charge converting by adding 0,2% of NaCO3 (w/v) under stirring for 5 H, followed by a pH correction with absolute acetic acid until pH=7. Afterwards, we proceed to the extraction of bio-based flocculant by adding ethanol (v/v) and centrifugation at 3500 rpm for 15 mn (centrifuge type ROTOFIX 32 A). The polymer residues are dried for 5 days in the oven (WTC binder) at a temperature of 45° C, and ground into powder [11,12].

The synthetic samples are fixed at 100 mg/L of pb2+ by dilution of a laboratory grade solution of pb (NO3)2, supplied by (Sigma Aldrich).

The eliminating process of pb^{2+} is based on Jar-test protocol using the floculateurs type (VILP JLT6). The residual of pb^{2+} ions during the treatment process was carried out by atomic absorption spectrometry (VARIAN AA 240 SS), after filtration on 0,45µm membrains. The turbidity of the suspended particules was measured by optical turbidimeter type (HACH 2100N).
The adjuvant of flocculation "BFM", was prepared by dissolving 1g/L of the powder in distilled water under stirring for 3 hours. The correction of pH was made by HCl(1M) and NaOH (1M).
- The removal percentage after treatment is calculated by the relationship:

$$\% \text{ removal } (T) = [Vi(T)-Vf(T)] / Vi(T)*100$$

Vi = initial value of the turbidity or pb2+ concentration, measured before treatment.
Vf = final value of the turbidity or pb2+ concentration, after treatment.

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3. Results and Discussion

3.1. Study of The Purification Performance of The New Bio-Based Floculant "BFM" Towards the Elimination of Lead Ions

3.1.1. PH effect on the Precipitation of Pb^{2+} Ions in Solution

To study the effect of pH on the precipitation of some heavy metal ions as pb^{2+}, reviewed in the current study, tests were performed using the Jar-test protocol, in which synthetic samples of 100 mg/l of pb^{2+} ions in solution, were treated under the same conditions of stirring speed and temperature while varying the pH of the reactionary medium increasingly by adding NaOH or HCl according to the requested pH. The Fig.1 below shows the removal percentage of pb^{2+} as a function of pH.

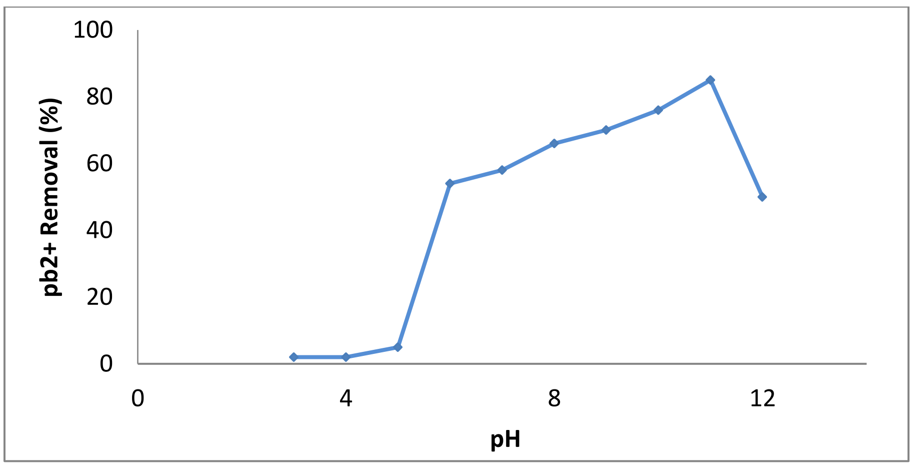

Figure 1 : Evolution of pb $^{2+}$ removal as a function of pH of reactionary medium, $[Pb^{2+}]_{int}$=100 mg/l

From Fig.1, we note that the removal of pb^{2+} ions is favored at basic pH than at neutral or acidic pH, because of the dominance of these metal ions in the acidic environment [13]. In fact, since pH 5, the percentage of removal of lead ions increased exponentially with the increase in pH, which is generally due to the formation of lead hydroxides Pb $(OH)_2$ characterized by a whitish cloud of fine crests that settle freely in the solution [14].

The curve marks an acute elimination pick that reaches a maximum of 85% at pH 11 relative to the optimal precipitation of hydroxides pb $(OH)_2$, beyond which the percentage of elimination begins to decrease. This regeneration of the pb^{2+} ions in the solution is explained by the inverse effect of the excess of (OH^-) ions which at pHs greater than 11, form other ionic forms of metallic ions, such as pb $(OH)^+$, pb $(OH)^-_3$, $pb(OH)_4^{2-}$, very soluble in the water. This result is in full agreement with several works. [15]

3.1.2. Effect of bio-flocculant "BFM" on the elimination of pb^{2+} ions

For the demonstration of the effect of the polymer "BFM" in the flocculation of preformed hydroxides by the reaction of NaOH with the pb^{2+} ions, we moved a little away on the optimum

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pH of precipitation mentioned above (pH 11). In this regard, and to create similar conditions to those of surface waters, which are generally included between 5 <pH <8.5, we have chosen to set the pH of all samples to 8. Thereafter increasing the injection of "BFM" under stirring, according to the Jar-Test protocol, allowed us to determine the purification performance of this bio-based flocculant.

Indeed the order of injection of reagents is decisive in the treatment process. The table below shows the evolution of the removal efficiency of pb^{2+} ions, for flocculant doses between 0 and 1 mg / l.

Table 1: Effect of the "BFM" dose on the removal of pb^{2+} ions.

[BFM] in (mg/l)	**0**	**0,2**	**0,3**	**0,5**	**0,8**	**1**
Flocs size	S	S	S	M	L	L
Pb^{2+} concentration (mg/l)	7,8	4,4	4,3	5	1,9	0,9
Removal rate of pb^{2+} (%)	70,2	95,6	95,7	95	98,1	99,1

Flocs size: (S: small; M : Medium ; L : large)

In the light of the results mentioned in Table 1, we can see clearly, the role of adjuvant "BFM" in the reduction of metal traces. Thus, the percentage of elimination increases from 70% for the control sample, up to 99.1% for the sample treated with 1 mg / l of studied biofloculant.

These results can be explained by the action of “BFM" at several levels. This advantage allows it, on the one hand, its large molar mass and its charge density which are capable of making purely covalent chemical bonds with all the opposite ions to its charge, or even by adsorption caused by electrostatic or Van Der Wals interactions [16,17]. On the other hand, the length and the flexibility of the polymer chains play a decisive role in the bridging phenomenon between the preformed micro-flocs. This last phenomenon contributes greatly to the maturation of the flocs of which the size improves progressively with the increase of the "BFM" doses as it is illustrated in Table 1, and consequently it increases the rate of sedimentation that we will study in the following of this Article. [17]

3.1.3. Study of the Sedimentation Rate of Pb $(OH)_2$ Hydroxides and Adsorbed Lead Ions Under the Effect of "BFM"

After determining the optimal dose of the bioflocculant (Table 1), we conducted a comparative study to follow the evolution of turbidity and the residual concentration of lead ions in synthetic samples, using as flocculating agents, the new bio-based flocculant "BFM" compared with commercial sodium alginate (ALG). The working pH is the optimum pH of flocculation (Ph 11). The initial concentration of lead ions in each sample remains at 100 mg/l. note that the samples are measured this time without filtration after treatment, to detect the fine suspended crystals in the solution. Figure 2 and 3 below illustrate the evolution of turbidity and the residual concentration of pb^{2+} ions in the treated samples.

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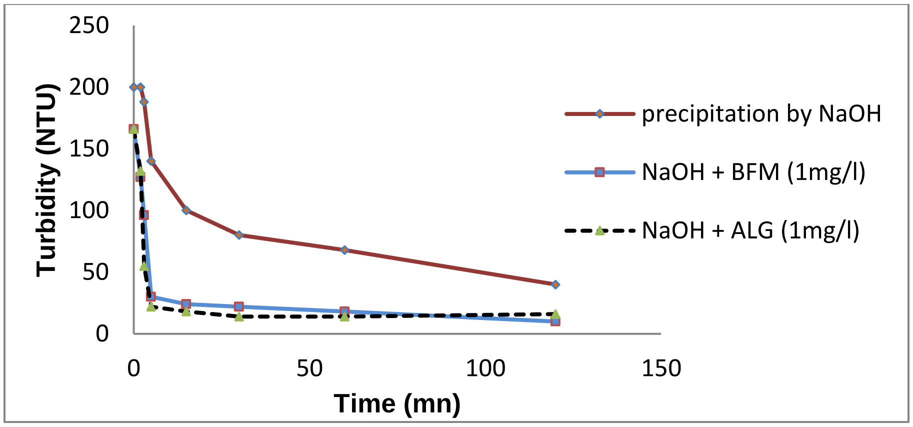

Figure 2: Evolution of the turbidity of lead's hydroxydes as a function of settling time, [BFM]=1mg/l, $[pb^{2+}]_{int}$=100mg/l, pH=11

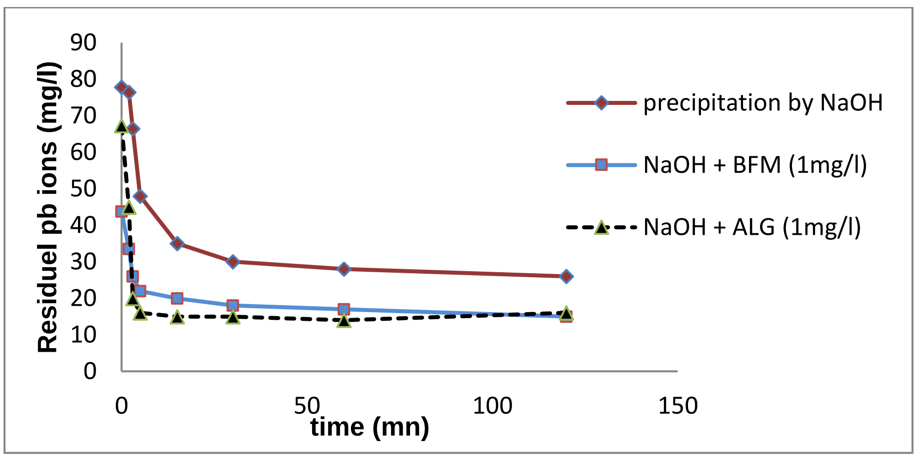

Figure 3: Evolution of the residuel concentration of all form of lead ions as a function of settling time, [BFM]=1mg/l, $[pb^{2+}]_{int}$ =100mg/l, pH=11

Figure 2 and 3, project the light on the role of bio-flocculant "BFM" in improving the treatment in the field of the reduction of turbidity and the residual concentration of metal traces. In fact, in terms of abatement of the metallic hydroxides turbidity, the sample treated with 1 mg / l of "BFM" has a turbidity-eliminating performance of more than 80%, in less than 5 min against more than 2 hours for the witness sample, for having the same goal. Regarding the lead residual ions elimination, their concentration decreases in parallel with the decrease in turbidity.

In comparison of "BFM" with the commercial sodium alginate (ALG), it can be said that they are closely convergent, with a slight superiority in favor of sodium alginate.

The appearance of curves on Fig.2 and 3 can be explained, on the one hand, by the primordial role of the flocculant "BFM" in the increase of the sedimentation rate, by bridging metallic hydroxide flocs, which size are more voluminous than those of the witness sample, and this generally due to the phenomenon of polymer bridging and adsorption. [17]

On the other hand, the high charge density of "BFM" also allows it to make other types of complexation with residual ionic forms of lead as pb^{2+}, pb $(OH)^{+}$, pb $(OH)_3^{-}$, $pb(OH)^{-}_4$ [18]. Indeed,

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thanks to the charge density, characterizing each polymer, it can occur chemical bonds with opposite charge ions, substitution of groups or exchange of ions with weakened hydroxyl (OH) functions. Several studies have investigated the influence of charge density, molecular weight, and length of polymeric chains on the removal of micro-pollutants [19,20,21]. The great problem in this process, based only on adsorption or complexation, sometimes gives a poor results especially with the metallic pollutants, in addition to the important quantities of the polymer involved in the purification, which influences the cost of treatment [22]. On the contrary, the use of "BFM" after the complixation reaction with NaOH, has given very relevant results, which exceed 99.5% if it is followed by a simple filtration after treatment. Otherwise prolonged decantation can also give high performance according to the economic and technical choice.

4. Conclusion

This new bio-flocculant draws its strength from its natural origin easily biodegradable in nature, unlike other synthetic polymers that are hardly biodegradable. In the same context this material, is extracted, as it is mentioned above in the methodology, from the flesh and the crust of the melon fruits, which presents an alternative for the recycling and the valorization of the organic waste, in view of their use in the production of biopolymers.

On the technical side, the new bioflocculant "BFM" showed a high purifying capacity toward metal traces, especially the pb^{2+} ions and their stereotypes, using the Jar Test method of coagulation and flocculation that Gave encouraging results that exceed 99.5%. This performance is also due to the fact that the "BFM" is not too sensitive to the pH of the medium.

In addition to the scoring elimination percentage, the biomaterial "BFM" qualitatively improves the sedimentation rate of the preformed flocs. Indeed, this parameter has a decisive importance in the field of dimensioning and engineering of water treatment.

At the economic level the "BFM" is extracted from fruit and crust of melon, which makes it very competitive with other commercial polymers. Adding to all this, the life of the powder and its ease of packaging.

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