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CLAY FLOCCULATION WITH A NATURAL POLYELECTOLYTE

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ABSTRACT

The flocculation performance by using biological flocculants (BFs) extracted from Moroccan cactus pads of Opuntia Ficus Indica (OFI) for turbidity removal was investigated. The results showed that BFs were able to eliminate turbidity from natural clay solution over a wide dosage range (initial turbidity about 1000 Nephelometric Turbidity Unit (NTU)). The removal efficiency with BFs reached 98.6 % on average at pH 12.4 adjusted with lime, higher than 62 % with a new Chelating-Soluble extract (CP) from cladode also. For bioflocculants, bridging flocculation other than charge neutralization should be responsible for turbidity removal. The combined applications of CP with H_2SO_4 increased overall turbidity up to -238 %; from an initial turbidity of about 76 NTU to 257 NTU. It was also shown that combination of BFs and H_2SO_4 was effective for removing turbidity from raw water and can achieve 94% with a residual turbidity about 10 NTU at pH 2.0. This study provides a proof-in-concept demonstration of BFs for water purification, which can in part reduce operational costs in flocculation treatment, as well, effectively reduce the concentration of residual metallic elements (e.g. aluminum) used as coagulant.

I. INTRODUCTION

Turbidity is a measurement of how cloudy water appears. Technically, it is a measure of how much light passes through water, and it is caused by suspended solid particles that scatter light. These particles may be microscopic plankton, stirred up sediment or organic materials, eroded soil, clay, silt, sand, industrial waste, or sewage. Bottom sediment may be stirred up by such actions as waves or currents, bottom-feeding fish, people swimming, or wading, or storm runoff. Coagulation/flocculation has been widely adopted as one of the most effective methods to remove colloidal particles in water or wastewater treatment. By adding highly charged cations, colloidal particles are destabilized, thereby, forming larger aggregates and flocs that can be effectively separated by subsequent sedimentation, flotation or filtration units. It is obvious that coagulant plays an extremely significant role in coagulation treatment. Chemicals used in coagulation and flocculation are referred to as either primary coagulants or as coagulant aids. The coagulant aids can be used to condition the water to add density to slow-settling flocs or toughness so the floc will break up for the use of the primary coagulants. Primary coagulants cause the particles to become destabilised and begin to clump together. The reagents currently used in coagulation and flocculation are inorganic products, natural polymers and synthetic polymers. The most widely used coagulants are aluminium or iron salts and less frequently used coagulants used are cationic polyelectrolytes. Aluminium and iron salts **[1]** are used because they are effective, relatively low cost, widely available and easy to handle, store and apply. Aluminium sulphate is still used widely even though there has been much concern over the possible effects to human health, such as Alzheimer's and possible have strong carcinogenic properties **[2, 3]**. Recently, numerous approaches have been studied for the development of

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cheaper and more effective flocculants containing natural polymers. Among these natural flocculants, polysaccharides deserve particular attention. These materials offer a better flocculant alternative because of their particular structure, physico-chemical characteristics, chemical stability, high reactivity and excellent selectivity towards aromatic compounds and metals, resulting from the presence of chemical reactive groups (hydroxyl, acetamido or amino functions) in polymer chains [4]. Natural polysaccharides such as such as starches [5, 6, 7] and amylopectin, guargum, xanthangum sodium alginates [8], kendu mucilage [9] find extensive application as flocculants. The majority of the cationic groups of polyelectrolytes are derived by introducing quaternary ammonium groups onto the polymer backbone, although polymers containing sulfonium and phosphonium groups are used to a limited extent. The most commonly used cationic polyelectrolytes are poly(diallyl dimethyl ammonium chloride) (polyDADMAC). In the anionic group of polyelectrolytes, mainly two types of polymers are used; one type is polymers containing carboxyl functional groups and the other containing sulfonic acid groups. A representative of the former is poly(acrylic acid) and its derivatives, of the latter poly(styrene sulfonic acid) (PSSA).
In this study, flocculation behaviors of natural two polyelectrolytes extracted from cactus cladode were determined by applying classical jar tests. The flocculation tests were performed in the presence of these two polymers at different polymer dosages and pHs. Then, the settling rates and residual turbidity values of suspensions were recorded.

II. MATERIALS AND METHODS

2.1. MATERIALS

A batch of fresh cladodes of OFI, was obtained from a plantation in Sidi el Aidi (7° 37′ 33″ W, 33° 8′ 0″ N), Morocco, and stored at 4◦C until BFs and NP extraction (period not exceeding 10 days). Harvesting of cladodes was carried out in December 2013. The chemicals used in the experiment were of analytical grade and were procured from the Sigma–Aldrich, Fluka, and Merck. Bi-distilled water was used throughout. Natural clay was used to prepare synthetic turbid water, the clay was obtained from a dry lake that lies in the province of Berrechid (7° 35′ 59″ W, 33° 14′ 18″ N).

2.2. METHODS

2.2. 1. PREPARATION OF SYNTHETIC TURBID WATER

The collected soil was used as a model suspension. Two hundred grams of soil was dispersed in 1 L of deionized water in a high-speed blender to prepare a stock solution. The synthetic raw water was prepared by mixing various volumes of a stock solution with distilled water, for four hours rapid mixing and then set to stand for 30 min. Second, the 500 mL supernatant from the high turbidity synthesized raw water was diluted into distilled water. The mixture was diluted to 1000 NTU, the various parameters analyzed in this study were Turbidity and pH. Turbidity measurements were conducted using Digital Nepheloturbidity Meter (HANNA LP2000-11). The pH was measured using a Digital pH multi-parameter (Consort C3050). The multiple stirrer speed was set to the rapid mixing rate values (75, 100, 150 and 250 rpm) and the extracts solutions were added. After the predetermined rapid mixing time (5 min.), the mixing speed was reduced to the flocculation or slow mixing value (30 rpm) for a specified duration (60 min.) and these values were

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held constant during the experiments. The pH of the synthesized water was adjusted using H_2SO_4 (0.1N) or lime $Ca(OH)_2$ (also used as natural coagulant) in the pH range of 3–12.4. Data were processed using Microsoft Excel, and the curve of turbidity *vs*. flocculation time was plotted.

2.2.2. BFS AND CP EXTRACTION

Prior to CP extraction, the fresh cactus pads were cleaned to remove thorns and cut into small pieces (1*1 cm) with a kitchen knife. Cactus pieces were heated in water at 85°C for 20 min to inactivate enzymes and left to cool to ambient temperature; neutralized to pH 7.5 from initial pH 4.0 in order to induce de-esterification of methoxyl groups and filtered through a cloth filter to extract as much BFs as possible. Then the solid residue was extracted by aqueous solution of 0.5% oxalate (0.25% oxalic acid + 0.25% ammonium oxalate) (2 × 2 hours at 85 °C) **[10].** All extracts were separated from the residues by filtering through a nylon cloth **[10],** and the solid products obtained were precipitated by centrifugation (30 min, 4500 rpm) with 2 volumes of acetone resulting in a Water-Soluble extract (BFs) and Chelating-Soluble extract (CP).

III. RESULTS AND DISCUSSION

3.1. DETERMINATION OF THE OPTIMAL pH

The experiments were performed with a fixed coagulant aid dose of 0.5 %.Wt (optimum dose condition (unpublished results)). Prior to the addition of the coagulant aid, experiments were carried out with different pHs in order to determine the optimal pH values for performing the experiments. These were found to be 11.3 and 12.4 for BFs (figure 1A and 1B). However, the polyelectrolyte CP doesn't show any elimination power at all pHs values (figure 2A and 2B).

Figure. 1A and figure. 1B show that BFs produces an appreciable removal of turbidity close to pH 2.0 and 11.3. Maximum removal observed was 93.5% after 20 min of flocculation, with a residual turbidity of 7 NTU for pH 2.0, and 98.3% with a residual turbidity of 3 NTU for pH 11.3 and the floc observed to be very coarse and settled easily. However, Figure. 2A and Figure. 2B, illustrate that CP has no effect on percentage removal of turbidity, and it found a maximum removal about 61.3% in the pH 11.5 (with a residual turbidity higher than 100 NTU). However, for other pHs turbidity increases, compared with that without the addition of CP (Figure. 2A). All the residual turbidities satisfies World Health Organization's (WHO) limit (5 NTU) for drinking water **[11].** It was clear from the present study that the BFs showed a good coagulating activity in conjunction with lime for synthetic turbid water.

The behavior of colloids in water is strongly influenced by their electrokinetic charge. Each colloidal particle carries a like charge, which in nature is usually negative. This like charge causes adjacent particles to repel each other and prevents effective agglomeration and flocculation. Visually, the flocs formed in the settling tests were very much smaller for CP than for BFs, suggesting that there was less extensive interparticle bridging by CP. Huber (1993) **[12]** indicated Ca2+ ions bind to the carboxylate groups of dissociated

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polyacrylates in aqueous solution and if the binding capacity is exceeded, an insoluble salt forms. Others have interpreted this as gelation from bond formation between the cation and polyacrylate chains and that addition of Ca2+ to partly neutralized polyacrylates causes a much stronger coil contraction than an equivalent amount of Na+ [13, 14]. Both Henderson and Wheatley (1987a) [15] and Sommerauer et al. (1967) [16] indicated that Ca2+ and Mg2+ form one-to-one complexes with carboxylate groups and therefore only have a minor influence on polymer conformation through the polyelectrolyte effect.
According to the results of our recent work [17, 18], we confirmed that our bio-flocculant soluble in water gives excellent removal efficiencies of colloids difficult settleable. We can suggest a mode of action of our high molecular weight polyelectrolyte according to the schematic of figure 3.

Fig. 1A- elimination power of BFs

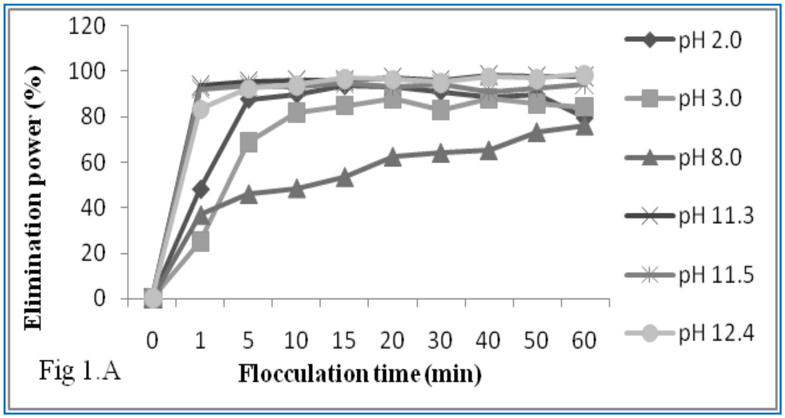

Fig. 1B - residual turbidity with BFs as coagulant aid

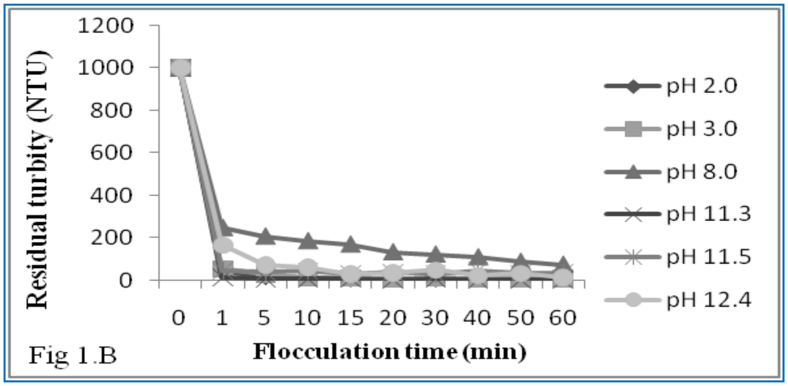

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Fig. 2A - elimination power of CP

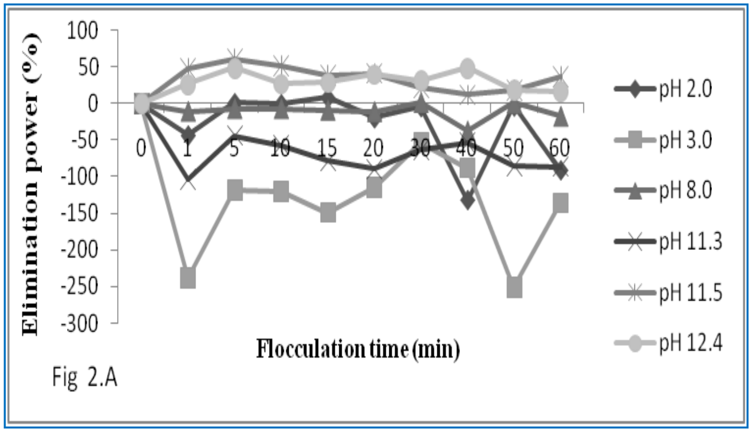

Fig. 2B - residual turbidity with CP as coagulant aid

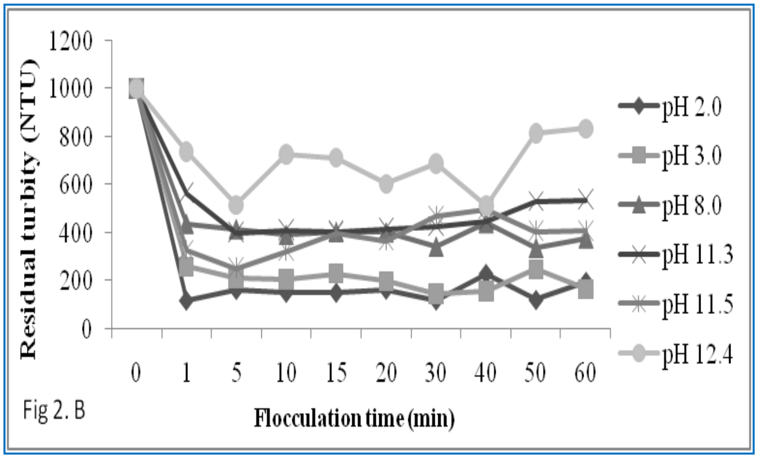

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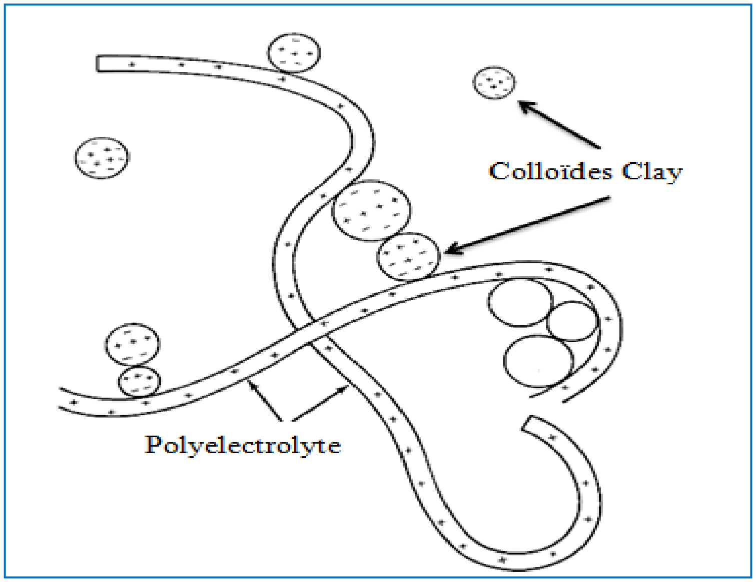
Fig. 3- mechanism of interaction between clay colloids and polyelectrolyte



IV. CONCLUSION

From the preceding results, it can be concluded that the flocculation efficiency of most of BFs have potential to replace synthetic flocculants. The words ‘‘Pollution’’, ‘‘Environment’’ and ‘‘Ecofriendly’’, have come into more and more frequent usage and the cleanliness of the world we live in has become the concern of all people. The experimental results of present study confirm that the turbidity removal efficiency by BFs was superior to that of CP. This flocculants may be composed of polysaccharide, proteins, lipids, lipoproteins, lipopolysaccharide…Etc. One obvious advantage of using renewable materials is the minimal net effect on global warming. Other advantages include biodegradability and sustainability.

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