International Journal of Scientific Engineering and Technology (ISSN : 2277-1581)
Volume No.3 Issue No.6, pp : 734-737 1 June 2014

Comparison of the Efficacy of Two Bioflocculants in Water Treatment

Belbahloul Mounir*, Zouhri Abdeljalil and Anouar Abdellah

Laboratory of Applied Chemistry and Environment, Faculty of Science and Technology of Settat
3 km, B.P.: 577 Road of Casablanca
*Email: belbahloulmounir@yahoo.fr

Abstract: ***The flocculating activity of mucilage and pectin extracted from cactus leaves of Opuntia Ficus Indica (OFI) was investigated. For the applications of mucilage or pectin, as bioflocculant, they showed more than 98% of the flocculating activity in Sanmix clay suspension. The presence of bivalent cations (Ca2+) did not enhance flocculating activity. The effect of mucilage on coagulation performance and floc characteristics with polyaluminum pectin was evaluated in synthetic turbid water treatment. The optimum dosage of mucilage and pectin was found to be 2~8 mL and 2~6 mL by one litre of turbid water, respectively. The optimum pH was found to be 3.0 for synthetic water.***

Keywords – cactus, pectins, mucilages, clay, water treatment, coagulation-flocculation

I. Introduction

Coagulation and flocculation, a well-established process in wastewater treatment, is used to remove suspended particles by aggregating small particles into larger-sized ones. Coagulants based on hydrolyzing metal salts are widely used. The metal salts hydrolyze rapidly to form various cationic species, which are adsorbed by negatively charged particles and cause charge neutralization. Bioflocculant is a kind of biodegradable macromolecular flocculant secreted by microorganisms and plants. Because of their biodegradability, harmlessness and lack of secondary pollution, bioflocculants have gained much wider attention and research to date **[1]**. Bioflocculants are widely useful in the treatment of water and wastewater, in downstream processing, and in processing of food and chemicals **[2]**. In wastewater treatment, bioflocculants have been used to treat dyes solution **[3,4]**, inorganic solid suspensions (bentonite, activated carbon, solid clay, Ca(OH)2 , and aluminum oxide) **[5-7]**, humic acids **[8]** and other suspensions which are synthetic **[9,10]**. Although chemical flocculants have been widely used because of their effective flocculating activity and low cost, they have neurotoxic and carcinogenic monomers, and their use is restricted **[11]**. In recent years, the use of bioflocculants has been promoted as a solution to environmental problems because their intermediates are harmless and biodegradable. Application of cacti species for water treatment is rather recent compared to other natural coagulants such as nirmali orM. oleifera. The most commonly studied cactus genus for water treatment is Opuntia which is colloquially known as 'nopal' in Mexico or 'prickly pear' in North America.

Several types of bioflocculants have been previously reported, and some of them showed efficient flocculating activities comparable to those of the synthetic flocculants for not only inorganic but also organic suspended particles **[12,13]**. However, they have the common problem of high production costs compared with the synthetic flocculants, because relatively expensive substrates such as glucose, fructose, sucrose and L-glutamate are necessary for their production **[14]**. In addition, final concentrations of bioflocculants after fermentations are also relatively low from an industrial point of view. The production of the biopolymer from inexpensive single carbon sources has potential for commercial production of biopolymers since it can address the critical problem of substrate costs as well as easier control of the bioprocess **[15]**. New possible sources of biopolymeric flocculant are pectins and mucilage **[16,17]**. Pectin can be described as a single extracellular matrix which is a complex structure that is formed continuously through the body of the plant. The cell matrix consists of various types of polysaccharides, protein and lignin. Pectin can be categorized as one of the anionic polysaccharides in the cell wall that consists of ''smooth"a-Dgalacturonic acid with 1–4 linkages region monomer **[18]**. Pectin can be extracted from outer cell layer of oranges, apples, grapes, peaches, etc. Pectin is extracted on an industrial scale from plant (waste) materials, e.g. apple pomace and citrus peel, and used by the food industry due to their ability to form gels under certain circumstances and to increase the viscosity of drinks.

Although most bioflocculants can be used to flocculate Kaolin suspension, they show different flocculating ability for other particles or colloids in aqueous solution. **Oh et al. 2001 [19]** reported that the bioflocculant produced by Paenibacillus sp. was successfully used to harvest Chlorella vulgaris from culture broth. **Deng et al. 2003 [20]** found a polysaccharide bioflocculant to be effective in the recovery of the organic solids from starch wastewater. In the present paper, we examine the removal of Sanmix clay in synthetics waters, by the mucilage and pectins extracted from cactus cladode OFI, depending on different growth stages of pads and at different pH.

II. Materials and methods

II .1. Materials

OFI, a species of the cactus was collected from a farmhouse in the region of Settat Morocco. The cladodes were neatly washed with water in order to remove dirt from the materials used before mucilage and pectins extraction. Pads obtained are classified according to their weight in four stages (**table 1**). Sanmix clay was used as a subject in suspension to evaluate the flocculating capability of a series of bioflocculants. Flocculation tests have been performed according to jar-test method, using a jar-test VELP Scientifica JLT6, equipped with six mixing posts. The pH was adjusted with a multi-parameters Consort C3050.

Table1. *cladodes ranked according to their weight*

Stage of growth	Weight (g)
1	<100
2	100-250
3	250-400
4	400<

II .2. Methods

a) Mucilage and pectins extraction

The fresh cactus pads were 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 mucilage as possible [21]. Pectic polysaccharides were extracted from residue by water (2 × 2 hours at 85 °C) [22]. The two series of bioflocculants were purified according to Belbahloul et al. 2014 [16].

b) Preparation of synthetic turbid water

Flocculation tests were conducted with suspensions of fine sanmix clay in water. The clay suspensions were prepared by adding appropriate amounts of sanmix powder (8 g per litre) into 500 mL tap water to obtain a solid concentration of 0.4% in suspension and stirred with jar-test for 60 min (200rpm). The turbidity of the synthetic water was approximately 1000 Nephelopmetric Turbidity Units (NTU). The natural pH value of suspension was about 8.0. The effects of pH on the flocculating activity of mucilage and pectins extracted from different stages of growth of pads were examined. To investigate the effect of pH on flocculating activity, the pH of the suspension was adjusted using HCl (0.1N) or lime solution in the pH range 3.0–12.4, by fast mixing (180 rpm) for 2 minutes, while flocculation step was done for 60 minutes, at 40 rpm. All tests have been performed in 1 liter cylindrical bakers, at ambient temperature. The bioflocculants used for flocculation are the mucilage and pectins extracted from cladodes, purified and finally suspended in distilled water at different dosages ranged from 1 to 6 ml of 0.2 % bioflocculant . Samples of synthetic turbid water were removed from the jar at specified time intervals of flocculation tests (60 min). Samples were always removed from exactly the same point in the jar. This point was 2 cm below the surface of the water in order to limit the influence of vertical aggregation.

We note that MP_i /WP_i: the mucilage/ pectin extracted from the cladode at growth stage i.

III. Results and discussion

III.1. Effects of pH on kaolin suspension without use of bioflocculants

Flocculation is due to decline of charge density by supplied cations, leading to inter-particle bridging between clay particles. The pH of reaction mixtures is also known to be a key factor influencing flocculating activity. Therefore, the effect of pH was determined by adding HCl or lime to suspension at different pH values without added flocculants. As shown Fig. 1, turbidity remains around 1000 NTU during the flocculation step for all pH range from 3.0 to 12.4, suggesting no synergistic effects with the addition of bivalent cations (Ca(OH)2) or H+.

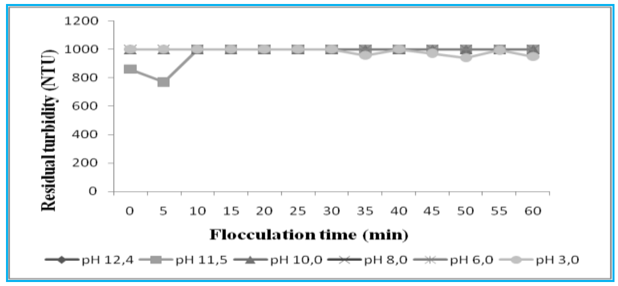

Figure 1. *Effect of pH on flocculating activity of kaolin without bioflocculants*

III.2. pH optimization for mucilage and pectin as bioflocculants

The experimental pH values of the synthetic water were set from 3.0 to 12.4. An equivalent amount of 4 mL/L bioflocculants (mucilage or pectin) was added and the flocculation activity was tested. Fig. 2 shows that pH has a great effect on flocculation activity. Flocculation activity is very poor under strong alkali conditions, i.e., small less than 60% for pH over than 10. For pH 10 and lower than and in acidic conditions, the flocculation activity reached 97.2% for mucilage and 98.8% for pectin at pH 3.0. The effect of pH on the flocculation activity in turbid water is probably caused by the charge property. For a natural pH of the clay (pH.8.0) and with the addition of only one of our two bioflocculants, elimination of the turbidity can reach 95.4%, 94.8% for the mucilage and pectin respectively (fig. 2b and 2d).

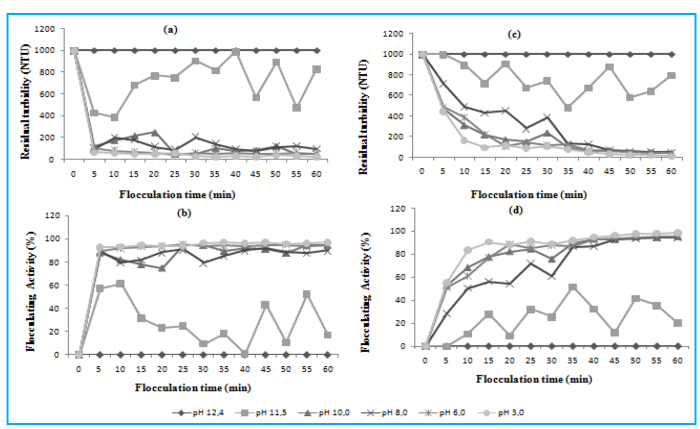

Figure 2. *Effect of pH value on the Removal of turbidity using (a,b) mucilage or pectin (c,d) bioflocculant.*

Some bioflocculants have more binding site and stronger Vander Waals forces than traditional flocculating agents, which strengthens its bridging ability between suspended clay particles. However, under an alkali condition the ionization of -COOH in bioflocculant will be blocked, restraining the bridging actions. While under an acidic condition,-COOH will be ionized into COO^-, and H^+ will be increased, both of them can promote the flocculating efficiency of bioflocculant.

III.3. Effect of bioflocculant concentration on flocculation activity

According to Gong et al. 2008 [23] inadequate dosage of bioflocculant will lead to a poor bridging phenomenon, thus resulting in low flocculating activity while excess input might induce re-stabilization of kaolin particles. We determined the effect of various flocculants concentrations on flocculation activity at pH 3.0. Fig. 3 shows that the bioflocculant concentration has, to a certain degree, an effect on flocculation. With a concentration of 2~8 mL/L for mucilage and of 2~6 mL/L for pectin, the flocculation activity achieved maximum and equilibrium. With the concentration greater than 8 or 6 mL/L for mucilage and pectin respectively (fig. 3c and 3d), the flocculation activity started to decline and the phenomenon “flocculation deterioration” appeared. Probably some colloidal particles were wrapped up by the highly concentrated flocculant and a “colloid protection function” formed, hence the flocculation activity reduced. These results could be clarified as follows: a) The incomplete dispersion of excess polysaccharide, only the clay particles around the polysaccharides participated in the flocculation reaction, therefore, other clay particles did not participate in the reaction [24], and b) The excess polysaccharide was oversaturated on many binding sites of the surface of clay particles, thus the attractive force of the other particles was reduced and the flocculation activity decreased [25]. Thus, either the deficiency or excess amount of polysaccharide and sanmix clay decreased or even prevented the flocculation activity (lee et al.1995) [26].

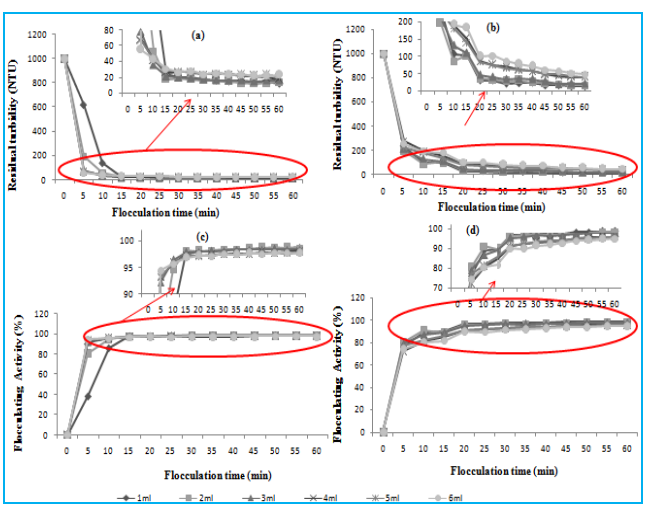

Figure 3. Effect of flocculant dosage on the removal of turbidity; conditions: pH value 3.0; bioflocculant dosage ranged from 1 to 6ml by 500ml of synthetic water

III.4. Effect of growth of cladode on the bioflocculant character of the mucilage and pectin

A comparative evaluation of different bioflocculants extracted from different growth stage was performed at optimum conditions. The flocs were very big and visible to the naked eyes when mucilage was used. Fig.4. shows the relationship between the growth of leaves and flocculation activities. It is important to notice than pectin gave more favourable results than mucilage. The flocculation efficiency with different extracts showed the same trend, which means that the age of the cladode has no effect on the character flocculants of these extracts and it was found that both bioflocculants were almost equally efficient, when the optimum conditions were applied. From the data obtained, it was observed the higher turbidity removal for WP_2 and WP_3 (reduction of 99.3 % after 50 min) followed by WP_4 (reduction of 99% after 50 min), WP_1 (reduction of 98.8% after 45 min), MP_1 and MP_3 (reduction of 98.6 after 45 min for MP_1 and 50 min for MP_3) and MP_2 and MP_4 (reduction of 98.4% after 50 min for MP_2 and 55 min for MP_4; fig.4a). In the experiments with MP_i and WP_i as bioflocculants, the lowest residual turbidity was 12 and 5 NTU, respectively (Fig. 4b) from initial turbidities of 1000 NTU. Water with a high turbidity can be very difficult or impossible to properly purify. These findings suggest that the bioflocculant could conveniently act as alternatives to many inorganic and synthetic flocculants.

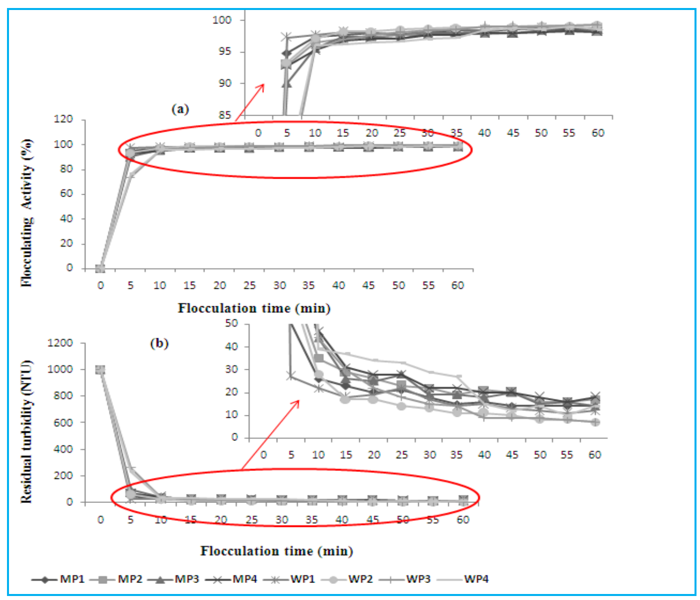

Figure 4. *Comparison of different flocculants on the Elimination of suspended matter with; MPi: mucilage extracted at growth stage i and WPi: pectin extracted at stage i*

IV. Conclusions

The effect of mucilage and pectin on flocculation behavior was assessed. Mucilage addition showed obvious positive effect on floc growth rate and floc size. Mucilage or pectin possesses several intrinsic properties such as its non-toxicity, its biodegradability and its outstanding chelation behaviour that make it an effective flocculant for the removal of contaminants in the dissolved state. It has the physico-chemical characteristics of both coagulants and flocculants, i.e., high cationic charge density and long polymer chains, leading to bridging of aggregates and precipitation.

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