Emerging plant-based flocculation treatment of phosphate clay: case study from Metlaoui-Gafsa (southwest Tunisia)

Feyda Srarfi, Raouen Rachdi, Karim Khela and Najet Slim Shimi

ABSTRACT

The objective of this study was to investigate the ability of cactus *Opuntia ficus-indica*, used as a natural flocculant in the treatment of phosphate clay as an industrial wastewater. It is a new process that has proven very promising in the removal of high turbidity from industrial effluents. The volume of clear water recovered (supernatant) is one of the characteristic features which allow us to judge the effectiveness of this bioflocculant. The following of the settling velocity on the one hand and the analysis of supernatant and sludge on the other hand allow us to compare the cactus-based flocculant effectiveness with that of a chemical flocculant (CF) of anionic polyacrylamide nature. The optimum pH required for maximum settling velocity was found to be 12. Obtained results indicated that after 900 seconds of settling, the highest volume of clear supernatant was obtained with the natural flocculant (740 mL/L), against 666 mL/L obtained with CF. Several analyses on recovered clear water (pH, turbidity, Cu, Zn, Fe, Cd and Cr) and on dry sludge (P_2O_5, CaO, MgO, organic C, SiO_2 and Cd) are highlighted.

Key words | cactus, clay of phosphate, flocculation, Metlaoui-Gafsa, mining industry, pH

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INTRODUCTION

Tunisian phosphate manufacturing plays a major role in the development and industrialization process of the country and its integration into the world economy. During this process, ground phosphate rock is firstly extracted from the mines and sent to recovery units to separate sand and clay and to remove impurities. Most of the processes are wet to minimize the emission of dust and to facilitate transport.

The activities of phosphate ore beneficiation need a large quantity of water and subsequently generate a significant discharge of polluted wastewater called 'phosphate clay'. These releases are extremely heterogeneous. They are loaded with various pollutants that can cause environmental degradation and endanger health. According to Galfati *et al.* (2011), these releases are rich in phosphate and trace elements; the average is around these values: P_2O_5: 10.96%, Cd: 25.83 ppm, Zn: 260.91 ppm, Cr: 387.7 ppm, Cu: 16 ppm, Ni: 26 ppm and Sr: 717.15 ppm. Soils adjoining these rejects present total concentrations in Cd, Zn and Cr higher than to the maximal contents tolerated in soils. The diversity of these effluents requires a specific treatment. To process them, the Gafsa Phosphate Company (GPC) uses a very expensive chemical flocculant (CF) which may cause environmental problems. The coagulation/flocculation process is used to remove pollutants (Miller *et al.* 2008). These materials can be classified into inorganic products and synthetic organic polymers. Several studies show that the use of this kind of synthetic chemical is very effective. But it has significant disadvantages in terms of health protection as well as the environment (Ben Rebah & Siddeeg 2017).

The use of conventional chemical-based coagulants increases residual levels of chemical products. That is why they are considered harmful to the environment and toxic to fauna and flora. In addition, they have a relatively high procurement cost (Rachdi *et al.* 2017).The cost and the environmental side-effects of these compounds led many researchers to investigate the possibility of using plant-based coagulants in water and wastewater treatment. Naturally occurring products are biodegradable and are presumed safe for human health (Miller *et al.* 2008; Theodoro *et al.* 2013). There have been numerous studies focused on the use of plant-based coagulants for treatment

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of turbid water but the application of these natural products for industrial wastewater treatment is still at the early stages.

Cactus is one such plant that has received a great deal of attention in recent years because it has multiple uses and benefits in different areas (cosmetics, medicinal, food, etc.). It shows a bright future because of its multifunction, biodegradation and abundant source (Miller *et al.* 2008). It allows, maybe, a fight against the aforementioned drawbacks. The cactus species *Opuntia ficus-indica* (OFI) has long been associated with multitude properties.

Cactus is known for its mucilage production. The mucilage is a complex polymeric substance of carbohydrate nature with a highly branched structure (Sepúlveda *et al.* 2007; Belbahloul *et al.* 2014) that contains polygalacturonic acid and five neutral sugars (L-arabinose, D-galactose, L-rhamnose, and D-xylose) (Trachtenberg & Mayer 1980; Betatache *et al.* 2014). These polysaccharides swell when dissolved in water, or in some cases form colloidal and very viscous suspensions or jellied masses (Sepúlveda *et al.* 2007). There are other minerals present, such as Ca^{2+} and K^+, carbohydrates and dietary fiber. The dried mucilage had on average 5.6% moisture; 7.3% protein; 37.3% ash; 1.14% nitrogen; 9.86% calcium and 1.55% of potassium (Sepúlveda *et al.* 2007).

In this research work, OFI was tested as flocculating agent. The objective of the present study is to investigate the potential use of this biomaterial as natural flocculant to treat phosphate clay, an wastewater. A commercial flocculant now used by GPC was also applied in this study in order to compare the flocculation performance with the natural flocculant. The effectiveness of this treatment was evaluated by the volume of clear water recovered in 60, 180 seconds and 900 seconds (an industrial specification). The optimal dose, the volume of clear water and the change of different chemical parameters were followed (P_2O_5, CaO, MgO, organic C, SiO_2 and Cd for the dry sludge and pH, turbidity, Cu, Zn, Fe, Cd and Cr for the recovered clear water). The physico-chemical studies on phosphate clay, after treatment, are very rare in the literature, so this study gives a new contribution in scientific terms.

MATERIALS AND METHODS

In Tunisia, Metlaoui is the most important mining city. It is attached to the governorate of Gafsa (southwest Tunisia): latitude 34.33333333°, longitude 8.36666667°. It is bounded by the cities of Mdhilla, Redayef and Om el Araies, and the governorate of Tozeur in the southwest (Figure 1).

Figure 1 | Location of study site.

Phosphate clay preparation

Mining exploits all layers with different qualities and a higher or lower pollution rate. So a preliminary washing of the ores, in the phosphate laundries, is necessary. This process is a means of enriching the phosphates. In fact, this enrichment is accomplished by releasing the phosphate grains trapped in clay and limestone clumps by mixing with water and by removing the coarse particles (greater than 2 mm). Grains less than 2 mm in diameter pass through the screen grid and will be recovered in a tray that is fed with clear water. To further enrich the phosphate ore, another cut known as 'low cut' eliminates grains with diameters less than 71 μm by cycloning. This fraction is called the phosphate clay.

In this study, all tests were performed on clay of phosphate of Kef schfaier. The clay was prepared in the laboratory of the Process and Valorization Division in the Research Center (RC) of the GPC. The procedure of clay preparation conformed to that described in the phosphate laundries for washing phosphate.

Plant material

The cactus OFI used in this study was collected during January 2015 from the region of El-Sned (in Gafsa in southwest Tunisia): latitude 34.47000000°, longitude 9.26694444°.

Preparation of cactus powder

The pads of cactus were washed and subsequently sliced into small pieces to facilitate drying. The sliced cactus was then dried in an oven at 80 °C. The dried cactus was milled into fine powders using a mortar and subsequently sieved to obtain a fine powder with granulometry lower than 250 microns.

Preparation of a stock solution of bioflocculant

A stock solution of cactus powder was prepared as needed by diluting 75 g into 1,000 mL of distilled water and the mixture was subjected to stirring at 100 rpm for 20 minutes. A working stock solution was prepared fresh for each experiment. The pH of the natural flocculant-based cactus (NFC) was acidic in the presence of water (in the range 3–4.5). The pH of the bioflocculant preparation was adjusted to value 12 by adding NaOH solution.

Preparation of a stock solution of chemical flocculant

A comparative study using an industrial flocculating agent (containing anionic polyacrylamide) showed that the natural flocculating agent had a very good competitiveness and strong capacity for flocculation. A stock solution of industrial flocculant was prepared as needed by diluting 3 g into 1,000 mL of distilled water and the mixture was subjected to stirring at 850 rpm for 20 minutes. A working stock solution was prepared fresh for each experiment. The pH of this CF preparation was neutral in the presence of water.

Experimental work

Flocculation tests were carried out to determine the flocculation properties of the plant-derived flocculants. Jar tests were used to determine the effectiveness of using cactus powder for treatment by flocculation of phosphate clay. The test was conducted via jar test apparatus (FC 6 S Series Flocculators VELP Scientifica) using 1 L capacity jars. Cactus powder with dosages of 15, 22.5, 26.25 and 30 g/L was tested. Following the addition of the flocculant dosages (CF and NFC), the samples were subjected to different speeds of agitation. Then the floc was allowed to settle undisturbed for 900 seconds. Effect of variation of pH on the effectiveness of the cactus was also studied by varying pH of turbid water. pH of the suspension was adjusted to the desired value by adding NaOH solution.

Measurement and analysis

To better ensure the flocculant activity of cactus as a bioflocculant, a set of analyses were performed. All analyses were carried out according to an internal protocol at the Chemical Analysis Laboratory (CAL) of the RC of the GPC. These analyses were realized in the Chemistry and Processing Division of the GPC RC. This center was certified according to ISO 9001 version 2000 in June 2006.

The supernatant samples were withdrawn using a pipette from a depth of 5 cm below the surface of each graduated cylinder, and chemical measurements were taken. The turbidity was measured as follows: after sedimentation for 15 minutes, 25 mL of the sample was collected from the middle of the beaker and residual turbidity was determined using a turbidimeter (DR/2010 Hach) and it was expressed in nephelometric turbidity units (NTU). The pH was measured using a pH meter (Hach brand, model ION1 direction). Fe, Cd, Zn, Cr, and Cu were analyzed using an atomic absorption spectrometer (Analytic Jenna Nova AA 400).

Analyses of dried sludge obtained after the treatment were performed too. P_2O_5 and CaO were determined with a continuous-flow auto analyzer (Technicon). The determination of organic carbon (C) in phosphates consists of an oxidation of organic C by potassium dichromate titrated in sulfuric acid medium. After dissolving the dried sludge sample with $HClO_4$, HF and HNO_3, the measurement of MgO was made by atomic absorption in an air-acetylene flame and a wavelength of 285.2 nm. SiO_2 and Cd were analyzed by atomic absorption spectrometer Perkin-Elmer Analyst 800.

Statistics analysis

All chemical analyses were measured and tabulated. Values of experimental results shown in tables and figures are the mean of at least three determinations (±standard deviation).

RESULTS AND DISCUSSION

Influence of the solution pH

To study the effect of pH, tests were conducted on turbid water with acidic pH, neutral pH and basic pH (varying from 10 to 12). The initial pH of the natural cactus in water was acidic, in the range 3–4.5. The presence of galacturonic acid (Miller *et al.* 2008; Torres *et al.* 2014) and acaraminic acid (Torres *et al.* 2014) cause this acidic pH. Firstly, tests were conducted on phosphate clay with this initial pH. For this part several doses were tested, but the results obtained showed a negative efficacy of cactus as a flocculant. At this pH there is no flocculation. This initial pH is not effective. The result of this study was very much comparable with the results of Miller *et al.* (2008).

Secondly, the efficacy of cactus in flocculation tests was also studied at a neutral pH. Adjustment of pH in a solution of natural cactus in water was conducted by the use of NaOH. The experiment showed very bad flocculation. So according to the literature, the best bioflocculating efficiency of cactus is obtained at basic pH. Miller *et al.* (2008) considered that the coagulation activity of *Opuntia* is greatest in basic waters (around pH = 10). Also, Belbahloul *et al.* (2014) considered that cactus produces appreciable reduction of turbidity only between pH 11 and 12.

For this study, the influence of basic pH of cactus solution was investigated in the following experiments. Dosage of OFI was 15 g/L at 150 rpm for 1 minute (arbitrary choice of the dose, used only to see if the pH has an effect on the phenomenon of flocculation by the use of cactus). The procedure was repeated over the pH range 10 to 12 of the NFC.

The results (Figure 2) show that the increase in pH value has positive effect on flocculation activities of cactus at high investigated turbidity of water (clay of phosphate). The flocculation activity of OFI is greatest at basic pH 12. So the flocculation process depends on pH value of the crude preparation of this biomaterial. This confirms the results obtained in several previous works (Zhang *et al.* 2006; Miller *et al.* 2008; Theodoro *et al.* 2013). They demonstrate that the performance of the cactus as bioflocculant at basic pH is improved.

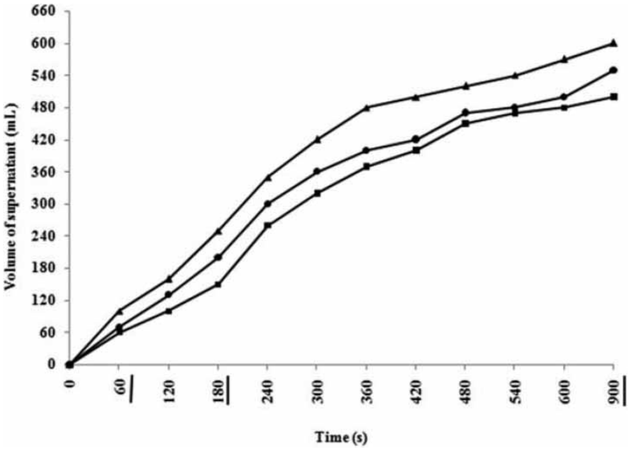

Figure 2 | Time course of water content under various pH conditions (pH = 10 (■); pH = 11 (●); pH = 12 (◄)).

The relation between basic pH and high efficiency can be explained by the coagulation mechanism described by Miller *et al.* (2008) as a mechanism of adsorption and bridging. The hydrogen bonding and dipole interactions are the main factors responsible for the adsorption for *Opuntia* cactus species. Mucilage also can contribute to the observed relation between pH and cactus flocculation efficiency. In fact, Trachtenberg & Mayer (1980) reported that the viscosity of the mucilage from *Opuntia* increases with pH increase. Fox (2011) found that the cactus extract viscosity increased with increasing pH, and explained this as being the result of a more expanded configuration for the mucilage. Many authors highlighted the cells' mucilage role in the coagulation mechanism (Trachtenberg & Mayer 1980; Miller *et al.* 2008; Fox 2011; Carpinteyro & Torres 2013; Theodoro *et al.* 2013; Torres *et al.* 2014; Nougbode *et al.* 2016). This mucilage, especially the galacturonic acid component may explain some of the turbidity reduction by *Opuntia* (Miller *et al.* 2008).

Effect of cactus OFI concentration

To determine the optimum dose of bioflocculant, we performed several tests while varying in each case the supplementary dose of cactus-based flocculant in one liter of phosphate clay concentrated at 60 g/L. Then the suspensions were left for sedimentation. So during this stage, the optimal dose, the volume of clear water and the evolution of different chemical parameters were followed. We tracked the volume of clarified water samples for 900 seconds.

Results on optimization of the bioflocculant dosage for phosphate clay are presented in Figure 3. With 150 rpm for 1 minute, the influence of cactus solution dose on flocculation activity was investigated in following experiments.

According to the GPC, the choice of the most efficient dose of flocculant is made according to the volume of clear water after 60 and 180 seconds of settling. The highest volume of clear supernatant obtained with the 26.25 g of NFC per one liter of phosphate clay was 210 and 470 mL/mL for respectively 60 and 180 seconds settling. After 900 seconds, the total volume of clear water recovered was 730 mL. The increase of flocculant dose increased flocculation activity of cactus. This sedimentation behaviour is typical of all observations with a variety of suspensions of

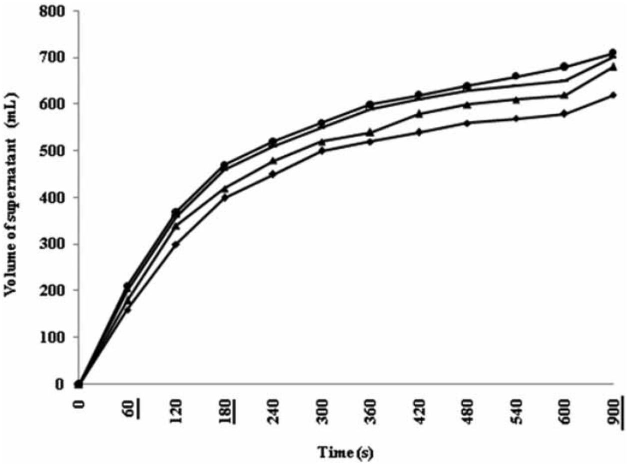

Figure 3 | Time course of water content under various bioflocculant concentrations: 15 g of NFC per one liter of phosphate clay (■); 22.5 g of NFC per one liter of phosphate clay (◄); 26.25 g of NFC per one liter of phosphate clay (●); 30 g of NFC per one liter of phosphate clay g/L (-).

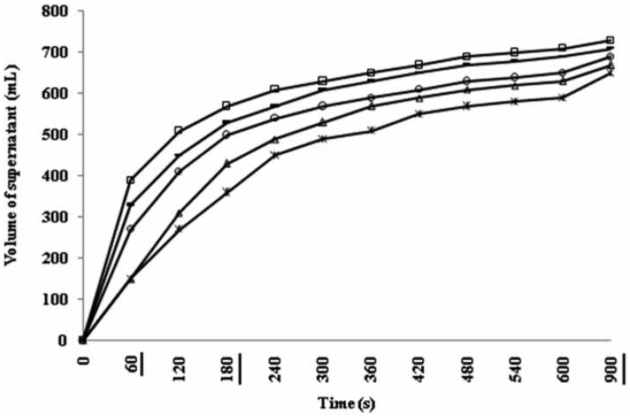

Figure 4 | Time course of water content under various frequencies of agitation: 30 rpm (-); 60 rpm (□); 90 rpm (○); 120 rpm (Δ); 150 rpm (*).

phosphate clays flocculated with a modified starch and gums (La Mer & Smellie 1958). At doses more than 26.25 g of NFC per one liter of phosphate clay, the increase of flocculant dose of cactus led to the decrease of flocculation activity. The observed reduction in coagulation activity when the flocculant dose is too low or too high is consistent with a bridge mechanism as a stoichiometric relationship between particle concentration and flocculant dose is expected (Miller *et al.* 2008). The excessive dose of the polymer flocculant prevents the formation of the linkage between colloidal particle and the chain of the compound of natural coagulant due to the lack of ionizable sites available (Theodoro *et al.* 2013). Observed floc stability and compactness after a few minutes of the flocculation process in this work give emphasis to an effective flocculation mechanism. Moreover, La Mer & Smellie (1958), contested the zeta potential control stability in the flocculation of phosphate suspensions. Also, Miller *et al.* (2008) excluded the zeta potential control in the flocculation by *Opuntia*. Rachdi *et al.* (2017) have found that the use of cactus in the flocculation process allows the formation of larger and heavier flocs which facilitate their sedimentation.

Effect of agitation on the flocculation of phosphate clays

It is necessary to carry out detailed systematic study of the effects of mixing intensity and agitation time. Floc size can be affected significantly by varying the agitation when all other factors are controlled (La Mer & Smellie 1958). So, tests were conducted on clay of phosphate with different speed of agitations varying from 30 rpm for 1 minute to 150 rpm for 1 minute. We used the optimal dose of NFC determined previously.

According to Figure 4, it was found that the natural flocculant produces higher clear water content of 370, 570 and 740 mL/mL for respectively 60, 180 and 900 seconds with 60 rpm for 1 minute. This stirring speed is sufficient for the natural flocculant to be dispersed in the sample to be treated and to well perform its function.

A comparison of chemical flocculant and cactus powder performances

We compared the efficacy of this bioproduct based on cactus with the efficacy of the chemical product based on anionic polyacrylamide. The tests were done on phosphate clay (industrial fine rejections samples prepared in the laboratory). The optimal dose of CF used for this type of sample was 0.6 g of CF per one liter of phosphate clay. It should be noted that the natural sedimentation was very slow.

At the beginning of the decantation phenomenon, the effect of CF was better than that of cactus. The highest volumes of clear supernatant obtained with the CF were 596 and 660 mL/mL for respectively 60 and 180 seconds. The volumes of clear supernatant obtained with the NFC were 310 and 510 mL/mL for respectively 60 and 180 seconds. But at the end of this phenomenon (after 900 seconds), the higher volume of clear content water was obtained with cactus (740 mL/L). When we used the optimal dose of CF, the volume of clear supernatant measured 666 mL/L.

The high settling rate obtained by the use of bioflocculant-based cactus is mainly related to the size and the floc formed form. With natural coagulant, as slow mixing proceeds, the threadlike floc produced at the beginning of the process, grows in length and circumference (Miller *et al.* 2008). At the end, the flocs are stable and never disintegrate even when subjected to rapid mixing. So under the influence of gravity, these larger flocs fall faster. Results of this study were very much comparable with the results of Young (2006).

It is obvious that cactus performs as a more efficient flocculant thanks to its ability to form larger flocs than the CF. This was compared with the finding of a study conducted by Yin *et al.* (2007). According to Belbahloul *et al.* (2014) the flocs obtained are very coarse and settled almost completely in less than 10 min.

The treatment with cactus powder as bioflocculant reduced significantly turbidity and suspended solids, but the apparent color remained slightly yellow. Similarly, Zhang *et al.* (2006) indicated that the final water content obtained with cactus had an obvious yellow color. The *Opuntia* bioflocculant does not eliminate organic matter responsible for the color of the water. Comparable results were found by Nougbode *et al.* (2016) with *Aloe vera*.

Characteristics of dry sludge

The quality of sludge produced by the use of NFC was observed to be denser (102.3 g/L) than the sludge produced by natural decantation (71.80 g/L) or by the use of CF (95.1 g/L). Bioflocculant produces denser sludge related to the nature of cactus mucilage. This was mucilage described by Miller *et al.* (2008) as a gummy substance. Carpinteyro & Torres (2013) note that *Opuntia* mucilage produced the maximum amount of sludge in comparison to many other bioflocculents and CF. Similar results were obtained in another study conducted by Madhukar & Yogesh (2013) by using other natural products.

It can be noted that the higher sludge production obtained with the use of the bioflocculant will have no negative effect on the subsequent treatment, as this sludge will be discharged into the hydrographical network by gravity, without any additional treatment.

It should be noted that the sludge production was higher as the polymer concentration increased. Torres *et al.* (2014) noted that sludge production (in mL/L) was very dependent on the coagulant/flocculant dose. As well, volumes of sludge were directly proportional to the pH value modification of the wastewater without the addition of any salt or polymer. This could imply that the sludge production was more related to the instability of the colloidal material at alkaline pH values.

Table 1 shows the characteristics of dry phosphate sludge obtained from raw phosphate clay as a blank (control), treated phosphate clay by CF and phosphate clay treated by the NFC after 900 seconds. The obtained results were very interesting.

The raw phosphate sludge represents the natural compounds considered as a reference to make comparisons. According to Table 1, P_2O_5, organic C and SiO_2 contents in sample treated by CF showed an increase with respect to the control. The rate of increase is respectively 1.43%, 0.11% and 2.03%. The concentrations for CaO, MgO and Cd showed a decrease with respect to the control. The percentage of reduction achieved was respectively 0.84%, 17.09% and 15.29%.

Compared to the sludge left over from natural decantation of phosphate clay (control), analysis of the clay of phosphate treated with cactus (NFC) showed a decrease in the contents of CaO (3.79%), SiO_2 (19.27%) and Cd (34.11%). Decreasing of concentrations of CaO, SiO_2 and Cd in the total amount of sludge is probably due to a bigger mass of natural flocculation sludge produced and a greater quantity of organic matter. However, P_2O_5, MgO and organic C are slightly increased. The use of natural flocculant may increase the organic load in sludge in water proved by Miller *et al.* (2008).

Recovered water measurements

A comparative study was made of water recovered at the end of treatment by the use of NFC and CF and the

Table 1 | Characteristics of dry sludge recovered from control (raw phosphate clay), CF (phosphate clay treated with chemical flocculant), and NFC (phosphate clay treated with natural flocculant-based cactus)

Parameters	Control	CF	NFC
P_2O_5 wt%	9.50 ± 0.56	10.93 ± 0.32	9.72 ± 0.12
CaO wt%	24.74 ± 0.62	24.53 ± 1.63	23.8 ± 0.50
MgO wt%	2.34 ± 0.08	1.94 ± 0.67	2.44 ± 0.17
Organic C wt%	1.89 ± 0.14	2.00 ± 0.20	3.21 ± 0.09
SiO_2 wt%	30.14 ± 0.39	32.17 ± 1.22	24.33 ± 0.55
Cd ppm	85 ± 1.03	72 ± 1.6	56 ± 1.5

Values correspond to the mean of three measurements ± standard deviation.

recovered water after natural decantation. The results are presented in Table 2 as a function of type of treatment.

According to Table 2, the pH variation was observed to be moderate. The pH of the industrial water sample (raw clay of phosphate) was 7.40 ± 0.42. The studies were conducted at this neutral pH. For CF, there was no significant change observed in the pH (7.25 ± 0.13). When the flocculation was completed with the solution of cactus, NFC appears to have no significant effects on the final pH of treated samples, it remained neutral (7.10 ± 0.29). In both cases the results are still within the range of standards recommended by the World Health Organization for drinking water (WHO) and Tunisian standards N.T 106.02 (1989) for the discharge of treated wastewater. So it does not require pH adjustment. Natural products are equally effective in treating water and are also unlikely to alter the pH of treated water. The Yin *et al.* (2007) study, involving surface water flocculation (estuarine and river water) by means of cactus *Opuntia*, showed marginal effect of increased cactus dosages on the water final pH (Yin *et al.* 2007). This result was also confirmed by Madhukar & Yogesh (2013).

From Table 2, the initial turbidity of the clear water recovered after natural decantation is high (68.9 ± 0.41 NTU). It could be seen that upon the application of flocculation treatment by the use of NFC the residual turbidity was in the range of 55.4 ± 0.99 NTU, while that of chemical product was in the range of 52.6 ± 0.81 NTU. In their study, Al-Saati *et al.* (2016) found that the water residual turbidity obtained with cactus remained high. This is a drawback of cactus that increases the organic matter in the water. Nougbode *et al.* (2016) note this fact with *Aloe vera* treatment of very turbid surface water. Also, the important alkalinity has an effect on the bioflocculant capacity of turbidity removal. According to Buttice (2012), in studies varying suspension water alkalinity, the turbidity removal decreased with increasing alkalinity.

Table 2 | Characteristics of clear water recovered from control (raw phosphate clay), CF (phosphate clay treated with chemical flocculant), and NFC (phosphate clay treated with natural flocculant-based cactus)

Parameters	Control	CF	NFC
T (C)	22.9 ± 0.1	22.86 ± 0.15	22.76 ± 0.05
pH	7.40 ± 0.42	7.25 ± 0.13	7.10 ± 0.29
Turbidity (NTU)	68.9 ± 0.41	52.6 ± 0.81	55.4 ± 0.99
Cu (mg/L)	0.806 ± 0.08	0.865 ± 0.10	0.810 ± 0.06
Zn (mg/L)	72 ± 0.80	32 ± 0.40	80 ± 0.30
Fe (mg/L)	1.36 ± 0.01	1.71 ± 0.03	1.45 ± 0.03
Cd (mg/L)	0.093 ± 0.006	0.10 ± 0.005	0.090 ± 0.002
Cr (mg/L)	7.1 ± 0.40	4.5 ± 0.30	6.0 ± 0.80

Values correspond to the mean of three measurements ± standard deviation.

Compared to the recovered water left over from the control (after natural decantation), the use of CF for treatment of phosphate clay caused Cu, Fe and Cd concentration increases. However, this treatment increased the rate of elimination of the turbidity, Zn and Cr by respectively 23.65%, 55.5% and 36.61%.

Table 2 shows that cactus has increased many element concentrations compared to the supernatant of the control sample, such as Zn, Fe and Cu. Carpinteyro & Torres (2013) showed that for all of the analyzed metals, such as and Zn, comparing many biopolymers, *Opuntia* mucilage showed the highest values. Using the NFC to flocculate phosphate clay decreases the rate of turbidity, Cd and Cr in the clear water recovered after this treatment. The decreases were respectively 19.59%, 3.22% and 15.49%.

The natural flocculant cactus resulted in the removal of Cu, Fe and Cd as compared to synthetic flocculant. It provides, also, better results than the control regarding the parameters turbidity, Cd and Cr. It is well-recognized that natural flocculants have particular macromolecular structures with a diversity of functional groups which facilitate the interaction with contaminants (Zhang *et al.* 2006; Lee *et al.* 2014). These works also reported that positively charged cationic macromolecules can destabilize the negative colloidal suspension by charge neutralization as well as by bridge formation.

It is speculated that polypeptides responsible for clarification also play the main role of metal sequestration through a complexation process. Cellulose can also sorb heavy metals from solution (Wan Ngah & Hanafiah 2008).

Results obtained through a comparative study of the cactus effect with other biomaterials such as *Aloe vera*, tannin, *Coccinia indica*, *Moringa oleifera*, and Nirmali seed widely used show that these biomaterials are similar in flocculation performance to cactus (Belbahloul *et al.* 2014; Al-Saati *et al.* 2016; Nougbode *et al.* 2013; Yin *et al.* 2007; Zhang *et al.* 2006; Diaz *et al.* 1999). The Tunisian cactus could be considered as a promising biomaterial to clarify wastewater.

CONCLUSIONS

For many convenience criteria, cactus-based flocculants are very attractive for wastewater treatment. Cactus plants are abundant, environmentally friendly, and biodegradable. It has been demonstrated that the powdered cactus OFI used as a natural flocculant was effective in treatment of phosphate mining wastewater with low cost. The following conclusions can be drawn from this ongoing study:

- The cactus powder has a solid form that allows its storage and industrial use.
- The cactus powder has a very good ability for flocculation at a basic pH without the need for pH correction of the clear water recovered.
- Based on the chemical analyses of dry sludge, the biomaterial shows decrease in several parameters comparing to natural decantation: CaO (3.79%), SiO_2 (19.27%) and Cd (34.11%), whereas P_2O_5, MgO and organic C are slightly increased.
- The biomaterial shows better removal for several parameters in dry sludge comparing to the industrial flocculant: Cd, SiO_2, CaO and P_2O_5. However, MgO and organic C show a decreasing ratio.
- The recovering of a high clear water volume (740 mL/L) by using the cactus powder shows that it could be potentially used as a bioflocculant instead of industrial flocculant (666 mL/L).
- Comparing to the natural decantation the biomaterial shows a decrease in Cr (15.49%), Cd (3.25%) and turbidity (19.59%), whereas it shows a slight increase in Fe, Zn and Cu. The slow natural decantation (24 hours) remains unprofitable for an industrial use.
- The biomaterial shows better removal for several parameters in the recovered water comparing to the industrial flocculant: Cd, Fe and Cu, whereas Cr, Zn and turbidity show a decreasing ratio.
- The criterion of biodegradability is very important in this case because the final destination of the sludge is the natural receiving medium. The sludge is deposited in settling tanks directly on the ground, then dried in the open air without further treatment.
- Sludge production was very dependent on pH value modification of the wastewater and the doses of flocculant employed.

However, the exploitation of cactus powder as a flocculant could be a very effective alternative. It has competitive characteristics such as being cost effective, easily available and in the strength of the flocs formed, thus making its use more reasonable. Further study should be made to improve flocculation efficiency of cactus as flocculant. So, exploration of the scaling up of this study from the laboratory scale to pilot plants and finally to industrial levels is needed.

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