Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2021.27342

228 (2021) 153–164
July

Comparative study between electrocoagulation and adsorption on the *Opuntia ficus indica* powder for industrial dairy wastewater treatment

Rahma Abrane*, Sabir Hazourli, Amina Eulmi

Laboratory of Water Treatment and Valorization of Industrial Wastes, Department of Chemistry, Faculty of Sciences, Badji-Mokhtar University, B.P. 12, Annaba 23000, Algeria, Tel. +213671525982; email: rahmaabrane148@gmail.com (R. Abrane), Tel. +213699287981; email: hazourlisab@yahoo.fr (S. Hazourli), Tel. +213776511362; email: eulmi94@gmail.com (A. Eulmi)

Received 23 November 2020; Accepted 9 April 2021

ABSTRACT

Dairy wastewater constitutes an essentially organic polluting load. Considering the environmental nuisances generated, treatment is essential. In the present study, two treatment techniques recognized for their easy and inexpensive applications have been optimized on real water from a local dairy industry namely electrocoagulation (EC) and adsorption on *Opuntia ficus-indica* powder: OFIP. The application of the cactus species for water treatment is relatively recent, even less for the adsorption process. The characteristic of this biomaterial, with high potential for recovery and available in many countries all year round, lies in the fact that it has considerable adsorbing power on its surface sites. Whether in EC or adsorption on OFIP, the results of monitoring the parameters continuously (chemical oxygen demand (COD), turbidity) and punctual (biochemical oxygen demand (BOD_5), Kjeldahl nitrogen, phosphorus, fat) are satisfactory. All the parameters measured after these treatments have values that meet the local standardization requirements for industrial aqueous residues. For comparison purposes, the EC gives turbidity (99%) and COD (80%) reduction rates higher than those of adsorption on OFIP but an operational cost 10 times more. However, given the advantages and disadvantages of each technique, the choice of the application of one or the other process requires a compromise to be made in relation to the objectives sought.

Keywords: Electrocoagulation; Cacti; Adsorption; Dairy wastewater; Treatment

1. Introduction

Milk and its derivatives (yogurt, cheese, etc.) have a privileged place in the dietary balance. The world demographic growth increases the need for these materials with high nutritional qualities. Animal production is no longer enough, especially in countries affected by a draught; this is why many dairy industries have been developed to reconstitute milk based on powder [1]. However, significant milk production requires high water consumption for the manufacturing, cleaning, and disinfection of production devices [2]. Unfortunately, a considerable volume of water in the form of wastewater is often not reused with an organic load essentially [3]. This organic load would be a vital nutritional supplement to the bacterial biomass conventionally present in this type of water [4], which can cause a biological degradation of the aqueous medium or even its possible eutrophication [5]. In a general way, this wastewater has a considerable negative impact on aquatic flora and fauna [6]; hence the need to treat it, to remedy this organic load problem. Many authors offer aerobic or anaerobic biological treatments [7,8]. Despite their effectiveness; these types of treatment are often excluded by many countries with modest means of investment. To meet this economic requirement while keeping the quality criteria of the treated water, physicochemical clarification processes are chosen. To this end,

* Corresponding author.

it is decided to clarify the wastewater from a local dairy, by two techniques: electrocoagulation (EC) and adsorption in the presence of a potential and promising adsorbent namely powder of *Opuntia ficus-indica* (OFIP), also known as prickly pear. The OFIP has been used for a long time because of its medicinal properties [9] and as a food intake [10]. The application of cactus species for water treatment is relatively recent, even less for the adsorption process [11–13].

Particular attention is paid to this natural biomaterial instead of traditional sorbents, because of its abundance in the world, especially in the Mediterranean region; at its low possible operating cost, and above all respectful of the environment.

Despite their use in dairy water treatment, the two techniques chosen for this study were not carried out under the conditions chosen in real water, and especially in the presence of OFIP for adsorption. Despite their seniority, they are still sought after in many industrial, medical, and other fields [14]. The reasons for the renewed attention and high uses are: efficiency, speed of treatment, easy application, as well as reduce the environmental nuisance in comparison with other techniques [15]. The EC is based on the principle of the soluble anode (Al or Fe). The application of a suitable current density in an aqueous medium generates an agglomeration of the cations formed (Al^{3+} or Fe^{3+}) with the organic matter resulting in decantation in two phases: clarified water plus mud [3]. For adsorption, it is a process of separation or filtration of adsorbate (organic or metallic materials) by an adsorbent (conventional material or biomaterial). The choice of adsorbent conditions the effectiveness of the treatment. This is why knowledge of the physico-chemical characteristics, structure, and texture of the material is necessary for any adsorption study [16]. The optimization of each of the two techniques was carried out on the basis of tests of the influences of a certain number of important operating parameters in[on] the treatment. For batch EC with two aluminum electrodes, the influences of the current density, temperature, and initial turbidity of the effluent were studied. For batch adsorption in the presence of OFIP, the mass of material, temperature, and initial turbidity are tested. The variation of pH has not been studied, to remain at free pH and close to neutrality and also avoid treating water at acid pH values causing phenomena of chemical precipitation of colloidal matter and not adsorption. For each of the chosen processes, the effectiveness of the treatment is measured by the parameters of turbidity and chemical oxygen demand (COD). Other parameters such as biochemical oxygen demand (BOD_5), phosphorus, fat, etc., are measured before and at the end of each treatment. In addition to the comparative efficacy results, mechanisms and operational cost calculations are discussed.

2. Materials and methods

2.1. Wastewater: sampling, parameters, and analytical methods

The wastewater sampling from the dairy studied is carried out at the main collector. The rhythm and the method of sampling wastewater at high and low flow rates are reported in the work of Hazourli et al. [17]. These waters are mainly composed of constituents of milk and its derivatives, but also residues of cleaning and disinfecting products from production installations. The sampling of an average volume of 50 L of wastewater spanned a full day of activity in the production workshops. The measurements of turbidity, COD, BOD_5, phosphorus, Kjeldahl nitrogen, and fats, are carried out according to standardized analysis methods [18]. All the used chemicals are of recognized analytical purity (Sigma-Aldrich®, UK). The ultra-pure water which is used to prepare the solutions has a resistivity of 18 MΩ cm. The characterization of the waters studied by Hazourli et al. [17] and Aitbara et al. [19] showed a similarity of the results with those obtained (Table 1). The turbidity and COD parameters analyzed continuously, have relative error averages of ±5% and 10% successively. The turbidity is carried out using a UV-visible spectrophotometer (Jenway 7315), whereas COD has carried out the method of chemical digestion of water (APHA, 2005). Whether in EC or adsorption on OFIP, the calculation of the pollution reduction rate of a given parameter X, expressed as a percentage TX(%), is based on the following equation:

$$\text{TX}(\%) = \frac{\left(C_i X - C_f X\right)}{C_i X} \times 100 \quad (1)$$

where C_iX and C_fX: values of a parameter before and after treatment successively.

Whether in adsorption on aluminum hydroxides (in EC) or in adsorption on cactus, the amount of adsorbed material is calculated according to Eq. (2):

$$q_t = \frac{\left(T_0 - T_f\right)V}{m} \quad (2)$$

where T_0 and T_f are the initial and equilibrium turbidity or COD measurement values respectively, V is the volume of water to be treated, m is the weight of OFIP (in adsorption), and weight of electrode dissolved (in EC), estimated according to Faraday's Law [Eq. (3)].

$$C_{\text{Al}} = \frac{M_w \times I \times \tau_{\text{react}}}{n \times F \times V} \quad (3)$$

where M_w is the molecular mass of electrode ($M_{w,\text{Al}}$ = 0.02698 kg mol^{-1}), t_{react} is operating time (s), n is the number of electrons transferred (n_{Al} = 3), and F is Faraday's constant (96.487 C mol^{-1}).

Table 1
Dairy wastewater properties

Average values	Wastewater before treatment
COD (mg O_2 L^{-1})	2,300
Turbidity (NTU)	1,000
BOD_5 (mg O_2 L^{-1})	1,260
Phosphorus (mg L^{-1})	45
Kjeldahl nitrogen	138
Total fat (mg L^{-1})	64

On the other hand, in EC, the consumed energy by the unit of treated wastewater volume is given by Eq. (4). [19,20].

$$E\,\frac{\text{kWh}}{\text{m}^3} = \frac{U \times I \times \tau_{\text{react}}}{V} \quad (4)$$

where U is cell voltage (V), i is current (A), t_{react} is operating time (h), and v is the volume (m^3) of the wastewater.

2.2. Preparation and characterization of OFIP for adsorption

The prickly pear snowshoes collected from local agricultural fields in the city of Tébessa (Algeria) were washed thoroughly with double-distilled water to remove dust and surface impurities. Once the thorns were removed, the racket was cut into approximately 1 cm^2 dice and then dried in an oven at 105°C for 72 h to evaporate all the residual moisture. The dried mass was ground and the particle size fraction less than 1 mm in diameter was kept for the adsorption tests (Figs. 1a and b). Fine grinding and sieving are made possible thanks to a JanKe and KunKel IKA labotechnik brand device. Part of the dry matter was intended for the characterization of the material, which is necessary to explain the adsorption mechanisms. Thus, the structure and texture parameters of OFIP were examined. The parameters tested are the specific surface analyzed according to the traditional method of Brunauer, Emmet, and Teller (BET) [21], using a device (Thermo Quest Sorptomatic 1990, Italy). Fourier transform infrared spectroscopy (FTIR) was performed by the standard method with KBr disk, at room temperature between 600 and 4,000 cm^{-1}, using a Shimadzu spectrometer (Japan). To visualize the morphology of OFIP, scanning electron microscopy (SEM) was used using a Philips XL-3 CP microscope (Belgium). X-ray diffraction (XRD) was performed on an X-ray diffractometer (Philipps X'PERT PANalytical, Almelo, Netherlands) with CuKα radiation at λ = 1.54 Å, operating at 50.0 kV and 200.0 mA. The point of zero charges of OFIP (PZC) was carried out from 50 mL of 0.1 M NaCl solutions transferred to a series of 100 mL beakers containing aqueous solutions adjusted to pH between 2 and 12 with HCl or NaOH (0.1 M). A mass of 0.1 g of OFIP was added to each beaker for stirring the suspension for 24 h at 150 rpm. The final pH is measured to determine the PZC of OFIP by plotting the curve of final pH-initial pH as a function of the initial pH [22].

2.3. EC equipment and experimental procedure

All the EC treatment tests for dairy wastewater were carried out in the batch reactor presented in Fig. 2. The choice of this equipment (dimensions of the electrodes and the reactor, methods of connecting the electrodes, and circulating the water to be treated) was motivated by the fact that it is already used successfully in our laboratory. It has shown its ability to remove food coloring [23] and to clarify industrial mining wastewater [24]. The assembly comprises a cylindrical glass reactor of 1 L capacity, thermoregulated, and in which two identical aluminum electrodes are immersed. The flat and parallel electrodes, of the total submerged surface of 45 and 36 cm^2, respectively, are spaced 1 cm apart in order to minimize the ohmic drop in the reactor. The connection between the electrodes is of monopolar type, where a given current density is applied by means of a potentiostat (Metrix-AX-502). Sufficient conductivity (3.2 ms cm^{-1}) of the solution to be treated was ensured by the addition of 1.5 g L^{-1} of NaCl in the reactor. After each test and in order to remove the residues and salt deposits mainly coming from the wastewater, the electrodes and the reactor are cleaned and then rinsed with HCl (0.1 M) and the double-distilled water successively. The reactor assembly and electrodes are then dried before being reused. The water to be treated is placed in the reactor with mechanical stirring at 200 rpm for a reaction time to be optimized.

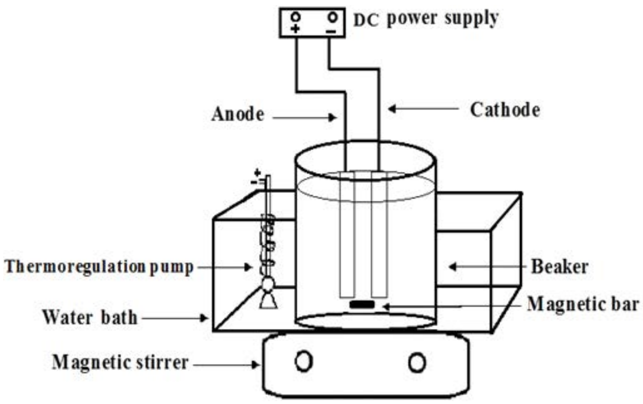

Fig. 2. Equipment used in EC.

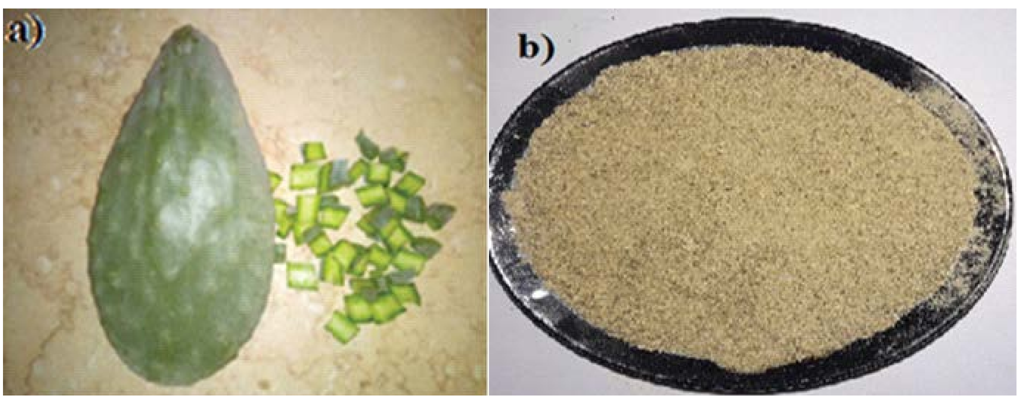

Fig. 1. Prickly pear racket (a) dried, crushed, and sieved (b).

At the end of each experiment, the treated water is decanted for 30 min minimum, in order to achieve good clarification. After decantation, approximately 50 mL of supernatant is sampled to measure the turbidity and the COD or the other chosen parameters for this study. Optimizing the EC required studying the influence of a number of important operating parameters such as current density and reaction time, initial water turbidity, and temperature.

2.4. Recovery and analysis of the mud formed after EC treatment

At the end of each EC test and after minimum decantation of 30 min of the treated water, the mud is measured in the reactor. This volume of liquid sludge is converted into dry sludge by introducing the liquid sludge in an oven at 80°C for 24 h until reaches a constant weight. On the dry mud obtained, the morphology and the elemental composition were studied using SEM (Zeiss Evo15) and EDS (EDX 5 detector), respectively. Some heavy metals recommended by the European Commission [25] such as chromium, copper, lead, nickel, and zinc were first extracted from 200 mg of dry sludge by oxidative mineralization (10 mL of 65% HNO_3 and 5 mL of H_2O_2 at 20%) on microwave (Ethos Milestone). The recovered suspension is filtered at 0.45 μm then adjusted to 50 mL with ultra-pure water of 18.2 MΩ cm. These mineralized elements were analyzed by the atomic emission plasma torch (ICPAES-Model Panorama 61). All measurements were reproduced on at least two identical samples of liquid or dry mud.

2.5. Adsorption equipment on OFIP and experimental procedure

This batch adsorption part required optimization tests where the particle size of the OFIP and the contact or equilibrium time were optimized beforehand and kept constant at 1 mm and 60 min successively for all subsequent tests of adsorption. Also, the pH of the solutions is not varied (pH_{free} = 7.03) to keep it within a pH range of natural waters in general, but also for comparison purposes with the EC treatment which is at its optimum efficiency at this pH. The tests concerned with the optimization are the influences of OFIP concentration, initial turbidity, and temperature. For the influence OFIP concentration, the masses tested are between 0.005 and 0.1 g; for the influence of the initial turbidity, the waters tested have turbidities of between 100 and 1,000 NTU; whereas for the temperature it is between 10°C and 40°C. For each of these influences, 50 mL of wastewater containing OFIP is stirred at 200 rpm for a contact time of 60 min. After this time, the mixture was filtered to analyze in the filtrate: turbidity, COD, etc. The calculation of the reduction rate for each of the parameters considered is expressed according to Eq. (1). While their quantities are fixed on the adsorbent by Eq. (2).

3. Results and discussion

3.1. Results of EC treatment of dairy wastewater

3.1.1. Influence of current density

It is well-known that the current density controls the EC process in terms of the quantity of coagulant distributed in solution, the speed and the size of the bubbles produced at the electrodes as well as the electrolysis time [19,20]. The influence of this parameter on the efficiency of the EC treatment was carried out at densities of 3–20 mA cm^{-2} while keeping constant: the free pH at 7.03 and the initial turbidity at around 1,000 NTU (Fig. 3). It can be noted that the efficiencies of water clarification and the reduction of COD increase with increasing current density. Thus, the electrolysis time is shorter the higher the current density. In this case, there is more coagulant (aluminum) available per unit of time resulting in maximum treatment efficiency. Consequently, the optimal density chosen for the subsequent experiments is that of 15 mA cm^{-2} with a short reaction time of 15 min.

3.1.2. Influence of initial turbidity

Dairy water is recognized as a colloidal solution composed of organic matter, especially protein. The study of the dilution of this water was necessary given the importance of the turbidity/quantity of colloidal particles relationship [26]. This study was carried out by carrying out, from wastewater at 1,000 NTU, dilutions of 100, 300, 500, 700, and 900 NTU. For each of these solutions, at a current density of 15 mA cm^{-2}, a reaction time of 15 min, and a free pH at 7.03, the results of the EC tests (Fig. 4), showed strong

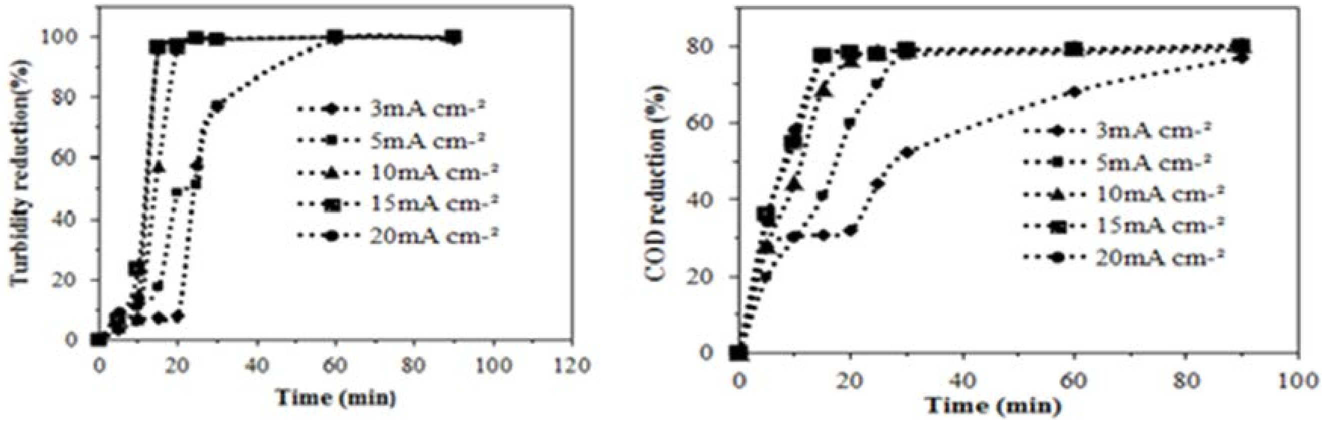

Fig. 3. Effects of current density and reaction time on the reduction of turbidity (a) and COD (b).

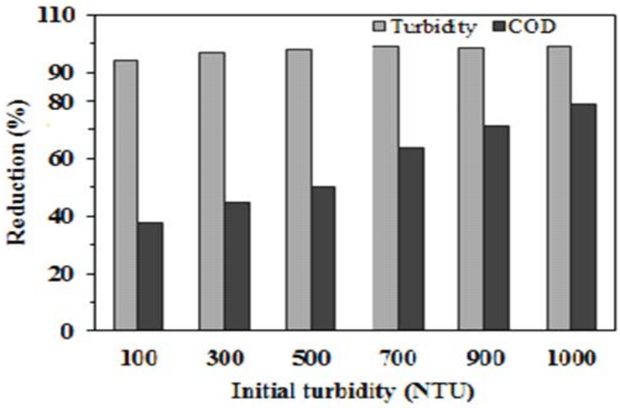

Fig. 4. Influence of the variation of the initial turbidity on the efficiency of the EC.

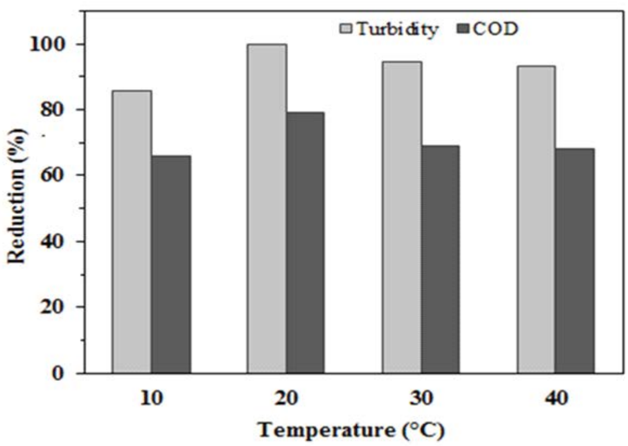

Fig. 5. Influence of the variation of the initial temperature on the efficiency of the EC.

reductions in turbidity regardless of the turbidity tested (>95%) and a marked improvement in the efficiency of COD removal from the least turbid to the most turbid solution (from 40% for 100 NTU to 80% for 1,000 NTU). For each of the turbidities tested, the reduction efficiency rate was high; it would be linked to the applied current density which is sufficient to supply the aluminum necessary for clarification, that is to say, the formation of flocs decantable aluminum hydroxides. For COD, the increasing reduction rate from low turbidity to highest would be attributed to the increase in degradable protein materials. This result was also reported by ŞengilI and Özacar [27] when reducing COD and fats from dairy wastewater in a batch system.

3.1.3. Influence of the initial temperature

The effect of temperature on the EC is very little studied, despite the fact that this process has been known for a long time and that industrial installations are often outside at room temperature or in premises with low heating. In this study, all the tests were carried out at room temperature. However, in order to observe the effect of the temperature on the treatment of EC, the temperatures ranging between 10°C and 40°C were tested by keeping constant the free pH of the solution (7.03), a current density at 15 mA cm^{-2}, a reaction time of 15 min, and initial turbidity of 1,000 NTU. The results compared to room temperature (Fig. 5) show an efficiency reduction of around 10% for turbidity and around 15% for COD corresponding to temperatures of 10°C, 20°C, and 40°C. This could be linked to the kinetics of formation of the flocks of aluminum hydroxides slowed down at low temperature, fast and stable at 20°C, but mobile, unstable, and dissociable beyond this temperature [28]. Reported that a temperature rise increased the solubility of the formed aluminum hydroxide precipitates. Similar results have been observed in a continuous treatment of dairy wastewater [19].

3.2. Data on the mud formed after EC treatment

One of the disadvantages of the CE technique is the production of sludge [14]. This production is closely related to the applied current density and the particles in the solution [29]. The tests (Fig. 6) showed that the volume of liquid mud formed at the end of EC treatment is proportional to the applied density. At optimum density, the volume of mud is between 200 and 250 mL L^{-1} of treated water, which corresponds to approximately 1 g of dry sludge per liter of treated water. This result is similar to that obtained by Aitbara et al. [19] to treat the same dairy water in EC at continuous mode. Despite the low mass of mud obtained, its recovery remains possible. This type of mud has long been valued; for example in poultry feed [30]. Characterization of the sludge formed after EC is necessary to assess the possibility of its reuse or treatment. For this, the mud recovered under optimal conditions of treatment efficiency by EC was analyzed by SEM, and the elemental composition by EDS as well as some heavy metals often sought in the sludge. The SEM image and the elemental composition of the sludge analyzed by EDS are shown in Fig. 7. The SEM image (Fig. 7a) showed granular clusters of particulate flocs (aluminum hydroxides/organic materials) which can serve as an adsorbent. Indeed Sassi et al. [31] have used dairy sludge as an adsorbent to eliminate by adsorption of Pb and Cd at 100 ppm in synthetic solution. On the other hand, the elemental composition of the sludge expressed as a weight fraction of the total weight of atoms in the sample (% by weight) (Fig. 7b) showed that carbon and oxygen represented the majority proportion compared to other elements. The presence of silicon was attributed to the glass slit used for the EDS analysis of the sample. The appreciable concentrations of calcium and aluminum are attributed successively to the calcium-rich whey discharged in the wastewater and to the aluminum electrodes used for the EC. Only aluminum would be problematic in the case of the use of sludge in the food sector; additional treatment of the sludge is therefore necessary. For example [32], treated textile sludge containing aluminum and chromium by electrokinetic or electromigration treatment. Nevertheless, in soil amendment, the presence of aluminum in the sludge can have rather beneficial effects. Indeed, a recent long-term incubation study has shown that aluminum has a sequestering power on reactive phosphorus and did not negatively affect plant-available phosphorus [33]. Aluminum can also have a positive effect on reducing ammonia volatilization and phosphorus losses through runoff without increased runoff and Al availability in soils or aluminum uptake by plants [34]. For the analysis of heavy metals in the sludge studied, the results showed very low concentration values of chromium, copper, lead, nickel, and zinc at 6.1, 39.2, 4.9, 3.8, and 325 mg kg^{-1} successively. Copper and zinc are in the majority but can constitute micronutrients necessary for plants [35]. All heavy metal values remain significantly lower than those recommended for an acceptable quality of compost derived from bio-waste ([36]: the best reference in the absence of a more specific norm).

4. Results of the adsorption treatment of dairy wastewater by OFIP

4.1. Characterization of OFIP

The characterization of the structure and texture of a material is necessary before any adsorption study.

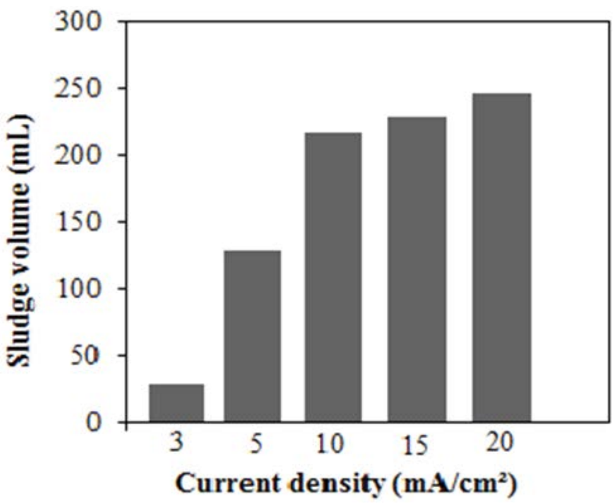

Fig. 6. Effect of current density on mud production after EC.

This would help better understand the phenomenon at the adsorbent/adsorbate interface. The surface structure and morphology of OFI powders were revealed by SEM (Fig. 8a), shows a structure with firm and rigid-looking laminated layers in the presence of cavities of disparate sizes favorable to adsorption. Microcrystallites arranged in a disordered manner can also be observed (Fig. 8b). According to Malainine et al. [37], these crystallites of millimetric sizes and star-shaped and spiny forms, are calcium oxalates or whewellite. XRD analysis (Fig. 9) indicates that OFIP contains these whewellite microcrystallites or complex polymorphous hydrated crystals. The signal intensity produced is negligible compared to metal. The OFIP has a specific surface (BET) of 0.41 m^2 g^{-1}. This surface value is close to that of an OFIP of Morocco found at 0.53 m^2 g^{-1} [38]. This small surface does not exclude the adsorbing power of OFIP given the presence on its surface of functions or sites confirmed by the IR spectrum. This IR spectrum (Fig. 10) shows that the surface of the material is lined with a variety of organic functional groups. Several bands are observed; the widest is between 3,200 and 3,600 cm^{-1} (conformation 3) corresponding to the elongation of the O–H bonds. The bands from 2,846.7 to 2,923.8 cm^{-1} (conformation 4) are due, respectively, to the asymmetric elongation vibrations of CH_2 and the symmetrical elongation of $–CH_3$ of aliphatic acids. The narrow and intense band at 1,700 cm^{-1} (conformation 5) is due to the vibrations of the bonds: C–O. The band at 1,500 cm^{-1} (conformation 6) is due to the vibration of elongation of the carboxylic groups. The band observed at 1,370.45 cm^{-1} (conformation 7) reflects vibrations of the symmetrical or asymmetric valence of the carboxylic groups of pectins. The narrowband at 1,319.2 cm^{-1} (conformation 8) comes from the vibration of elongation of the –OH groups of the phenolic compounds. The band at 1,026 cm^{-1} (conformation 9) could be due to the vibration of the C–O–C or –OH groups and of the polysaccharides. Absorption bands in the region of wave numbers less than 800 cm^{-1} (conformation 10 and 11) can be attributed to nitrogen bioligands. The point of zero charge (PZC) of OFIP is obtained at pH 5.6 (Fig. 11). Above this pH value, the surface of the material is negative

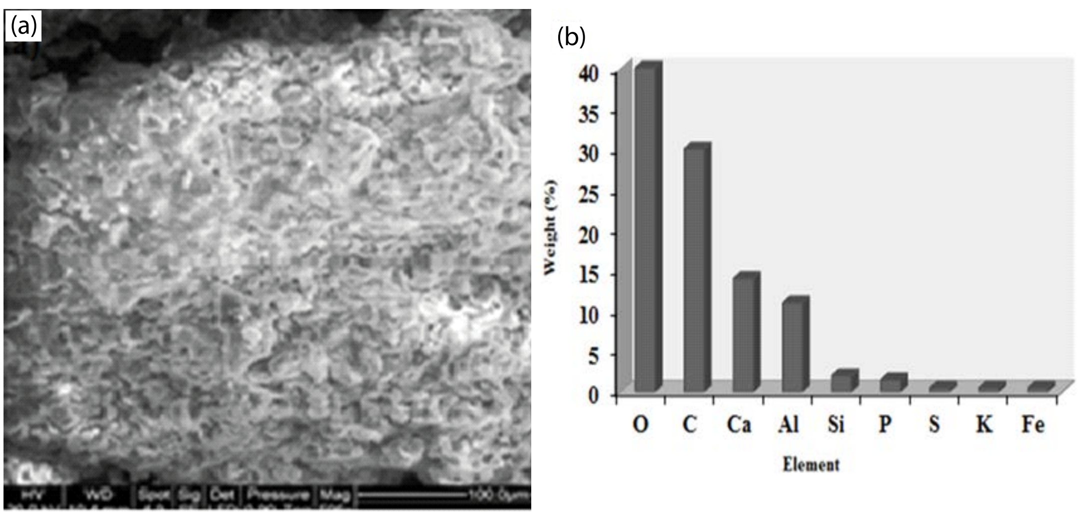

Fig. 7. SEM image (a) and the weight composition of mud formed after EC (b).

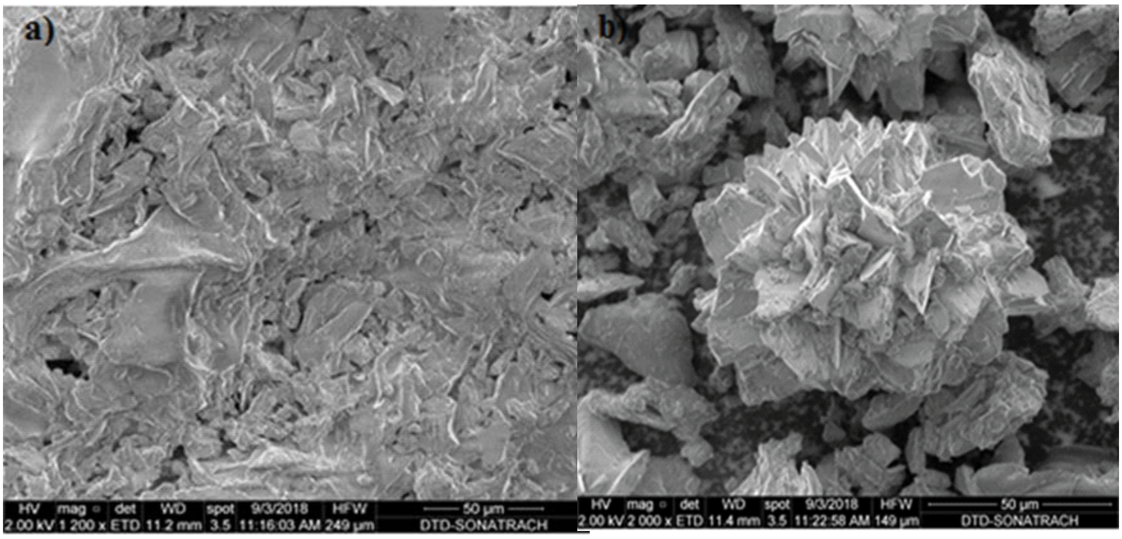

Fig. 8. SEM images of OFIP (a) at 1,200× magnification and (b) at 2,000× magnification.

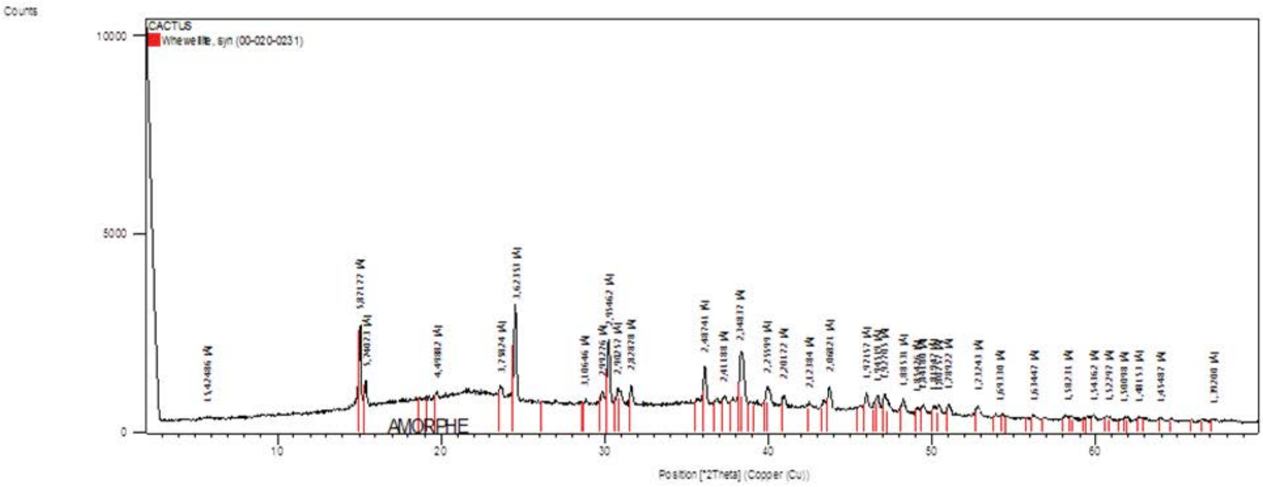

Fig. 9. Diffractogram of the OFIP.

but below, its surface is positive. The PZC value is in agreement with the free pH of the OFIP solution which is 4.7.

4.2. Optimization of operating parameters

4.2.1. Influence of OFIP concentration

The tests are carried out at concentrations between 0.1 and 2 g L^{-1} in OFIP while keeping the following parameters constant: initial turbidity at 1,000 NTU, a free pH at 7.03, an ambient temperature at around 21°C, an optimal contact time at 30 min, and a particle size of the material at 1 mm. The results presented in Fig. 12 show that the optimal OFIP concentration is 1 g L^{-1} for an efficiency rate of 55% for turbidity and 50% for COD; which corresponds to 544 NTU g^{-1} and 1,188.16 mg COD g^{-1} successively. Below this adsorbent concentration, the yield is approximately 50% for turbidity and 40% for COD. This behavior is often associated with an increase in the number of surface sites available with the increase in the biosorbent [39]. On the other hand, beyond the optimal concentration of adsorbent, a reduction in the yield of at least 5% is observed, whether for turbidity or COD. This would be the consequence of a partial aggregation of little dissociated organic particles, which results in a reduction in the specific surface available for adsorption. Various authors have also reported this decrease in adsorption after optimization of the adsorbent concentration [38].

4.2.2. Influence of initial turbidity

The effect of the initial turbidity was tested between 100 and 1,000 NTU corresponding to a COD of between 259.4 and 2,300 mg L^{-1}, a free pH at 7.03, an ambient temperature at around 21°C and an optimal time 30 min adsorption in the presence of 1 g L^{-1} of OFIP. The results

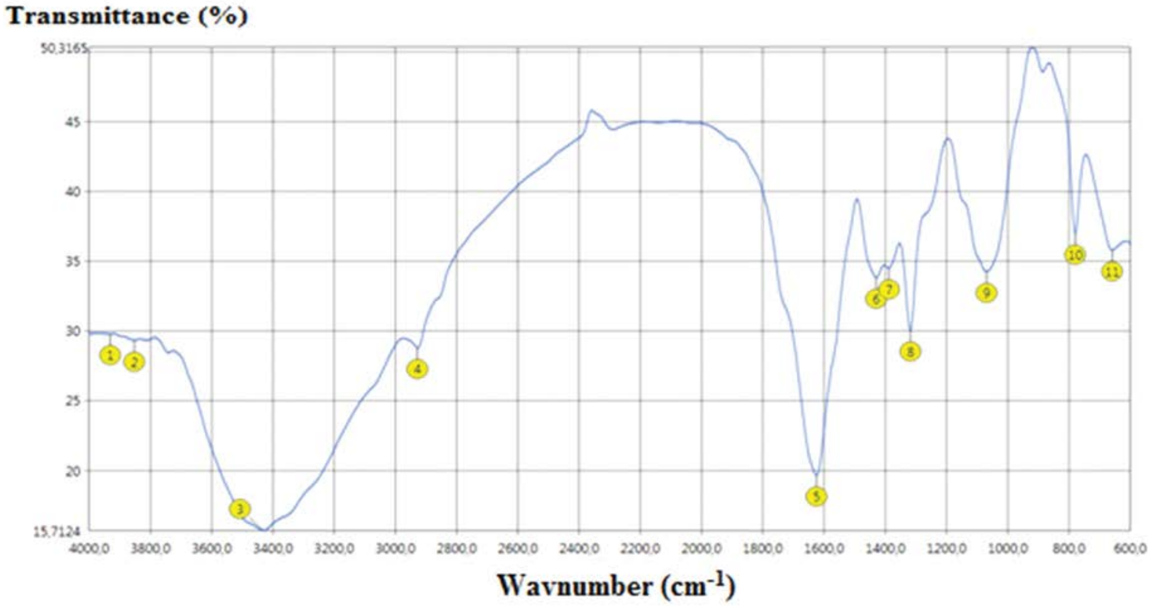

Fig. 10. IR Spectrum of OFIP.

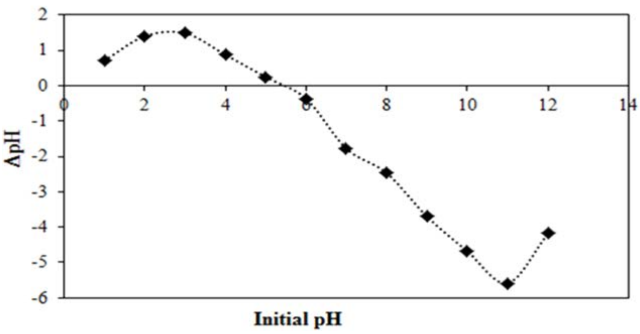

Fig. 11. Point of zero charges of OFIP.

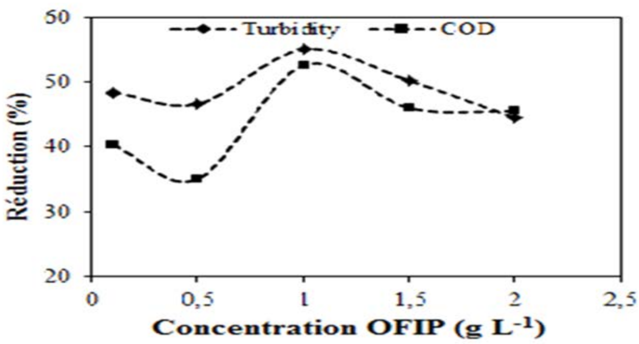

Fig. 12. Effect of OFIP concentration on the effectiveness treatment of turbidity and COD.

(Fig. 13) show that the absorption rate of turbidity decreases slightly but remains between 55% and 60%. For COD, the reduction rate increases with increasing initial turbidity; the reduction rate doubles at the extreme values of turbidity; 25% for the initial turbidity 100 NTU and 50% for 1,000 NTU. For turbidity, the decrease in adsorption efficiency at high turbidity (1,000 NTU) and its increase at low turbidity (100 NTU) could be explained in a similar way as for the effect of the concentration of the biosorbent. At low turbidity, there would be an increase in the number of surface sites available, and at high turbidity, an effect of partial aggregation of little dissociated organic particles and reduction of the specific surface available for adsorption[38,39]. For the gradual increase in the efficiency of the COD with the increase in the initial turbidity, it would be linked to the strong gradient of negatively charged organic particles leading to their attractions from the aqueous solution to the surface sites of OFIP. Similar adsorption behavior for dairy wastewater has been reported by [29] but for commercial activated carbon.

4.2.3. Influence of the initial temperature

The effect of the initial temperature was tested between 10°C and 40°C, for initial turbidity at 1,000 NTU corresponding to a COD of approximately 2,300 mg L^{-1}, a free pH at 7.03, an optimal adsorption time of 30 min, in the presence of 1 g L^{-1} of OFIP. The results (Fig. 14) show that at low (10°C) and high (30°C and 40°C) temperatures, the reduction rates of turbidity and COD decrease. The optimal reduction rates are obtained at room temperature close to 20°C; 55% for turbidity and close to 50% for COD. At high temperatures (30°C and 40°C), the reduction in the attraction forces of the adsorbent for organic particles in an aqueous solution (low viscosity, high mobility) would rather favor repulsion. At low temperatures (10°C), the viscosity of water is higher, thus limiting the interaction between organic particles and OFIP. Pathak et al. [40] reported a similar discussion on dairy waters with rice husk as an adsorbent. Similarly, Chakraborty et al. [41] remove a dye from modified rice husk.

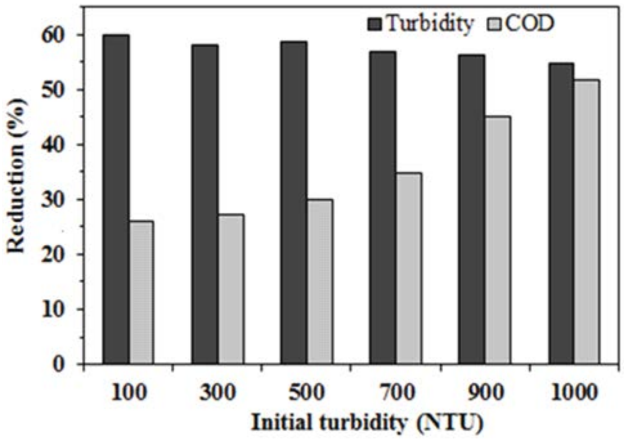

Fig. 13. Effect of variation of initial turbidity on the treatment effectiveness of turbidity and COD.

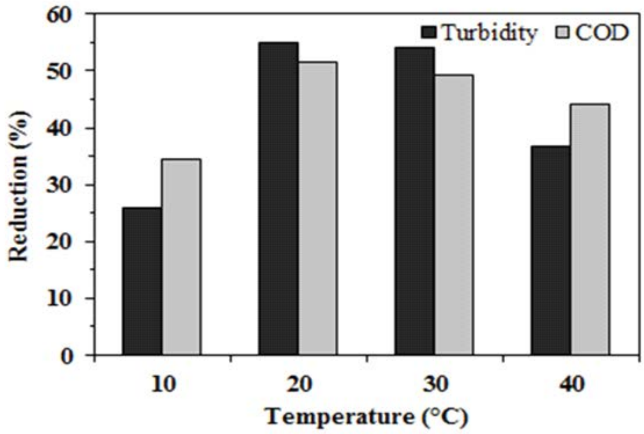

Fig. 14. Effect of variation in water temperature on the treatment effectiveness of turbidity and COD.

4.3. Comparative results of EC treatments of adsorption and mechanisms

4.3.1. Comparative efficacy of EC and adsorption treatments on OFIP

The quantitative analysis of the turbidity parameters, COD, BOD_5, phosphorus, Kjeldahl nitrogen, and total fat, is essential and often carried in the search of quality control of dairy wastewater [3,29,42]. The analysis results of the water studied (Table 2) show a very significant reduction in the initial pollution for all the parameters considered; whether for EC treatment or for adsorption on OFIP. The residual values of the parameters at the end of each treatment are for the majority, lower than the country's industrial rejection standards [43]. This treated water could be reused for agricultural needs or discharged into rivers without major risks for the environment. With regard to the choice of OFIP for the adsorption of dairy water, for the parameters and operating conditions considered, Table 3 shows that OFIP could be used as a potential adsorbent all the more since it is abundant and environmentally friendly.

4.3.2. Comparative study of energy consumption and cost of EC and adsorption treatments on OFIP

This comparative study of energy consumption and cost of the two treatment processes studied under optimal conditions of efficiency took into account the consumption of aluminum for the EC and energy consumption essentially. In EC or adsorption, the prices of the agitators were not taken into account in this economic evaluation. They are included in the fixed ratios. Thus, the equations for calculating operational costs are represented by Eq. (5) for the EC (sum of Eqs. (3) and (4) and the energy consumed by the agitator) and Eq. (6) for adsorption on OFIP.

$$\text{OC} = a \cdot E + a \cdot E_{\text{Stirrer}} + b \cdot C_{\text{Al}^{3+}} \quad (5)$$

$$\text{OC} = a \cdot E_{\text{Stirrer}} + c \cdot \text{Quantity}_{(\text{OFIP})} \quad (6)$$

where (a) and (b) are ratios for the calculation of international market prices for energy and chemicals for the year 2011. They are successively 0.05 US \$ kWh^{-1}, or ~ 4 DZD kWh^{-1}, and 3.08 \$ kg^{-1}, or ~ 240 DZD kg^{-1} of aluminum. The c.$\text{Quantity}_{(\text{OFIP})}$ part of Eq. (6) may be overlooked since OFIP is not currently considered a marketable product and therefore the ratio (c) is zero. The operational cost for adsorption on OFIP is then represented by Eq. (7).

$$\text{OC} = a \cdot E_{\text{Stirrer}} \quad (7)$$

where E_{Stirrer} is the energy consumed by the agitator for optimal agitation time; the power of the agitator used is that

Table 2
Dairy wastewater analyzes before and after a treatment EC or adsorption on OFIP

Parameters	Wastewater before treatment	Reduction (%) after EC treatment	Reduction (%) after adsorption treatment	Standard norms in Algeria: maximum concentration allowed For industrial wastewater discharge
COD (mgO_2 L^{-1})	2,300 ± 230	80	50	120
Turbidity (NTU)	1,000 ± 50	99	55	–
BOD_5 (mgO_2 L^{-1})	1,260 ± 126	98	60	35
Phosphorus (mg L^{-1})	44.5 ± 2.2	80	70	10
Kjeldahl nitrogen	138 ± 6.9	84	65	30
Total fat (mg L^{-1})	460 ± 23	97	48	20

in heating therefore overestimated (380 W). The results (Table 4) show that, despite a moderate reduction in pollution, adsorption on OFIP has a negligible operational cost compared to treatment with EC. In this study, the EC process has an operational cost of around 10 times more, compared to other work on dairy waters but with different compositions [45,46,17]. This difference in cost would be linked to the presence of fats in the water studied (500 mg L^{-1}) which would increase the resistance in the EC reactor, therefore the voltage and the current and the energy consumption. Thus the choice of treatment by adsorption on OFIP or EC would be a compromise to be made in relation to the objectives targeted by the use of the first or second treatment.

4.4. Mechanisms

Due to the multiplicity of parameters involved in the treatment of EC or adsorption on OFIP, it is difficult to propose a mechanism that takes into account all of the phenomena involved in the first or second treatment. However, the mechanisms proposed (Fig. 15) for each of the studied treatments are different, they take into account the main constituents of dairy water, reactions with aluminum electrodes for EC, the structure and texture for adsorption on OFIP. Dairy wastewater mainly consists of proteins (colloidal casein and soluble proteins: albumin, and globulin) and milk sugar (soluble lactose) [47]. For the OFIP, despite a low specific surface of 0.41 $m^2\ g^{-1}$, nevertheless, according to the IF analysis (Fig. 10), it has a surface filled with surface sites which allows it to have an interesting adsorption power. Many studies have shown the presence of complex sugars in OFIP such as l-arabinose, d-galactose, l-rhamnose, dxylose, and galacturonicacid [48]. According to Nharingo et al. [49], Galacturonicacid is one of the main agents involved in adsorption; it showed that Pb and Cd adsorb on the polysaccharide chains serving as a "bridge" on which the particles adsorb. The OFIP zero charge point curve (Fig. 11) confirms its adsorption power since it can adsorb anionic or cationic substances depending on the pH of the medium. For the EC, the mechanisms are explained in a similar way as those of a study carried out in our laboratory on dairy waters but in dynamic mode [29]. Interactions are possible between the reactive and formed species at the aluminum electrodes with the colloidal (CM) and organic (OM) particles successively specified by the insoluble casein and the soluble lactose (Fig. 5, Eqs. (9)–(11)). According to the Pourbaix diagram, complex aluminum species ($AlOH^{2+}$, $Al(OH)_4^-$) can reside depending on the pH of the medium; the formation of the flocculating species $Al(OH)_3$ is found at a pH between 6 and 7.5 [50]. At the optimum of clarification, the $Al(OH)_3$ and residual aluminum species become the majority. Several mechanisms can coexist together or separately such as the trapping of (CM) (Fig. 15A), the adsorption of (CM) and (OM) on the amorphous $Al(OH)_3$ formed (Fig. 15B), the destabilization of (CM) by neutralization of the colloidal surface by existing positive aluminum species (Fig. 15C) or by the complexion and precipitation of Al-OM which can be removed by separation (Fig. 15D). For the adsorption part on OFIP, the turbidity reduction mechanisms or COD would be attributed to surface sites and not to the low porosity and specific surface of OFIP. Thus, the physical adsorption dipole–dipole via the hydroxyl of the lactose molecule (OM), the amines of casein (CM) with the carboxylic forms of OFIP, would be privileged (Fig. 15E).

Table 3
Comparison of the effectiveness of OFIP with other biomaterials for the treatment of dairy wastewater

Adsorbant	Operating conditions adsorbent dose (g L^{-1})/pH/ contact time (min)	Reduction (%)					References
		COD (mg O_2 L^{-1})	BOD_5 (mg O_2 L^{-1})	Turbidity (NTU)	Phosphorus (mg L^{-1})	KN (mg L^{-1})	
Tamarind kernel	4/7.8/35	68	–	57	–	–	[40]
Water hyacinth	0.3/8.0/10	84	–	94	80	90	[41]
Multi-walled carbon nanotube	4/6.5–7.1/15	40	–	–	–	–	[42]
Modified dried activated sludge	7/6/60	75	65	–	65	90	[43]
Crab shell chitosan	0.15/5/50	75	–	90	–	–	[44]
OFIP	1/7.03/30	50	60	55	70	65	This study

Table 4
Comparative study of the operational cost between the EC and the adsorption on OFIP

Parameter	CAl_3^+ (kg m^{-3})	EC			Adsorption OFIP	
		E (kW m^{-3})	$E_{Stirrer}$ (kW m^{-3})	OC ($ m^{-3})	$E_{Stirrer}$ (kW m^{-3})	OC ($ m^{-3})
Turbidity or COD	0.030	421.308	0.190	21.1	0.380	0.019

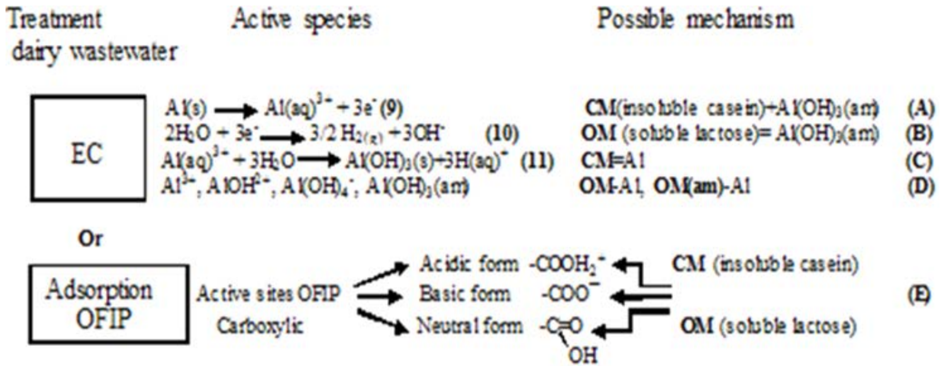

Fig. 15. (A–E) Possible mechanisms of EC and adsorption on OFIP of dairy wastewater.

A similar approach has been described by Pathak et al. [40] but for the adsorption of wastewater by the husk of rice.

5. Conclusion

Dairy wastewater has essentially organic pollutant which can harm the environment, particularly the aquatic environment when it is discharged without prior treatment. This water deserves special attention due to a level of pollution that sometimes exceeds that of domestic wastewater. Each technical treatment used (EC or adsorption) has been optimized based on important operating parameters. The results showed a reduction in the initial pollution of the parameters analyzed continuously (turbidity, COD) and punctual (BOD_5, phosphorus, Kjeldahl nitrogen, and fat). Whether for EC or adsorption on OFIP, all the measurements carried out after treatment meet local standards for industrial aqueous discharges. However, the EC has higher turbidity and COD treatment efficiencies than those of adsorption on OFIP but an operational cost 10 times more, and the disadvantage of the mud formed after EC to be taken into account for removing aluminum. Also, the use of OFIP in adsorption is advantageous for more than one reason; it is a material that has shown adsorption of organic pollutants due to its composition and specific texture, inexpensive, abundant in many countries in large quantities throughout the year, respectful of the environment. In conclusion, the use of EC or adsorption on OFIP could be recommended as a treatment for organic pollution. However, given the advantages and disadvantages of each technique, the choice of the application of one of the methods requires a compromise to be made with the objectives sought.

Acknowledgments

The authors acknowledge the financial support of the Ministry of Higher Education and Scientific Research (Algeria) (Project of research No. E01120140052).

References

[1] S.T. Chamango, C.P. Nanseu-Njiki, E. Ngameni, D. Hadjiev, A. Darchen, Treatment of dairy effluents by electrocoagulation using aluminium electrodes, Sci. Total Environ., 408 (2010) 947–952.

[2] F.K. Mostafapour, E. Bazrafshan, D. Balarak, M.J. Tahsini, Survey efficiency of dairy wastewater treatment by combined chemical coagulation and Fenton oxidation process, Sci. J. Environ., 4 (2015) 159–166.

[3] A. Hamdani, M. Chennaoui, O. Assobhei, M. Mountadar, Characterization and treatment of a dairy effluent by coagulation and decantation, Dairy Sci. Technol., l84 (2004) 317–328.

[4] S. Garcha, N. Verma, S.K. Brar, Isolation, characterization and identification of microorganisms from unorganized dairy sector wastewater and sludge samples and evaluation of their biodegradability, Water Resour. Ind., 16 (2016) 19–28.

[5] B.V. Raghunath, A. Punnagaiarasi, G. Rajarajan, A. Irshad, A. Elango, G. Mahesh kumar, Impact of dairy effluent on environment–A review, M. Prashanthi, R. Sundaram, Eds., Integrated Waste Management in India, Environmental Science and Engineering, Springer, Cham, 2016, pp. 239–249.

[6] I. Kabdaşlı, I. Arslan-Alaton, T. Ölmez-Hancıand, O. Tünay, Electrocoagulation applications for industrial wastewaters: a critical review, Environ. Technol. Rev., 1 (2012) 2–45.

[7] B. Demirel, O. Yenigun, T.T. Onay, Anaerobic treatment of dairy wastewaters: a review, Process. Biochem., 40 (2005) 2583–2595.

[8] H. Yahi, N. Madiand, K. Midoune, Contribution to biological treatment of dairy effluent by sequencing batch reactor (SBR), Desal. Water Treat., 52 (2014) 2315–2321.

[9] E.S.S. Abdel-Hameed, M.A. Nagaty, M.S. Salman, Bazaid phytochemicals: nutritionals and antioxidant properties of two prickly pear *Cactus cultivars* (*Opuntiaficus-indica* Mill) growing in Taif, KSA Food Chem., 160 (2014) 31–38.

[10] P.I. Angulo-Bejarano, O. Martínez-Cruzand, O. Paredes-Lopez, Phytochemical content: nutraceutical potential and biotechnological applications of an ancient Mexican plant: Nopal (*Opuntia ficus-indica*), Curr. Nutr. Food Sci., 10 (2014) 196–217.

[11] T. Nharingoand, M. Moyo, Application of *Opuntia ficus-indica* in bioremediation of wastewaters: a critical review, J. Environ. Manage., 166 (2016) 55–72.

[12] N. Adjeroud, F. Dahmoune, B. Merzouk, J.P. Leclercand, K. Madani, Improvement of electrocoagulation–electroflotation treatment of effluent by addition of *Opuntia ficus-indica* pad juice, Sep. Purif. Technol., 144 (2015) 168–176.

[13] A.A. Pelaez-Cid, I. Velazquez-Ugalde, A.M. Herrera-Gonzalez, J. García-Serrano, Textile dyes removal from aqueous solution using *Opuntia ficus-indica* fruit waste as adsorbent and its characterization, J. Environ. Manage., 130 (2013) 90–97.

[14] P.K. Holt, G.W. Barton, C.A. Mitchell, The future for electrocoagulation as a localized water treatment technology, Chemosphere, 59 (2005) 355–367.

[15] A. Dermouchi, M. Bencheikh-lehocine, S. Arris, V. Nedeffand, N. Barsan, Aspects regarding the electrocoagulation applications in the water and wastewater treatment, J. Eng. Stud. Res., 210 (2015) 26–33.

[16] E.H. Ezechi, S.R. Kutty, A. Malakahmad, M.H. Isa, Characterization and optimization of effluent dye removal using a new low cost adsorbent: equilibrium, kinetics and

thermodynamic study, Process Saf. Environ. Prot., 9 (2015) 16–32.
[17] S. Hazourli, L. Boudiba, D. Fedaoui, M. Ziati, Prétraitement de coagulation floculation d'eaux résiduaires d'une laiterie industrielle, J. Soc. Alg. Chim., 17 (2007) 155–172.
[18] APHA, Standard Methods for the Examination of Water and Wastewater, 21st ed., American Public Health Association, Washington DC, 2005.
[19] A. Aitbara, M. Cherifi, S. Hazourli, J.P. Leclerc, Continuous treatment of industrial dairy effluent by electrocoagulation using aluminum electrodes, Desal. Water Treat., 57 (2016) 3395–3404.
[20] M. Kobya, E. Demirbas, Evaluations of operating parameters on treatment of can manufacturing wastewater by electrocoagulation, J. Water Process Eng., 8 (2015) 64–74.
[21] S. Brunauer, P.H. Emmett, E. Teller, Adsorption of gases in multimolecular layers, J. Am. Chem. Soc., 60 (1938) 309–319.
[22] F.Z. Khelaifia, S. Hazourli, S. Nouacer, R. Hachani, M. Ziati, Valorization of raw biomaterial waste-date stones-for Cr(VI) adsorption in aqueous solution: thermodynamics, kinetics and regeneration studies, Int. Biodeterior. Biodegrad., 114(2016) 76–86.
[23] M. Bendaia, S. Hazourli, A. Aitbara, N. Nait Merzoug, Performance of electrocoagulation for food azo dyes treatment in aqueous solution: optimization, kinetics, isotherms, thermodynamic study and mechanisms, Sep. Sci. Technol., 55 (2020) 1–17, doi: 10.1080/01496395.2020.1806883.
[24] S. Touahria, S. Hazourli, K.H. Touahria, A. Eulmi, A. Aitbara, Clarification of industrial mining wastewater using electrocoagulation, Int. J. Electrochem. Sci., 11 (2016) 5710–5723.
[25] Official Journal, Council directive on the protection of the environment and in particular of the soil when sewage sludge is used in agriculture, Off. J. Eur. Union, 181 (1986) 6–12.
[26] A. Maréchal, M. Aumondand, G. Ruban, Mise en œuvre de la turbidimétrie pour évaluer la pollution des eaux résiduaires, Houille Blanche, 5 (2001) 81–86.
[27] A. ŞengilI, M. Özacar, Treatment of dairy wastewaters by electrocoagulation using mild steel electrodes, J. Hazard. Mater., 137 (2006) 1197–1205.
[28] H. Perry Robert, W. Green Don, Perry's Chemical Engineers' Handbook, 7th ed., McGraw-Hill Professional Publishing, New York, NY, 1997, p. 2640.
[29] A. Eulmi, S. Hazourli, R. Abrane, M. Bendaia, A. Aitbara, S. Touahri, M. Chérifi, Evaluation of electrocoagulation and activated carbon adsorption techniques used separately or coupled to treat wastewater from industrial dairy, Int. J. Chem. Reactor Eng., 17 (2019) 1–12.
[30] International Dairy Federation, Disposal and utilization of dairy sludge, Bull. Int. Dairy Fed., 356 (2000) 3–34.
[31] M. Sassi, B. Bestani, A. Hadj Said, N. Benderdouche, E. Guibal, Removal of heavy metal ions from aqueous solutions by a local dairy sludge as a biosorbant, Desalination, 262 (2010) 243–250.
[32] M. Cherifi, S. Hazourli, S. Pontvianne, F. Lapicque, J.P. Leclerc, Electrokinetic removal of aluminum and chromium from industrial wastewater electrocoagulation treatment sludge, Desal. Water Treat., 57 (2016) 18500–18515.
[33] O. Flynn, C.J. Fenton, O. Wall, D. Brennan, R.B. McLaughlin, M.J. Healy, Influence of soil phosphorus status, texture, pH and metal content on the efficacy of amendments to pig slurry in reducing phosphorus losses, Soil Use Manage., 34 (2018) 1–8.
[34] P.A. Moore, T.C. Daniel, D.R. Edwards, Reducing phosphorus runoff and improving poultry production with alum, Poultry Sci., 78 (1998) 692–698.
[35] S.M. Ashekuzzaman, P. Forrestal, K. Richards, O. Fenton, Dairy industry derived wastewater treatment sludge: generation, type and characterization of nutrients and metals for agricultural reuse, J. Cleaner Prod., 230 (2019) 1266–1275.
[36] European Commission, Compliance With Limits Required for Compost from Source Separated Bio-Waste Only, 2008, p. 34.
[37] M.E. Malainine, A. Dufresne, D. Dupeyre, M. Mahrouz, R. Vuong, M.R. Vignon, Structure and morphology of cladodes and spines of *Opuntia ficus-indica*, cellulose extraction and characterization, Carbohydr. Polym., 51 (2003) 77–83
[38] N. Barka, S. Qourzal, A. Assabbane, A. Nounah, Y. Ait-Ichou, Adsorption of disperse blue SBL dye by synthesized poorly crystalline hydroxyapatite, J. Environ. Sci., 20 (2008) 1268–1272.
[39] N. Barka, S. Qourzal, A. Assabbane, A. Nounah, Y. Ait-Ichou, Removal of reactive yellow 84 from aqueous solutions by adsorption onto hydroxyapatite, J. Saudi Chem. Soc., 15 (2011) 263–267.
[40] U. Pathak, P. Das, P. Banerjee, S. Datta, Treatment of wastewater from a dairy industry using rice husk as adsorbent: treatment efficiency, isotherm, thermodynamics, and kinetics modelling, J. Thermodyn., 2016 (2016) 1–7.
[41] S. Chakraborty, S. Chowdhury, P. Das, Adsorption of Crystal Violet from aqueous solution onto NaOH-modified rice husk, Carbohydr. Polym., 86 (2011) 1533–1541.
[42] J. Hambly, Environmental – ecological impact of the dairy sector (literature review on dairy products for an inventory of key issues – list of environmental initiatives and influences on the dairy sector), Int. J. Dairy Technol., l64 (2011) 145–146.
[43] JORA Journal Officiel de la République Algérienne du 23 Avril, Annexe des Valeurs Limites Maximales des Paramètres de Rejet des Installations de Déversements Industrielles, n° 26, 2006.
[44] B. Shoba, R. Sakthiganesh, S. Raju, Treatment of dairy wastewater using tamarind kernel adsorbent, Int. J. Innovative Res. Eng. Manage., 3 (2015) 221–223.
[45] F. Falahati, M. Baghdadi, B. Aminzadeh. Treatment of dairy wastewater by graphene oxide nanoadsorbent and sludge separation, using *in situ* sludge magnetic impregnation (ISSMI) pollution, 4 (2018) 29–41.
[46] O. Moradi, M.S. Maleki, Removal of COD from dairy wastewater by MWCNTs: adsorption isotherm modeling, Fullerenes Nanotubes Carbon Nanostruct., 21 (2013) 836–848.
[47] E. Bazrafshan, F.K. Mostafapour, M. Alizadeh, M. Farzadkia, Dairy wastewater treatment by chemical coagulation and adsorption on modified dried activated sludge: a pilot-plant study, Desal. Water Treat., 57 (2016) 8183–8193.
[48] M. Geetha Devi, J.J. Dumaran, S. Feroz, Dairy wastewater treatment using low molecular weight crab shell chitosan, J. Inst. Eng. (India) Environ. Eng. Div., 93 (2012) 9–14.
[49] H.C.L. Geraldino, J.I. Simionato, T.K.F. Souza Freitas, J.C. Garcia, O. Carvalho Júnior, C.J. Correr, Efficiency and operating cost of electrocoagulation system applied to the treatment of dairy industry wastewater, Acta Sci. Technol., 37 (2015) 401–408.
[50] G.F. Silva Valente, R.C.S. Mendonça, J.A.M. Pereira, The efficiency of electrocoagulation using aluminum electrodes in treating wastewater from a dairy industry, Ciênc. Rural, 45 (2015) 1713–1719.
[51] C. Agabriel, J. Coulon, B. De Rancourt, Composition chimique du lait et systèmes de production dans les exploitations du Massif, INRA Prod. Anim., 2 (2001) 119–128.
[52] G. Vijayaragharan, T. Sivakumar, K. Vimal, Application of plant based coagulant for waste water treatment, Int. J. Adv. Eng. Res. Stud., 1 (2011) 89–93.
[53] T. Nharingo, M.T. Zivurawa, U. Guyo, Exploring the use of cactus *Opuntia ficus-indica* in the biocoagulation–flocculation of Pb(II) ions from wastewaters, Int. J. Environ. Sci. Technol., 12 (2015) 3791–3802.
[54] P. Cãnizares, C. Jiménez, F. Martínez, M.A. Rodrigo, C. Sáez, The pH as a key parameter in the choice between coagulation and electrocoagulation for the treatment of wastewaters, J. Hazard. Mater., 163 (2009) 158–164.