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Adsorption of organic pollutants from slaughterhouse wastewater using powder of *Moringa oleifera* seeds as a natural coagulant

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ABSTRACT

The seed of *Moringa oleifera* Lam. (*Moringaceae*) comes from a tropical plant containing important quantities of edible oils and water-soluble proteins with excellent coagulation properties which can be used in wastewater treatment. These proteins are non-toxic natural organic polymers and biodegradable. The main objective of this work was to use the powder of seeds of *M. oleifera* Lam. as a natural coagulant for the adsorption of organic pollutants from slaughterhouse wastewater. The effects of adsorption time, initial pH, slaughterhouse wastewater concentration and dosage of seed in powder were evaluated. The results indicated that 180 min is necessary for a high adsorption. The greatest removal efficiency measured as chemical oxygen demand (COD) was 5,614 mg/L (64%) and this was reached using 7 g/L powder of seed, pH 9 and 8,772 mg/L of pollutant in wastewater. This study elucidates that the sorption process follows second-order kinetics and the values of constant are in the range $0.0427 \leq k_2$ (g pollutant organic adsorbed/g of *M. oleifera* min) ≤ 0.0516, with correlation coefficients above 0.98. The adsorption data were fitted to the Langmuir and Freundlich isotherm equations. The maximum adsorption capacity of 0.523 g COD/g powder suggests a good affinity between the organic pollutants and the powder.

Keywords: Moringa oleifera; Slaughterhouse wastewater; Natural coagulant; Bioadsorbent

1. Introduction

Pollution by organic and inorganic contaminants is an important environmental problem due to their toxic effects and possible accumulation throughout the food chain and hence in the human body [1]. The search for new and low-cost techniques is very important for the removal of organic and inorganic contaminants from drinking water and industrial wastewater. Biosorption is becoming a potential alternative to traditional treatment processes used for the removal of organic pollutants; this represents a biotechnological innovation as well as a cost-effective and excellent tool for capture contaminant compounds from aqueous solutions [1–3].

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Many coagulants are widely used in conventional processes for wastewater treatment. These coagulants can be classified as inorganic coagulants, naturally occurring coagulants and synthetic organic polymers [4,5]. These compounds exhibit different chemical compositions depending on their application and the characteristics of the residual water. The inorganic polymer known as polyaluminium chloride (PAC) and inorganic salt alum (aluminium sulphate) are the most widely used coagulants in the physicochemical treatment of wastewater for removal of volatile suspended solids [1,4,5]. However, some studies have reported that residual aluminium, which is the main component of PAC and alum, may induce Alzheimer or contribute to various diseases [6]. It has also been reported that monomers of some synthetic organic polymers such as acrylamide have neurotoxic and strong carcinogenic properties. These concerns, along with the adverse environmental effects generated by these compounds, are their main drawbacks when compared with natural materials; however, their cost is economical [7–10].

Currently, various naturally occurring alternatives for the production of coagulants are being explored, because the performance of some plant and animal products is excellent [7,11]. Indeed, the use of biological materials for the treatment of wastewaters containing organic and inorganic contaminants is growing. This relatively new technology has received considerable attention in recent years as it has many advantages over traditional methods. It uses inexpensive and abundant renewable materials with good ability for the recovery of organic pollutants [6].

The removal of organic pollutants from aqueous solution by biomaterials is an innovative and promising technology. In recent years, research about biosorption mechanisms has been intensified as various biomasses can be employed to capture organic and inorganic pollutants from industrial effluents. The efficiency of the biomass used depends upon the capacity, affinity and specificity related to its physical chemistry property [1,3].

A large variety of biosorbents have been tested for the removal of both organic and inorganic compounds, but the seeds from the *Moringa oleifera* tree (*M. oleifera*) have particularly attracted attention in the environmental science community because they are capable of clarifying turbid surface water through two action levels: as a coagulating and antibacterial agent [1,12]. The seeds of *M. oleifera* represent a viable alternative like natural coagulant by virtue of its low cost, not only in developing countries, but also in the world because of the efficiency shown [11].

The trees of the genus *Moringa Adans* are tropical and subtropical plants belonging to the family *Moringaceae* with 14 different varieties, found throughout India, Asia, Africa and Latin America, where the most familiar being *M. oleifera* Lam. [3,13,14]. Its seeds contain edible oil and water-soluble proteins. It is estimated that each tree can produce up to 25,000 seeds annually with an average weight of 0.3 g per seed. This material in powder or extract form is the natural substance most widely used as coagulant to clarify superficial waters with high turbidity in developing countries and is also used in the food, cosmetics and pharmaceutical industries [13,15,16].

The first paper published about *M. oleifera* was written in 1935 by Puri [17], from this year and until end of 2013, 1,300 reports have been published. Moreover, since 1979 to the current, 134 reports have been written only about the use of its seeds to treat wastewater; however, they principally report the reduction of turbidity and colour in surface water and only a small part of these depict the depuration of organic pollutants present in industrial wastewater [6,10,11].

The most cited and most important scientific report makes the description of the mechanisms involved when *M. oleifera* is applied in the treatment of turbid waters was published in 1995 by Ndabigengesere [18]. This suggests that the active agents that perform coagulation are dimeric cationic proteins with molecular mass between 12 and 14 kDa and isoelectric point between 10 and 11, having as its main mechanism particle coagulation, adsorption and subsequent charge neutralization [13,19]. The document initiated widespread interest in the scientific community for the simplicity and clarity in the mechanisms that were discussed. Although there is not a general consensus on what is the precise mechanism of adsorption and type of protein, the efficiency of the seed of *M. oleifera* about these systems is significant [19].

The study of parameters influencing the biosorption process with *M. oleifera* is crucial for the evaluation of sorption potential of pollutant material. The mechanism of binding in the biomass depends not only on the chemical nature of contaminant, age of biomass, its preparation and its specific surface properties, but also about operating conditions such as initial pH, temperature and ionic strength. Other factors influencing the adsorption include *M. oleifera* dosage, size of particle, agitation rate and reaction time [1,13,19].

Agro-industrial wastewater contains organic compounds with an extensive variety of physical and chemical characteristics, which directly affect the behaviour of effluent and the capacity to remove pollutants. The slaughtering, processing and preserving activities required for meat production in municipal slaughterhouses generate great quantities of wastewater and solid waste. It is estimated that for every cow and pig processed, 700 and 330 L of wastewater are generated, respectively [20]. Slaughterhouse wastewater is a complex mixture of proteins, organic compounds and fats. The organic load of 5,000–15,000 mg/L, measured as chemical oxygen demand (COD), includes fats and oils at concentrations in range of 100–300 mg/L and isoelectric point between 3 and 4 [21].

The objective in this study was to investigate the adsorption of organic pollutants (measured as COD) from slaughterhouse wastewater when *M. oleifera* Lam. seed was employed as a natural coagulant. The variables of adsorption time, initial pH, slaughterhouse wastewater concentration and powder dosage were varied in order to better understand the sorption processes.

2. Experimental section

2.1. Wastewater sampling and analyses

The slaughterhouse wastewater used in this research was obtained from a municipal slaughterhouse without prior treatment located in Coatepec, Veracruz, Mexico (19˚ 21´ N, 96˚ 47´ W). The average volume of wastewater generated in one working day is 32 m^3. The liquid waste comes from the slaughter of animals and the final wash of the work area. The effluents generated are accumulated in a 35 m^3 pit, wastewater is removed every day to a nearby river in the night. Wastewater samples were obtained during intervals of 60 min throughout a work day of 8 h, to form a composite sample of 40 L, which was transferred to the laboratory and kept refrigerated at 4˚C for analysis and use in the experiment. The isoelectric point of the slaughterhouse wastewater was identified as 3.8, and the physicochemical characterization was carried out according to standard methods [22]. These results together with standard deviations are presented in Table 1.

2.2. Preparation of powder of M. oleifera seeds

Dried *M. oleifera* seeds were classified and supplied by the Autonomous University of Chihuahua. They were reaped in the Yaqui Valley that is located south of Sonora (27˚ 30´ N and 110˚ 15´ W), Mexico, and stored at room temperature (25˚C). The seeds used were harvested and employed during the first month like is suggested by Katayon and co-workers to prevent the reduction in natural coagulant [23]. The seeds were shelled by hand just before use, and the kernel was reduced to a fine powder using a food processor (Moulinex, France). They were then sieved to obtain a bioadsorbent with homogenous particle size. The white seed kernels with mesh size 0.51 mm were selected for use in the adsorption tests like is suggested in the literature [24]. According to official methods of analysis [25], four bromatology analyses in dry basis were performed to the seed in powder showing the following results (see Table 2):

2.3. Batch adsorption studies

In all the experimental set-ups, the doses in weight of biosorbent were in the range of 3–7 g/L; this range

Table 1
Physical chemistry characterization of slaughterhouse wastewater

Parameter	Unit	Value (average)	Standard deviation	Method
pH	PU	695	0.5	4,500-H$^+$ B
Alkalinity (in CaCO$_3$)	mg/L	1,750	135	2,320 B
Conductivity	ms/cm	10.3	0.2	2,510 B
COD$_T$	mg/L	8,772	193	5,220 D
COD$_S$	mg/L	6,621	102	5,220 D
BOD	mg/L	3,230	114	5,210 B
TS	mg/L	8,565	595	2,540 B
VS	mg/L	7,634	127	2,540 E
TSS	mg/L	713.9	44	2,540 D
N$_{org}$	mg/L	320.5	85	4,500-N$_{org}$
N-NH$_3$	mg/L	180.2	28	4,500-NH$_3$

Note: PU: potentiometric unit; COD$_T$: COD$_S$ total and soluble COD, respectively; BOD: biological oxygen demand; TS: total solids; VS: volatile solids; TSS: total suspended solids; N$_{org}$: organic nitrogen and N-NH$_3$: ammonia nitrogen.

Table 2
Bromatology analysis of the *M. oleifera* powder in dry basis (%)

Parameter	Value average (%)	Standard deviation
Humidity	5.80	0.3
Protein (N × 6.25)	44.24	3.4
Ash	4.37	0.5
Fat (ether extract)	37.15	2.4
Total carbohydrates	8.13	0.7
Crude fibre	0.31	0.05

is consistent with the dose reported in the literature, which suggests a range of 0.5–6.0 g/L [26]. Experiments were conducted at 25 ± 1˚C; in all cases, the *M. oleifera*/slaughterhouse wastewater mixture was well stirred for homogenization and adsorption equilibrium was reached in 12 h. The contact time for the adsorption process (10–180 min) was selected considering the results of the kinetics for organic compound removal reported previously by Akhtar and co-workers, who proposed a time of 5–120 min [6]. Different operation conditions were investigated during the study to establish their influence on the adsorption process. Here were tested initial pH in range of 5–9 and slaughterhouse wastewater concentration in values of 4,386–8,772 mg/L of COD. The last condition is justified because the wastewaters come from the slaughter of animals and are diluted constantly in the pit by wash waters from the work area, which have the same type of pollutants but in low concentrations. For this study, the dilutions of slaughterhouse wastewater in the laboratory were carried out employing distilled water.

Adsorption tests were carried out using a jar test apparatus (Phipps & Bird, model PB-700) with six beakers of 2 L of capacity. The coagulation–flocculation process was carried out as follows: in the beginning, a vigorous shaking was applied to homogenize the effluent (100 rpm); after five minutes, the adsorbent was introduced into each of the beakers. The rapid mixing was maintained for five minutes, and then, the mixing speed was reduced to 20 rpm for twenty minutes to perform the adsorption process. After this, the apparatus was turned off. Finally, the sedimentation process took 180 min and carried out according to APHA [22]. After every 10 min of adsorption time, an aliquot of 20 mL was sampled from the beakers and COD was determined. An adsorption test with no bioadsorbent was conducted like a process control. To adjust the initial pH of the medium, 0.1 N solutions of NaOH and HCl were used during this study.

2.4. Analytical methods

The pH, dissolved oxygen and conductivity measurements were made with a multiparameter digital metre (HACH HQ 40d). The COD values were determined using HACH DR/2010. The measurements of settled sludge volume were performed with an Imhoff cone, as suggested by the method 2710 C [22].

2.5. Determination of removal efficiency

The quantification of organic compounds measured as COD before and after the adsorption processes was determined. Below, the method used for calculating the removal efficiency or percentage adsorption is shown. In this case, it was calculated according to Eq. (1), where C_i and C_t are the initial and any time t (min) concentrations, respectively, expressed in mg/L in COD [27].

$$\text{Removal efficiency } (\%) = \frac{(C_i - C_t)}{C_i} \times 100 \tag{1}$$

2.6. Capacity of adsorption

The capacity of adsorption was determined by means of Eq. (2); the uptake of pollutants (q_e) was calculated from a mass balance. Here, (C_i) and (C_e) are the initial and equilibrium concentrations of pollutants adsorbed, respectively, expressed in mg/L in COD.

$$q_e\ (g/g) = \frac{(C_i - C_e)V}{1{,}000\ \mathrm{W}} \tag{2}$$

In this case, q_e is the adsorption capacity in equilibrium in COD (g pollutant organic adsorbed/g of *M. oleifera*), V is the volume of solution (L), and W is the amount of dry sorbent powder (g). Each experiment was conducted in triplicate to ensure the reproducibility of results; the data represent the average of these experiments along with 95% of confidence in standard deviations. Statistical analyses were performed using the statistical functions of Microsoft Excel® version Office XP (Microsoft Corporation, USA) [28].

3. Results

Since the application of powder from *M. oleifera* in slaughterhouse wastewater treatment is a recent technical achievement, it has not been reported extensively. Consequently, there is no way to compare these results with others. It must be highlighted that no chemical or thermal treatment was made on *M. oleifera* seeds; this procedure makes the adsorption process simpler and more directly applicable in every case.

The study of powder of *M. oleifera* as a natural adsorbent for industrial wastewater treatment is still recent, particularly when applied to liquid effluents of slaughterhouses. Moreover, the reported results usually present disagreements about the variables used in adsorption process with *M. oleifera* [4,27–29]. Another point to consider is the fact that natural compounds may contain variations in their composition, which can be attributed to the usage of seeds collected from different geographic locations as were reported by Narasiah and co-workers, which interfere with its adsorption power [15].

3.1. Kinetic of pollutant adsorption

Many times, the primary goal of coagulation–flocculation was organic compound removal; of the most important physicochemical parameters for the evaluation of the adsorption process is the sorption equilibrium and the kinetic of reaction. For this research, a kinetic study was first done [27]. In order to investigate the mechanisms of the adsorption process, two different kinetic models were proposed. The first- and second-order Lagergren rate equations were applied to describe the kinetics of adsorption of organic pollutants onto *M. oleifera* powder [8]. The first-order Lagergren model is one of the most widely used expressions describing the adsorption of solute from a solution. The first-order model is generally expressed as follows Eq. (3) [8,10,27]:

$$\frac{dq}{dt} = k_1\ (q_e - q_t) \tag{3}$$

where q_e and q_t (g pollutant organic adsorbed/g of powder of *M. oleifera*) are the amounts of organic pollution adsorbed on the adsorbent at equilibrium and at any time t (min), respectively, while k_1 (min^{-1}) is the rate constant of the first-order model. The integrated form of the above equation is rearranged to obtain the following linear function Eq. (4):

$$\log(q_e - q_t) = \log\ q_e - \frac{k_1 t}{2.303} \tag{4}$$

The first-order model considers the rate of occupation of the adsorption sites proportional to the number of unoccupied sites. The second-order rate equation is expressed as Eq. (5) [8,10,27]:

$$\frac{dq}{dt} = k_2\ (q_e - q_t)^2 \tag{5}$$

Here, k_2 (g pollutant organic adsorbed/g of *M. oleifera* min) is the rate constant for the second-order kinetic model. The integrated form and linearized form of previous equation are as follows Eq. (6):

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \tag{6}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{7}$$

where q_e and q_t are the amount of removed organic pollutant by *M. oleifera* at equilibrium and in any time t (min), respectively. As shown in Fig. 1, the effect on

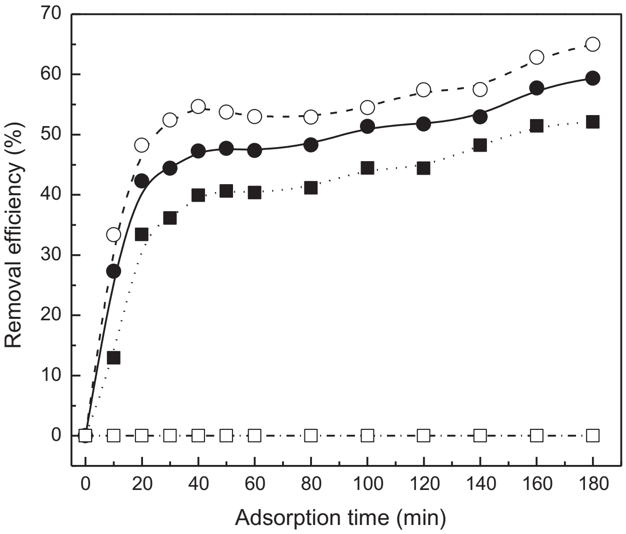

Fig. 1. Influence of adsorption time on removal efficiency of COD_T with slaughterhouse wastewater concentration at 8,772 mg/L using a powder dose of 7 g/L at pH 7 (●) and pH 9 (○); a dose of 3 g/L at pH 9 (■) and control system without powder at pH 9 (□).

kinetic of sorption of organic pollutants with powder from *M. oleifera* was studied from 10 to 180 min for different conditions.

For COD, the removal efficiency of pollutants gradually increased with the increase in adsorption time from 10 to 40 min. The values near to equilibrium throughout the adsorption process were showed in 180 min, for this reason, the proposed optimum value through time was 180 min, because most of the contaminants were captured at this time. Important increases were observed in the equilibrium, and in most cases, the equilibrium concentration showed values near of 92% after 12 h, while the control system that did not contain *M. oleifera*, not shown contaminant adsorption. Fig. 2 shows a spectrum of absorbance for slaughterhouse wastewater with 8,772 mg/L in equilibrium employing 7 g of powder of *M. oleífera* at pH 9 and without *M. oleifera*. Similar equilibrium times were reached by Akhtar et al. [6] for the removal of organic pollutants using *M. oleifera* pods and Kumari et al. [26] for the removal and recovery of arsenic from aqueous system using *M. oleifera* seed powder.

To define the kinetic parameters of pollutant adsorption, the Fig. 3 was elaborated by employing the linearized form of the equation of Lagergren. In this study, the better equation of fitting to the experimental data was the second-order kinetic. The values of k computed from the slope of the linear plots for both models are depicted in the Table 3.

This observations elucidates that the sorption process follows second-order kinetics and the values of k_2 are in the range $0.0427 \le k_2 \le 0.0516$ (g pollutant organic adsorbed/g of powder of *M. oleifera* min). The correlation coefficients for the second-order kinetic model obtained for this study are above 0.98 in all the cases analysed. These results confirm that this adsorption system is well represented by the second-order kinetic model. The results of k_2 obtained here are congruent in order of magnitude with the reported by Akhtar and co-workers for the removal of organic pollutants such as benzene, toluene, ethylbenzene and cumene in aqueous solutions [6].

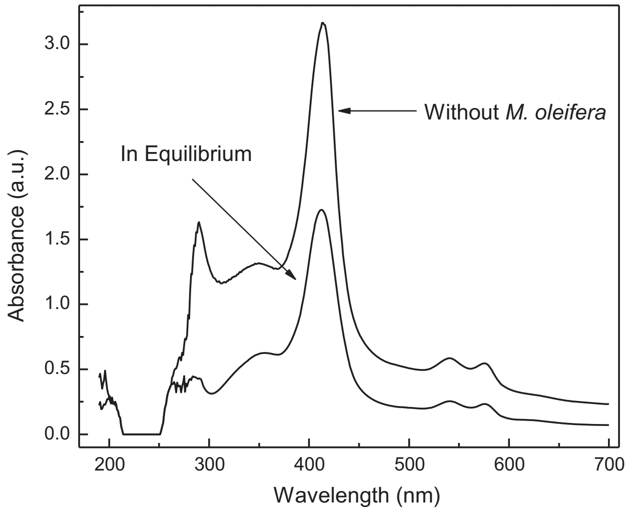

Fig. 2. Spectrum of absorbance for slaughterhouse wastewater employing 8,772 mg/L in COD_T, pH 9 and with 7 g of powder of *M. oleífera* in equilibrium and without powder seed.

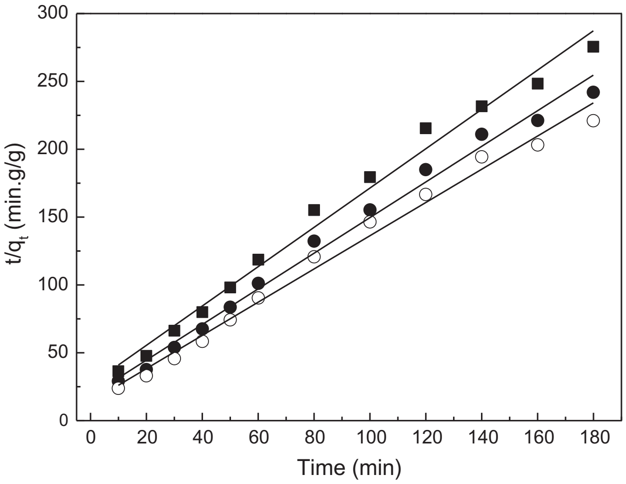

Fig. 3. Second-order kinetics for pollutant adsorption from slaughterhouse wastewater in concentration of 8,772 mg/L using a powder dose of 7 g/L at pH 7 (●); pH 9 (○) and dosage of 3 g/L at pH 9 (■).

Table 3
Comparison between the k calculated for different operating conditions for the equations first- and second-order

pH	*M. oleifera* powder (g/L)	k_1 (min^{-1})	R^2
First-order kinetic			
9	7	0.0251	0.873
7	7	0.0228	0.871
9	3	0.0186	0.792
Second-order kinetic		k_2 (g/g min)	
9	7	0.0516	0.988
7	7	0.0484	0.990
9	3	0.0427	0.987

3.2. Effect of initial pH

The powder of *M. oleifera* seeds contains cellulose, hemicellulose, lignin and crude fibre. It is a matrix complex that contains carboxylic and carbonaceous fibre and amino functional groups. These groups may be dissociated at different initial pH values and consequently take part in the adsorption process. Therefore, it is logical to assume that the initial pH influence the adsorption process of the pollutants with *M. oleifera* [27]. Fig. 4 illustrates the effect of initial pH on the removal efficiency in COD. Different slaughterhouse wastewater concentrations were used with powder *M. oleifera* dose of 7 g/L and initial pH in range of 5–9. These results were carried out in 180 min of adsorption as was suggested in the previous sections.

For an initial pH in range of 5–9, a reduction greater than 19% in COD was reached in all cases. However, the better conditions of operation are when the initial pH was basic. The per cent reduction in COD increased with increase in initial pH, from 45% at pH 5 to 64% at pH 9 employed 8,772 mg/L (100% v/v), but when the concentration in wastewater is diluted to 5,263 mg/L (60% v/v), the adsorption process is inverse. On the other hand, when the pH is 7, all cases show the minimum capacity of adsorption, this process can be attributed to changes in the protein conformation to pH 9, because ionic strength is affected by the dilution, the mechanism suggests that the proteins are denatured, as is proposed in the literature [30].

The experimental results suggest that the maximum adsorption capacity is achieved in the upper pH range; however in this zone decreases the adsorption capacity when the wastewaters are diluted, this behaviour is consistent with that reported in the literature because that the isoelectric point is between 10 and 11 and shows as its main mechanism particle coagulation, adsorption and subsequent charge neutralization [13,19,30]. This same behaviour is coherent with that reported in the literature for the treatment of dairy wastewater and wastewater samples collected at a pumping station in the percentage of removal efficiency [15,28].

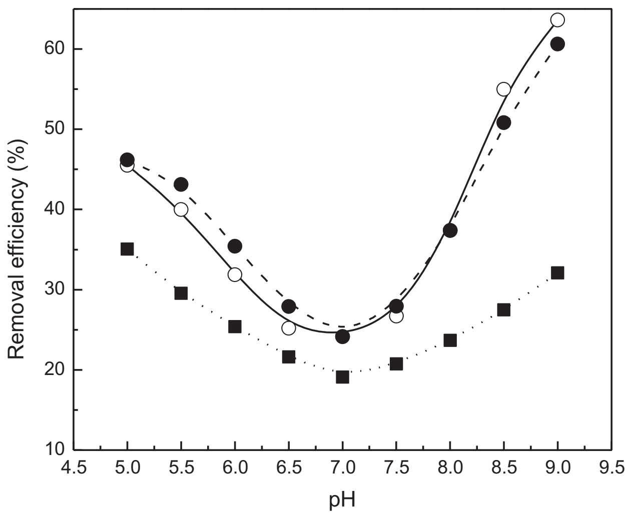

Fig. 4. Effects of initial pH on removal efficiency of COD_T with slaughterhouse wastewater concentration of 8,772 mg/L (○); 7,895 mg/L (●) and 5,263 mg/L (■) using powder dose 7 g/L and 180 min of adsorption.

In this study, the best results were obtained when the initial pH values were handled in 9, which suggest that the protein was not fully denatured by the effect in the initial pH change. On the other hand, the dilution in the concentration of slaughterhouse wastewater improved the performance of the *M. oleifera* at low pH values. This last behaviour may be attributed to the presence of more OH ions at $pH < 7$, resulting in an increased uptake of slaughterhouse wastewater components by the sorbent surface.

The results obtained in this study show that the powder of *M. oleifera* seed keeps its adsorption power when pH is within a range of 5–9. Furthermore, because the natural pH of slaughterhouse wastewater is around 7, it is necessary to adjust this variable in order to make the adsorption process more efficient [6].

3.3. Influence of dosage of M. oleifera *powder*

The influence of dosage of *M. oleifera* seed powder on treatment of slaughterhouse wastewater is illustrated in Fig. 5. Here, COD removal efficiency is shown in function of the dose of powder *M. oleifera* (3–7 g/L) and various concentrations in slaughterhouse wastewater at pH 9.

The figure shows that a higher dose of powder of *M. oleifera* causes increased in COD removal efficiency, but does not produce an important difference with the dilutions of slaughterhouse wastewater except to the dose greater than 4.5 g/L of bioadsorbent. Although the removal efficiency with doses of *M. oleifera* in the low range (3–4.5 g/L) was approximately equal in their behaviour with the dilutions, this performance is very different after 5 g/L with larger dilutions.

The maximum removal efficiency obtained for COD was with 7 g/L of *M. oleifera* powder, since these characteristics shows the greatest difference in the removal of contaminants, starting in 38 and ending in 64% with the greatest amount adsorbent employed; these results are consistent with data report in the literature for organic pollutants such as benzene, toluene and other [6,31]. On the other hand, the extraction of the active coagulant component from *M. oleifera* seed has been employed for water and synthetic wastewater treatment by many authors [4,23,27]. The total organic carbon (TOC) reported and turbidity removal by coagulant *M. oleifera* was up to 50–85 and 80–95%,

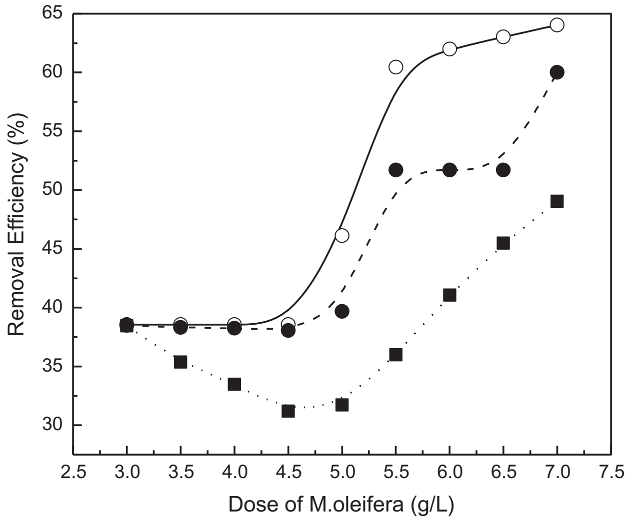

Fig. 5. Influence of dosage of *M. oleifera* powder on removal efficiency of COD_T with slaughterhouse wastewater concentration of 8,772 mg/L (○); 6,140 mg/L (●) and 5,263 mg/L (■) in pH 9 and 180 min of adsorption.

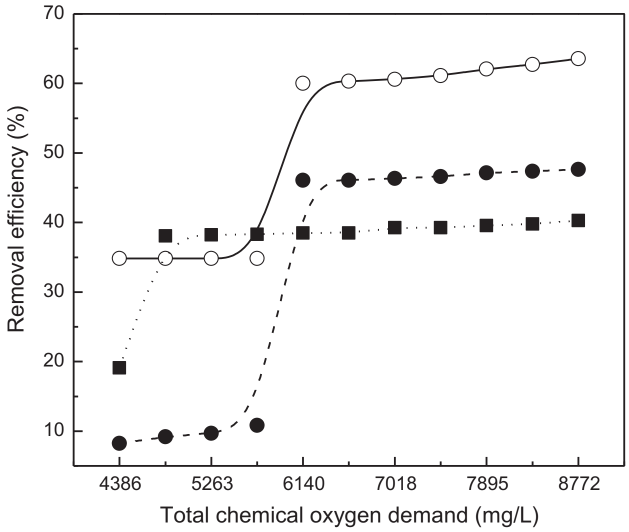

Fig. 6. Influence of slaughterhouse wastewater concentration on removal efficiency of COD_T with *M. oleifera* powder of 7 g/L (○); 5 g/L (●) and 3 g/L (■) in pH 9 and 180 min of adsorption.

respectively, but in all cases, the initial turbidity of the synthetic water was lower than 300 NTU and the level of pollutants is not great (TOC < 1,750 mg/L). In this study, the slaughterhouse wastewaters are a matrix more complex and your depuration is less efficient.

Considering aspects like slaughterhouse wastewater concentration, initial pH and biomass dosage, the adsorption process with extract of *M. oleifera* is as efficient as the coagulation process using powder of *M. oleifera* without previous treatment. Another advantage present when using *M. oleifera* powder as bioadsorbent is the operational simplicity when compared with the traditional coagulation process with inorganic adsorbents or when is compared with the process of extraction of active component from *M. oleifera*, because in all cases analysed here the efficiency is similar.

3.4. Effect of slaughterhouse wastewater concentration

The variation in the sorption of pollutant components as a function of initial slaughterhouse wastewater concentration is depicted in Fig. 6. This shows removal efficiency of COD as a function of concentration from 4,386 to 8,772 mg/L in COD, with various dosages of *M. oleifera* powder and pH 9 in 180 min of process.

In general, it is observed that removal efficiency in COD is good for all cases (upper to 35%) after of 6,140 mg/L; however for 7 g/L of *M. oleifera* powder, the depuration efficiency was better, because reaching 64% in removal efficiency of COD with the maximum concentration of slaughterhouse wastewater 8,772 mg/L. The depuration efficiency when used 7 g/L de *M. oleifera* in the range of concentration of slaughterhouse wastewater from 4,386 to 8,772 mg/L in COD passed from 35 to 65%, respectively. Moreover, the purification efficiency obtained when 5 g/L of *M. oleifera* powder was used, improved from 8 to 42% employing the same range of COD in slaughterhouse wastewater, respectively.

The influence of the initial slaughterhouse wastewater concentration upon the removal efficiency was relevant. The Fig. 6 shows that, if the initial concentration of wastewater increased until 6,149 mg/L in COD (70% v/v), the removal efficiency of organic pollutants is highest. However, after this value, the change in the efficiency of removal drops significantly. In the reports of the literature, the extract obtained of *M. oleifera* seeds is used to purify superficial water through reduction in turbidity; however, the organic load is not taken into account due to the fact that they handle synthetic water without concentrations high of organic pollutant [4,23,28]. In this study, it is observed that when applying high concentrations in COD with pH 7, the capacity for depuration of organic pollutants by *M. oleifera* powder tends to increase significantly after 6,149 mg/L, but after this value, the behaviour is constant in all cases. These findings may suggest that the sorption sites of the sorbent are being limited, which may have the effect of an insufficient capability to accommodate the increasing number of pollutants molecules available to be adsorbed into the sorbent

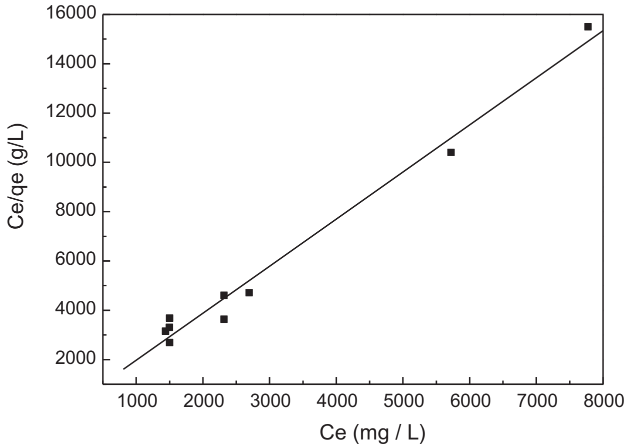

Fig. 7. Linearized Langmuir isotherm plot for sorption of organic components (COD_T) by *M. oleifera* powder. Experimental data (■), fitting of model (—).

surface. This same behaviour is similar to the results reported by Akhtar et al. [6].

3.5. Estimation of sorption capacity using isotherms

In order to understand the adsorption processes, the Langmuir isotherm was used to represent the equilibrium relationships in experiments with different initial concentrations of slaughterhouse wastewater and initial pH, using the COD data with better removal efficiency obtained in tests. Fig. 7 shows the experimental data and fitting of the regression employed to obtain the constants of the Langmuir model [32].

The Langmuir model represents monolayer adsorption on a set of adsorption sites having the same sorption energies independent of surface coverage with no interaction between adsorbed molecules and incoming molecules [2]. The data of adsorption were subjected to the linearized form of Langmuir Eq. (8) where $q_{\max}$ (g/g) and K_L (L/g) are the Langmuir model constants like is recommended by Conney and another authors [2,12]. Physically, $q_{\max}$ represents the concentration of the adsorbed species on the surface when one complete monomolecular layer of coverage is achieved. The best straight line through the data is usually obtained by a linear least-squares fitting procedure [2,12].

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{C_e}{q_{\max}} \tag{8}$$

The Freundlich sorption isotherm is the most commonly used empirical expression describing the sorption from solutions and deals with surface heterogeneity, exponential distribution of active sites of sorbent and their energies towards sorbate [33]. The linearized form of Freundlich model is described in Eq. (9) where K_f (g/g) and n (dimensionless) are constants [2,12].

$$\log\ q_e = \frac{1}{n} \log\ C_e + \log\ K_f \tag{9}$$

The constants obtained by isotherms of Langmuir and Freundlich are tabulated in Table 4. Straight lines were obtained by plotting values of C_e/q_e vs. C_e for the wastewater. The data employed for applicability of both models were the sorption data with the better removal efficiency in all analysed. The estimated values of $q_{\max}$ and K_f, respectively, come from the slope and intercept of the Y-axis from the graphic. The magnitude of $q_{\max}$ represents the maximum saturation capacity of organic components that the powder of *M. oleifera* can adsorb. In this case, a value $q_{\max}$ of 0.523 g of pollutant adsorbed/g powder of *M. oleifera* was achieved.

The Table 4 shows that the Langmuir model performs well for this system because the coefficient of determination (R^2) by COD was greater than 0.99, indicating that the constants ($q_{\max}$ and K_f) adequately describe the experimental data from the experiments of biosorption. Additionally, the plot of log q_e vs. log C_e for the organics components in the effluent, expressed in COD (see Fig. 8), was developed in order to calculate the constants generated by the Freundlich model from the sorption data.

Table 4
Parameters of Langmuir and Freundlich isotherms for slaughterhouse wastewater uptake by *M. oleifera* powder

	Model			
	Langmuir		Freundlich	
Wastewater component	$q_{\max}$ (g/g)	K_L (L/g)	n (dimensionless)	K_f (g/g)
COD_T	0.523	0.0318	4.74	0.102
R^2	0.9914		0.8018	

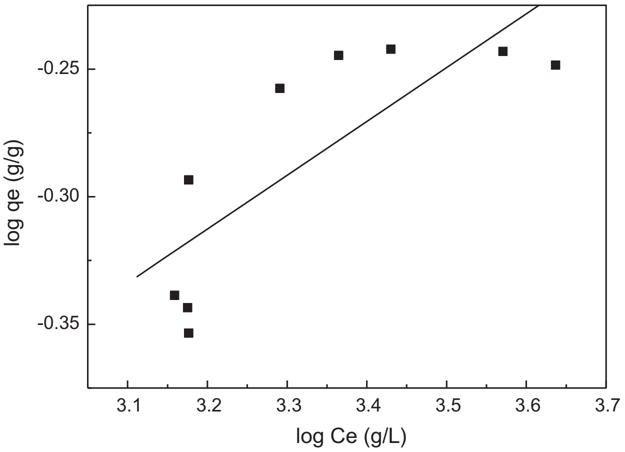

Fig. 8. Linearized Freundlich isotherm plot for sorption of organic components (COD_T) by *M. oleifera* powder. Experimental data (■), fitting of model (—).

From Table 4, it is apparent that the value n for the Freundlich model obtained for these systems indicates that process adsorption is favourable. The results published by Marquetotti et al. demonstrate that, when the value lies between 1 and 10, the effectiveness is of good quality [27]. Agreeing with this, the behaviour that *M. oleifera* powder has as a biosorbent for the removal of organic pollutants present in slaughterhouse wastewater is acceptable, because the coefficient of determination (R^2) by COD in this case was 0.8018.

On the other hand, the linearized Freundlich model did not give a good correlation for COD removal from slaughterhouse wastewater with *M. oleifera* powder, indicating that the adsorption of organic pollutants is better fitted by the Langmuir model than by the Freundlich model.

4. Conclusion

The use of *M. oleifera* powder in the treatment of slaughterhouse wastewater proved to be a natural efficient coagulant because it reduces considerably the initial values of the COD. The coagulant powder is more effective with slaughterhouse wastewater concentrations of 8,772 mg/L in the COD with adsorption times in the range of 180 min for a maximum adsorption of organic pollutants. The powder of *M. oleifera* seeds showed its sorption power in the range of initial pH suggested (from 5 to 9), but it was demonstrated that the best results are obtained at high pH levels. The greatest removal efficiency in COD was 64%, reached using 7 g/L powder of *M. oleifera*, pH 9 and 8,772 mg/L COD slaughterhouse wastewater concentration. Finally, the Langmuir model fitted well with the sorption data and demonstrated a higher value for coefficient of determination than the Freundlich model. The use of powder *M. oleifera* seeds can be considered advantageous and a promising step towards improving the processes of wastewater coagulation/flocculation.

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