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Treatment of refinery waste water using modified sludge—Effect of processparameters, sorbent characterization and kinetic studies

N. Rajamohan[a,*], Amal Al-saadi[b], K.P. Ramachandran[b]

[a] *Faculty of Engineering, Chemical Engineering Section, Sohar University, Sohar, Oman, email: natrajmohan@gmail.com*
[b] *Department of Process Engineering, Caledonian College of Engineering, Muscat, Oman, emails: eng.alsaadiamal@gmail.com (A. Al-saadi), kpramachandran@caledonian.edu.om (K.P. Ramachadran)*

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ABSTRACT

This research study focuses on the feasibility of the application of modified activated sludge as an adsorbent to treat refinery effluent was tested at different conditions. The sorbent was characterized using Fourier transform infrared spectroscopy and scanning electron microscope analysis. Maximum chemical oxygen demand (COD) removal of 84% was observed at pH 8.0, sorbent dosage 8 g L^{-1}, temperature 35°C shaking speed 300 rpm and initial COD 3,400 mg L^{-1}. Experimental data were analyzed using pseudo-second-order, power function, and Elovich kinetic models to identify the mechanism of COD removal. Pseudo-second-order model was found to represent the COD removal kinetics very well and the kinetic constant was estimated as 0.7×10^{-4} g mg^{-1} min^{-1} with the actual effluent. Maximum COD uptake of 153.846 mg g^{-1} was observed in this study.

Keywords: Refinery; Activated sludge; Uptake; Kinetics

1. Introduction

Petroleum refineries represent one of the chemical process industries that consume large quantities of water and produce substantial quantities of contaminated wastewater. The volume ratio of effluent produced to crude oil processed was reported to be in the range of 0.4–1.6 [1]. With an estimated contribution of 32% of the world's energy supply by crude oil (projected by the year 2030), continuous and increased released of refinery waste waters is a major challenge [2]. The refinery effluent is reported to contain a wide variety of pollutants like phenol, benzene, toluene, ethylbenzene and toluene along with oils. Many oil and petroleum-producing countries are water stressed and are more focused on identifying energy and cost-efficient methods to remove the pollutants in order to supplement their limited fresh water resources [3]. The selection of an appropriate remediation method for a specific industrial wastewater is a difficult task. Selection of the best treatment option for the remediation of a specific industrial wastewater is a highly complex task. The choice of one or more processes to be combined in a certain situation depends on the quality standards to be met and the most effective treatment with the lowest reasonable cost. Therefore, the main factors that must be considered in the decision on the wastewater treatment technologies to be applied are as follows: the characteristics of the original wastewater, the removal of parent contaminants, conventional treatment choices, treatment flexibility and the facility

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*Corresponding author.

decontamination capacity. It is clear that the study of real wastewater is inevitably compromised by the amount and quality of information available. If the exact composition of the original effluent is hard to find, the identification of all the reaction intermediates of any applied treatment is impracticable, and therefore, the kinetics must be based on dissolved organic carbon or chemical oxygen demand (COD) measurements [4]. Various treatment methods tried for refinery wastewater include chemical oxidation [5], coagulation [6], wet air oxidation [7], and biological methods [8]. These methods do not ensure complete elimination of organic compounds and suffer from demerits like low efficiency, slow reaction rates, and excessive sludge production [9,10]. Adsorption has been tried as an alternative method over the conventional physicochemical methods for mitigating water pollution. The application of this method is highly denied because of the expensive cost of the conventional adsorbents such as activated carbon. This has led to the search of novel, cheap and easily available adsorbent material [11]. Application of natural plant-based adsorbent and biosorbents gained importance recently. Studies involving biosorbents reported application of both living and dead cells as potential sorbents effective for the removal of contaminants. Toxicity associated with the wastewater does not favor the use of living cells. In addition, the use of living cells involve addition of nutrients which lead to increase in BOD and COD values [12]. Easy regenerability, reduced cost, and maintenance favor the application of biosorbent for the removal of contaminants from wastewaters. El-Naas et al. [13] investigated the potential application of date pit activated carbon for COD removal in refinery wastewater and reported approximately 90% removal efficiency. Mohan et al. [14] reported a COD removal of 74% using activated carbon derived from coconut shell fiber and rice husk. Refinery effluent treatment has been tried using a three-phase flow airlift loop bioreactor and the influence of airflow rate and retention times on COD removal were studied [15]. The objective of this research study are to: (i) evaluate the sorption potential of modified activated sludge (MAS) for the treatment of refinery wastewater, (ii) study the characteristics of the produced adsorbent using Scanning Electron Microscope (SEM) and Fourier transform infrared analysis, (iii) study the effect of environmental factors on COD removal efficiency and (iv) study the kinetics of the COD removal experiments to identify the mechanism of removal.

2. Materials and methods

2.1. Preparation of adsorbent

The activated sludge was collected from the secondary treatment of unit the municipal sewage treatment plant. The settled sludge was separated from the supernatant and washed several times with tap water. The sludge was washed again using double-distilled water till the COD of the supernatant water was less than 10 mg L^{-1}. The removal of metal ions present on the sludge was verified with the filtrate using ethylene diamine tetraacetic acid (EDTA) test. The chloride test was conducted by the addition of 0.1 M $AgNO_3$ to the filtrate and absence of turbidity confirms the halogen-free filtrate. The filtered sludge was then dried in an oven at 110°C for 24 h. The dried sludge was ground in a mixer and sieved to particle size in the range of 125–212 μm. The organic content was estimated using the methods explained [12] and was found to be 0.698 kg kg^{-1} on dry weight basis. The sieved sludge powder was activated using chemical activation with 0.1 N HCl and the activated powder is termed as MAS.

2.2. Characteristics of the adsorbent

The characteristics of the adsorbent were studied by recording the micrographs using SEM (JEOL, Japan) with an accelerating voltage of 20 kV at high vacuum mode.

Fourier Transform Infrared Spectroscopy (FTIR) spectra of the MAS were obtained for both fresh and treated samples using KBr pellets method performed using FTIR spectrophotometer (Perkin Elmer, USA) in the spectral range 400–4,000 cm^{-1}.

2.3. Batch experiments on COD removal

The batch experiments were conducted in a temperature-controlled orbital shaker operated at fixed conditions of speed and temperature. The petroleum refinery effluent was collected from the nearby refinery at the entry of effluent treatment plant. The physicochemical characteristics of the refinery effluent were given in Table 1. The effect of initial pH of the effluent was studied in the range of 4.0–10.0 at fixed concentration, adsorbent dose, shaking speed, and temperature. The influence of adsorbent dosage was studied by mixing various amounts of MAS (0.5–10.0 g L^{-1}) in conical flasks containing 100 mL of the raw effluent. The effect of initial effluent concentration

Table 1
Physicochemical characteristics of the refinery wastewater

Parameters	Value
pH	8.04
Suspended solids (mg L^{-1})	60
Dissolved solids (mg L^{-1})	1,132
Total solid (mg L^{-1})	1,192
Dissolved oxygen	Nil
Chemical oxygen demand (COD) (mg L^{-1})	3,400
Biochemical oxygen demand (BOD) (mg L^{-1})	260
Chlorine	Nil
Ammonia, (mg L^{-1})	10
Ammonium (mg L^{-1})	11.1
Oil and grease (mg L^{-1})	880
Conductivity (mS cm^{-1})	7.89

on the COD removal was studied in the COD range of 850–3,400 mg L^{-1} at optimal conditions of other process parameters. The effect of shaking speed was studied in the range of 0–400 rpm at optimal conditions of pH and sorbent dosage at a fixed metal concentration of 100 mg L^{-1}. The effect of temperature was studied in the range of 30–40°C by shaking the flasks in a thermostatic water bath shaker operating at 400 rpm for 120 min to ensure the attainment of equilibrium. All the experiments were conducted at room temperature of 35°C unless or otherwise specified. Samples of solutions were filtered through filter paper and then the filtrates were collected and analyzed for remaining COD using spectrophotometric methods. The amount of COD adsorbed during the contact time with MAS powder was estimated using % COD removal defined in Eq. (1) and COD uptake defined in Eq. (2):

$$\%\text{COD removal} = \left(\frac{C_0 - C_e}{C_0}\right) \times 100 \tag{1}$$

$$q_e = \frac{V(C_0 - C_e)}{w} \tag{2}$$

where q_e (mg of COD removed/g of adsorbent) is the amount of COD adsorbed on the selected adsorbent, C_e and C_0 (mg L^{-1}) are the initial and equilibrium COD values, respectively, V is the volume of the sample solution (L) and w is the mass of the adsorbent (g). All experiments conducted were using actual effluent if otherwise specified. Kinetic studies were performed to identify the mechanism of COD removal.

3. Results and discussion

3.1. Characteristics of the sorbent

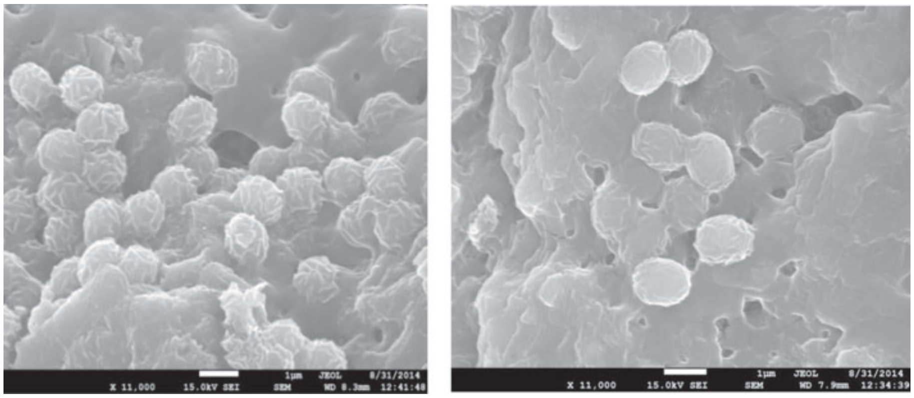
The SEM images shown below in Fig. 1 confirm the heterogeneity and irregularity of the sorbent surface. In addition, it shows the presence of micro pores and macropores which were responsible for the removal of solute molecules. While Fig. 2(a) shows the microstructure of fresh DAS, the surface covered by adsorbed molecules was represented by Fig. 2(b).

3.2. Effect of pH

The activated sludge is reported to have negative surface charges by nature and could prefer to adsorb the positive ions from the sorbate [16]. The wastewater pH plays an important role by the way of creating more surface charges through proton additions. The effect of pH was studied in the range of 4.0–10.0, while the actual effluent pH is 8.0. pH changes were made by acid (HCl) or base (NaOH) addition and the change in COD values were recorded. Fig. 2 presents the variation in COD removal percentages at different pH, while the other operating parameters are fixed. The removal efficiency increased from 70 to 80% in the pH range of 4.0–6.0. The effluent pH did not influence the COD removal efficiency significantly in the pH range of 6.0–8.0 and the maximum efficiency of 84% was obtained at a pH of 8.0. Reduced removal at lower pH could be due to the competition between the protons and the other organic and inorganic sorbate molecules for the same sorption sites. Studies on the sorption of COD by date pit-activated carbon also reported a similar behavior and the optimal pH was found as 8.0 [13]. The removal of COD in sugar industry effluent through adsorption also reported identical results [17].

3.3. Effect of sorbent dosage

The surface area made available for the contact with the sorbate is decided by the amount of sorbent used. In this set of experiments, the adsorbent dose of MAS was varied in the range of 0.5–10.0 g/L and its influence on COD removal percentage and uptake were studied. From Fig. 3, it was observed that the removal efficiency increased from 28 to 84% when the dose of sorbent increased from 0.5 to 8.0 g L^{-1}. Better COD removal percentage at higher dosage was attributed to the availability of more surface area. When the sorbent dose was further increased to 10 g/L, no further increase in efficiency was observed. At fixed solution volume and initial metal concentration,



Fresh MAS Treated MAS

Fig. 1. SEM micrographs of MAS.

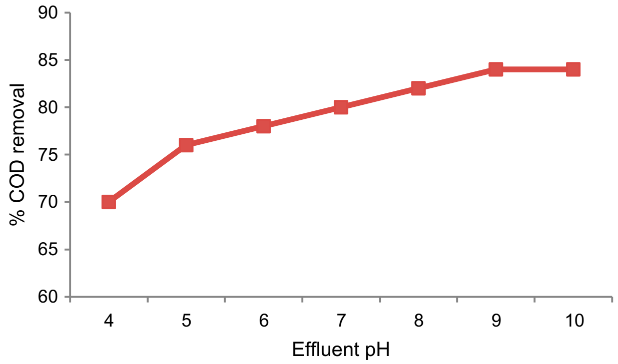


Fig. 2. Effect of pH on the COD removal by MAS ($COD_0 = 3{,}400$ mg L^{-1}; $w = 8$ g L^{-1}; $T = 35$°C; speed = 300 rpm).

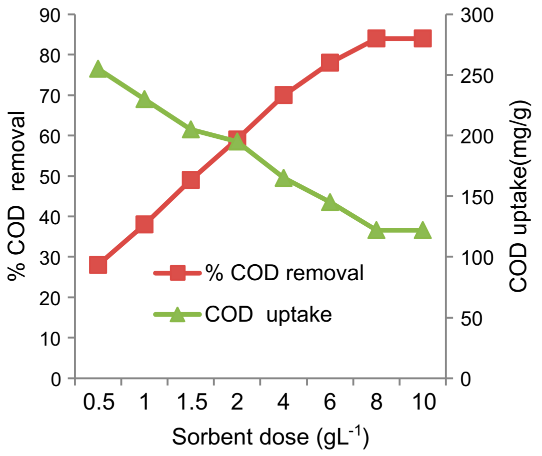


Fig. 3. Effect of MAS dose on the COD removal and uptake ($COD_0 = 3{,}400$ mg L^{-1}; pH 8; $T = 35$°C; speed = 300 rpm).

unsaturation of sorption sites is expected to occur at higher sorbent dosages. Superficial sorption onto the surface sites was reported to occur at higher sorbent–sorbate ratios [11]. An inverse relationship was found to exist between COD uptake and adsorbent dose which resulted in poor uptakes at higher dosages. The reasons for this effect could be electrostatic interactions, interference between binding sites and improper mixing at high adsorbent concentrations [6]. Removal of heavy metal ions using activated sludge as adsorbent reported similar effects on percentage COD removal [12].

3.4. *Effect of contact time and initial effluent concentration*

The influence of contact time on the adsorption process efficiency was studied in order to establish a time dependence relationship. The experimental studies measuring the effect of contact time and initial effluent COD on the batch removal of COD was performed using four different initial COD concentrations namely 850, 1,700, 2,550, and 3,400 mg L^{-1} at optimal conditions of pH, sorbent dose, shaking speed and temperature. As shown in Fig. 4, it could be inferred that the general COD removal rate was fast during the initial phase of 90 min followed by relatively slower phase of removal. The initial rapid uptake rate may be due to physical adsorption or ion exchange at the sorbent surface and due to complexation and microprecipitation of the binding sites during the later phase resulted in reduced COD removal [18]. The COD removal percentages decreased with increase in initial COD concentrations of the effluent which was proved by the results of 98% with 750 mg L^{-1} COD and 84% with 3,400 mg L^{-1} COD. Limited availability or availability of the same number of sorption sites at

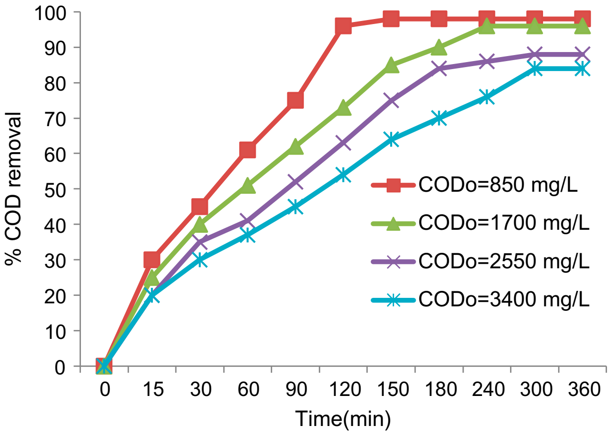


Fig. 4. Effect of effluent concentration on the COD removal by MAS (pH 8; $T = 35$°C; $w = 8$ g L^{-1}).

higher effluent concentration is responsible for this reduction in removal efficiency. The COD uptakes achieved were 36.5, 70.4, 101.5, and 125 mg g^{-1} with 850, 1,700, 2,550, and 3,400 mg L^{-1} COD values respectively. These results demonstrate the removal capacity of the adsorbent produced to handle a wide range of effluent concentrations. The COD uptake observed in this study were comparable with the values reported for refinery effluent treatment using date-pit activated carbon [5].

3.5. Effect of speed of agitation

To examine the effect of speed of agitation on the COD uptake, adsorption experiments were conducted at different shaking speeds ranging 0–400 rpm at optimal conditions of pH, sorbent dose, and temperature. As shown in Fig. 5, the COD uptake by MAS increased from 10.0 to 122.0 mg g^{-1} when the shaking speed increased from 0 (static condition) to 300 rpm, as shown in Fig. 5. The external mass transfer rate through the film is reported to be better at high speed along with reduction in the boundary layer thickness. When the speed was increased further to 400 rpm, a decrease in COD uptake was observed. Lack of homogeneity in the sorbate–sorbent system could be the reason for this effect [19].

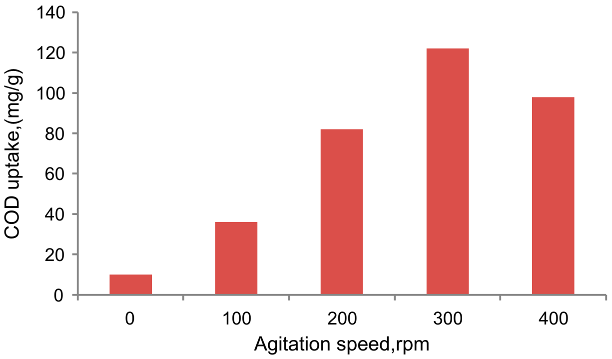


Fig. 5. Effect of agitation speed on the COD removal by MAS (pH 8; $T = 35$°C; $w = 8$ g L^{-1}).

3.6. Effect of operating temperature

Temperature is always a vital operating variable for any separation process driven by concentration gradients. The effect of temperature on the percentage COD removal was studied by conducting three different sets of experiments at 30, 35 (actual effluent temperature during the period of study), and 40°C at predefined conditions of pH, sorbent dose, and shaking speed. Fig. 6 presents the change in COD removal percentages at the selected temperatures and the results proved the process as exothermic in nature. The COD removal percentage decreased from 89 to 74% when the temperature increased from 30 to 40°C. The reason attributed for this behavior is decrease in surface activity at higher temperatures and also due to escape of adsorbed sorbate molecules from the active sites. Similar observations were reported with studies on removal of dye [20] and Cu(II) biosorption by dried activated sludge [21].

3.7. Kinetic studies

Design of wastewater treatment requires proper understanding on the COD removal mechanism. The adsorption data were fitted to the pseudo-second-order equation (Eq. (3)) to analyze the adsorption kinetics of COD removal:

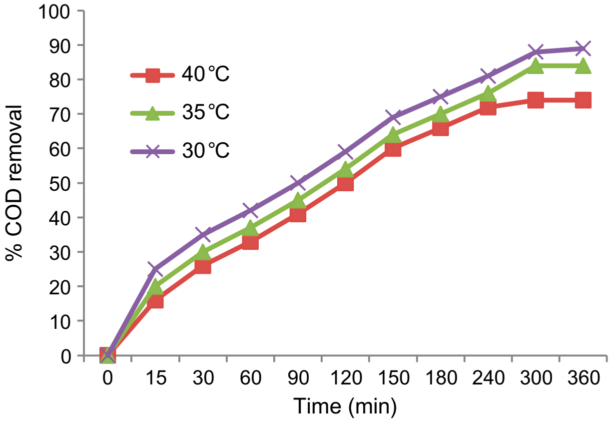


Fig. 6. Effect of operating temperature on the COD removal by MAS (pH 8; speed = 300 rpm; $w = 8$ g L^{-1}).

$$\frac{t}{q} = \frac{1}{k_1 q_1^2} + \frac{1}{q_1} t \tag{3}$$

where q_1 (mg g^{-1}) is the maximum adsorption capacity and q (mg g^{-1}) is the COD adsorbed at time, t, and k_1 (g (mg min) $^{-1}$) is the equilibrium rate constant for pseudo-second-order adsorption. The power function model is represented as:

$$q = k_p t^n \tag{4}$$

where k_p and n (usually positive and <1) are model constants. Eq. (4) is empirical except when $n = 1/2$, where it is a parabolic diffusion equation [22].

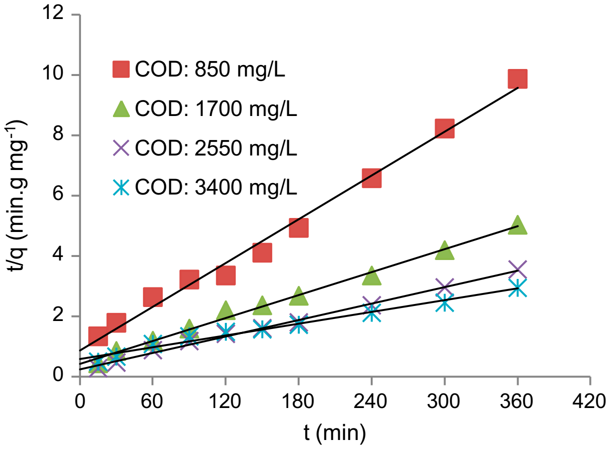


Fig. 7. Pseudo-second-order model plot for the COD removal using MAS.

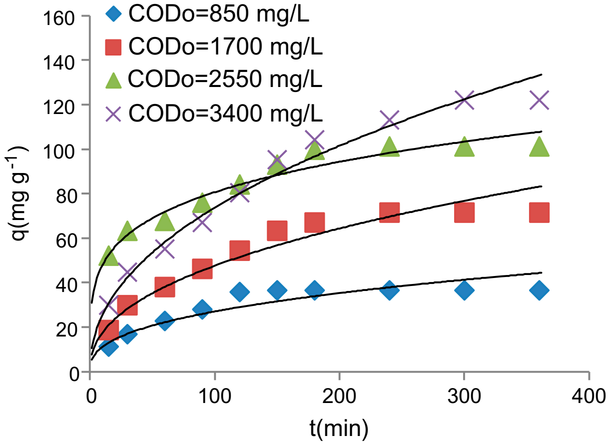


Fig. 8. Power function model plot for the COD removal using MAS.

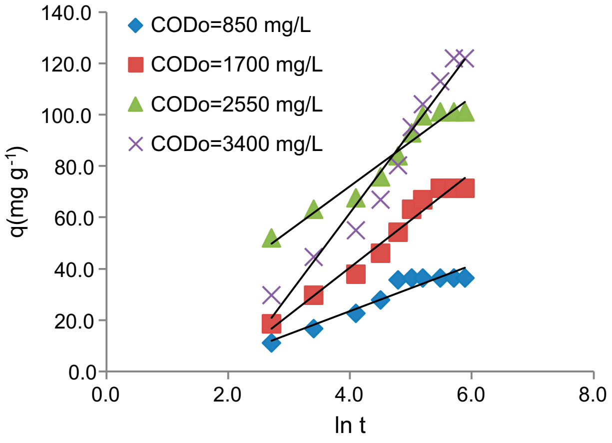


Fig. 9. Elovich model plot for the COD removal using MAS.

Elovich model represented by Eq. (5) in its linearized form was used to represent the kinetic data:

$$q = \frac{1}{b}\ln(ab) + \frac{1}{b}\ln t \tag{5}$$

where a denotes the initial adsorption rate (mg/g min) and b denotes the desorption constant (g/mg) and this model relates the activation energy and extent of surface coverage for chemisorption [23].

Figs. 7–9 represent the kinetic plots of the models mentioned above. Among the models tested, Pseudo-second-order model was found to represent

Table 2
Kinetic constants for refinery wastewater treatment

	Initial effluent concentration (mg L^{-1})			
COD$_0$ (mg L^{-1})	850	1,700	2,550	3,400
Pseudo-second-order				
k_1 (g mg^{-1} min^{-1}) x 10^4	6.7	3.7	3.3	0.7
q_1 (mg g^{-1})	41.322	78.740	109.890	153.846
R^2	0.990	0.991	0.995	0.979
Power function				
k_p (mg g min$^{-1/2}$)	4.553	6.4001	28.407	8.7685
n	0.387	0.436	0.227	0.462
R^2	0.902	0.964	0.961	0.976
Elovich				
b (g mg^{-1})	0.112	0.054	0.058	17.349
a (mg g^{-1} min^{-1})	2.287	3.050	20.343	4.084
R^2	0.912	0.970	0.948	0.958

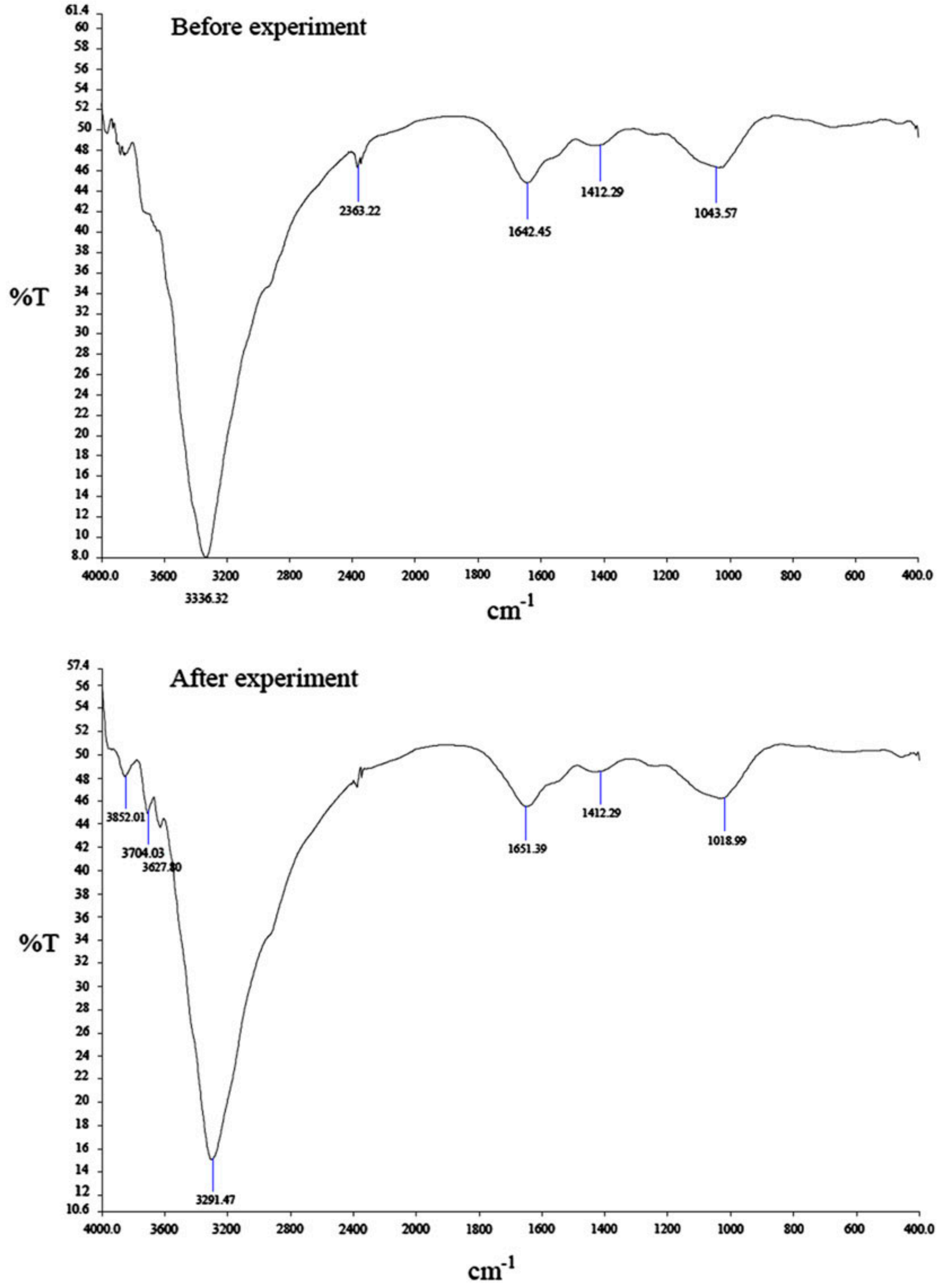


Fig. 10. FTIR spectra of MAS.

the COD removal kinetics in a better way with comparatively higher values of R^2 (>0.97). In this model, the rate-determining step is the surface adsorption which involves chemisorption. The removal of sorbate from the solution is assumed to occur due to physicochemical interactions between the phases [22]. The constants in the kinetic models were presented in Table 2. The model constants with power function and

Elovich model were evaluated from the slopes and intercepts of Figs. 8 and 9.

3.8. FTIR characterization of MAS

The FTIR spectra presented in Fig. 10 reflects the surface chemistry of the samples and functional groups involved in the sorption process. The spectra present a number of absorption peaks which indicate the heterogeneity and the complex nature of the sorbent surface. From the peaks shown, the major functional groups present on the sorbent surface were identified as O–H carboxylic acid, C–O stretch, N–H stretch and bonded O–H groups [21]. The band at 3,300 cm^{-1} represents the O–H stretching of the activated sludge polymeric compounds [22]. Appearance of new peaks at 3,627.80, 3,704.03, and 3,852.01 cm^{-1}, representing amine and amide N–H stretch, respectively, after the sorption experiment confirmed the transfer of contaminants onto the sorbent surface.

4. Conclusion

In this study, the utilization of MAS as an adsorbent for the removal of COD from refinery wastewater was successfully demonstrated. The SEM studies showed the surface microstructure clearly while the FTIR spectra indicated the active functional groups present on the sorbent surface. The initial pH of the wastewater was found to be less influential whereas increase in sorbent dose resulted in increased removal efficiencies and decreased COD uptake capacities. Higher temperature was unfavored confirming the exothermic nature of sorption process. The pseudo-second-order model fitted well (with $R^2 > 0.97$) for the kinetic data and the constants were evaluated at different wastewater COD values. The proposed COD removal mechanism is to due to physicochemical interactions between the phases. From this study, we conclude that MAS merits further research to be employed in large-scale continuous systems to evaluate the practical applicability of its use in refinery effluent treatment units.

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