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Colour and COD Removal from Real Textile Wastewater by Using Diatomite

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Abstract The aim of this study was to investigate the adsorption performance of a low-cost adsorbent, diatomite, for the treatment of real textile wastewater. Effect of adsorbent dosage, contact time and particle size on colour and COD removal was investigated. The results showed that colour removals were achieved within a relatively short time and while COD removals increased with increasing contact time. Diatomite dosage was found to be a critical parameter especially for the COD removal. COD removal increased from 37% to 57% with an increase in diatomite dosage from 10 g/L to 150 g/L. Particle size, on the other hand, presented different removal trends. As colour removal was slightly increased (<5%) with decreasing particle size, a higher COD removal (70%) was observed for the smallest particles size (<425 mm). The influence of thermal and acid/alkaline pre-treatments on the performance of the natural diatomite was also evaluated. Thermal treatments significantly decreased the medium EC, while colour and COD removals were not significantly changed. Similarly, acid and alkaline pre-treatments seem not to increase the adsorption performance of natural diatomite.

Key words: *textile industry, wastewater, treatment, diatomite, adsorption*

Introduction

The textile industry is one of the major industrial activities that consumes large amounts of water and produces highly polluted wastewaters. Textile industry uses different amounts of water, dyes, chemicals and surfactants in various processes in order to produce high quality textile products (Kamaruddin *et al*., 2013). The treatment of textile wastewater poses considerable difficulties due to the presence of dyes and persistent organic and inorganic compounds. The methods used in the treatment of textile effluents include biological treatment, coagulation-flocculation, ozone oxidation, adsorption and membrane processes (Kausar *et al*., 2018; Özacar & Şengil, 2003). Adsorption is one of the effective treatment processes for the removal of dyes from textile wastewater. A great number of low-cost adsorbents have been used for the removal of textile dyes (Özcan & Özcan, 2004; Doğan *et al.,* 2006; Lin *et al*., 2007; Patra *et al*., 2015).

Diatomite is a siliceous rock composed of the fossilised skeletal remains of aquatic plants called diatoms (Erdem *et al*., 2005). Diatomite has been used for the adsorption of various pollutants from water and wastewaters, either in natural or modified form obtained by chemical or thermal modifications (Reza et al., 2015; Calıskan et al., 2011). The surface of diatomite contains silanol groups that spreading over the silica matrix (Figure 1). The silanol groups are very active groups and can react with various polar organic compounds (Al-Ghouti *et al*., 2003).

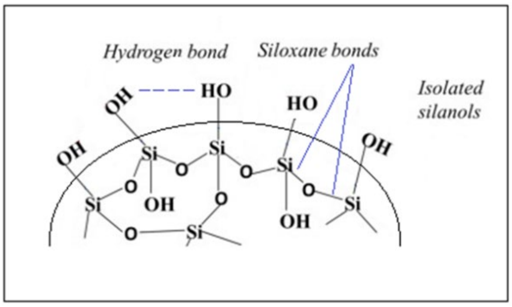

Figure 1. Structure of silica surface involving bonds types and silanol groups (Al-Ghouti et al., 2003)

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In this study, colour and chemical oxygen demand (COD) removal from real textile wastewater using diatomite was investigated by varying the contact time, diatomite dosage and particle size. The influence of thermal, acid and alkaline treatments on the performance of natural diatomite was also evaluated.

Materials and Methods

Textile Wastewater

The raw textile wastewater samples were obtained from a textile industry located in Kayseri Turkey. Different reactive dyes and various chemicals were used during various treatment stages resulting in the complex composition of textile wastewater. The wastewater is directly discharged into the wastewater collection system of industrial zone without any pre-treatment. Sample collection has been done several times during this study. All samples have been kept at 4°C and have been used without any pre-treatment. The characteristics of raw textile wastewater are presented in Table 1.

Table 1. Textile wastewater characteristics

Parameters	Raw textile wastewater	
	Range	Average
COD (mg/L)	101-687	378.7
TOC (mg/L)	12-202	95.1
Colour (Pt-Co)	394-1126	734.1
Conductivity (mS/cm)	3.36-3.56	3.42
pH	7.12-8.60	7.85

Adsorption Studies

Diatomite used in the experimental studies was obtained from Kazan-Ankara. Before use in the adsorption experiments, it was crushed and sieved into different particle sizes. SEM image and XRD spectra of natural diatomite were shown in Figure 2. SEM image shows high porous structure of diatomite and XRD spectra shows the amorphous nature of diatomite. Batch adsorption experiments were conducted using natural diatomite and real textile wastewater on Julabo SW23 mechanical shaker. The influence of contact time (5-1440 min; diatomite <425 mm), adsorbent dosage (10-150 g/L; diatomite <425 mm) and particle size (<425, 425-600 and 600-1180 nm) was determined. All adsorption experiments were carried out in 250 mL flasks with 100 mL of wastewater at 30±2°C without any other adjustment.

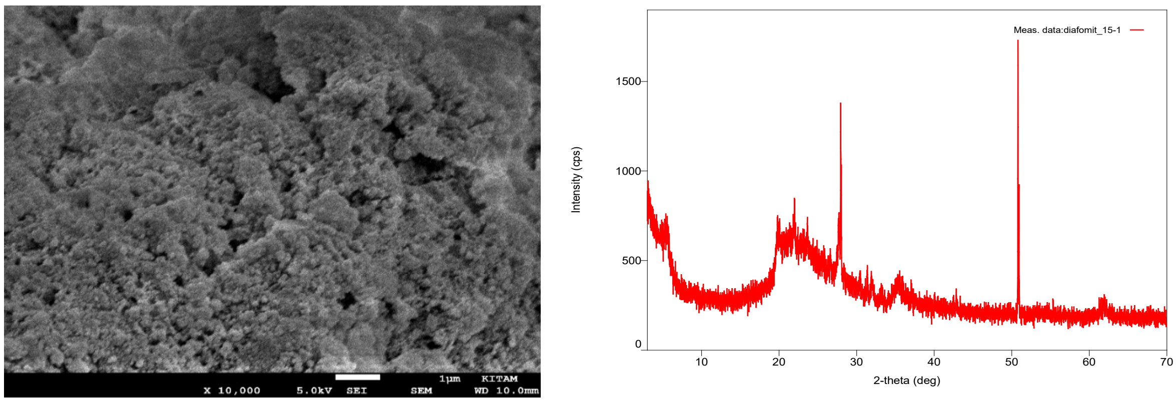

Figure 2. SEM image and XRD spectra of natural diatomite

The adsorbent performance of natural diatomite has been investigated by thermal and acid/alkaline treatments. Thermal treatments were done by keeping the natural diatomite with a particle size below 425 mm at temperatures varying between 300 and 900°C for one hour. Acid and alkaline treatments were performed by keeping the adsorbent (diatomite <425 mm) at 30°C in 2 M H_2SO_4 or NaOH solutions for one hour followed by a washing step with distilled water and a drying step (24 h at 70°C). The performance of adsorbent after all experiments was evaluated by differences in COD, colour (Pt-

Co unit), electrical conductivity (EC) and pH. COD experiments were carried out according to APHA-AWWA-WPCF (1998).

The pseudo-second order model was used for the modelling of the kinetic data obtained for the colour and COD removals. The linearized form of pseudo second-order kinetic model is given by Eq. (1) as:

$$\frac{t}{qt} = \frac{1}{k.qe^2} + \frac{1}{qe}t \qquad (1)$$

where k is the rate constant (g/mg min), qe is the sorption capacity at equilibrium (mg/g). The values of k and qe were obtained from the slope and intercept of the plots of t/q_t against t (Zhanga et al, 2018).

Results and Discussion

Effect of Contact Time

The influence of contact time on the adsorption of textile wastewater constituents and medium conditions was investigated using natural diatomite with a particle size below 425 mm. As can be seen from Figure 3, variation of colour and COD removal with contact time revealed different trends within time. An initial fast colour removal of approximately 60% was observed within 5 min. An additional increase of only 7% was achieved at the end of 1440 min. On the other hand, the initial COD removal was about 40% but increased with time, reaching a value of 78% at the end of 1440 min. These results show that the sorption sites on diatomite have different affinities for different constituents present in the textile wastewater. It can be seen from Figure 3 that; EC and pH of medium revealed an insignificant change (± 0.1) implying that the interaction of textile wastewater with diatomite didn't cause to a release of ionic constituents from the adsorbent.

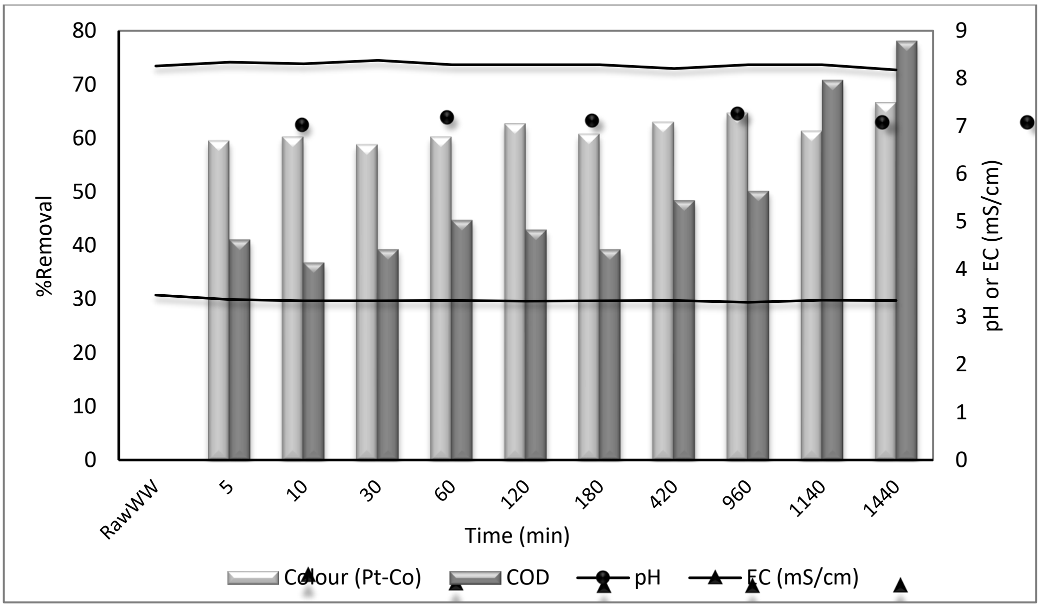

Figure 3. The effect of contact time on EC, pH, colour and COD removal

Effect of Adsorbent Dosage

It can be observed from Figure 4 that colour and COD values that the removal of both parameters represented an increase with increasing diatomite dosage. When the adsorbent dosage increased from 10 to 100 g/L colour removal increased from 37% to 57% and COD removal increased from 49% to 63%. These results showed that the reactive sites of diatomite have a higher affinity to reactive dyes present in the textile wastewater than other organic constituents. The influence of diatomite concentration on the medium conditions can also be seen in Figure 4. Both EC and pH represented a slightly decreasing trend with increased adsorbent dosage. When the spectra of treated wastewater were analysed it can be seen from Figure 5 that the absorbance at 292 nm decreased with an increase in diatomite concentration from 10 to 150 g/L. This result showed that the aromatic moieties of dyes in the textile wastewater were adsorbed on the diatomite surface.

Effect of Particle Size

Figure 6 shows the variation of colour and COD removals and pH and EC with particle size. It can be stated that particle size has not an important influence on colour removal (4%). In the study by Ngulube *et al*. (2017) on the adsorption of textile dyes, it was similarly reported that the particle size of diatomite had little effect on the removal of dyes. COD removal data reveals a different trend with particle size. The highest removal was observed for the smallest particles size (<425 mm). The lowest COD removal was observed for the 425-600 mm fraction, for which the highest pH rises and lowest EC drop was observed.

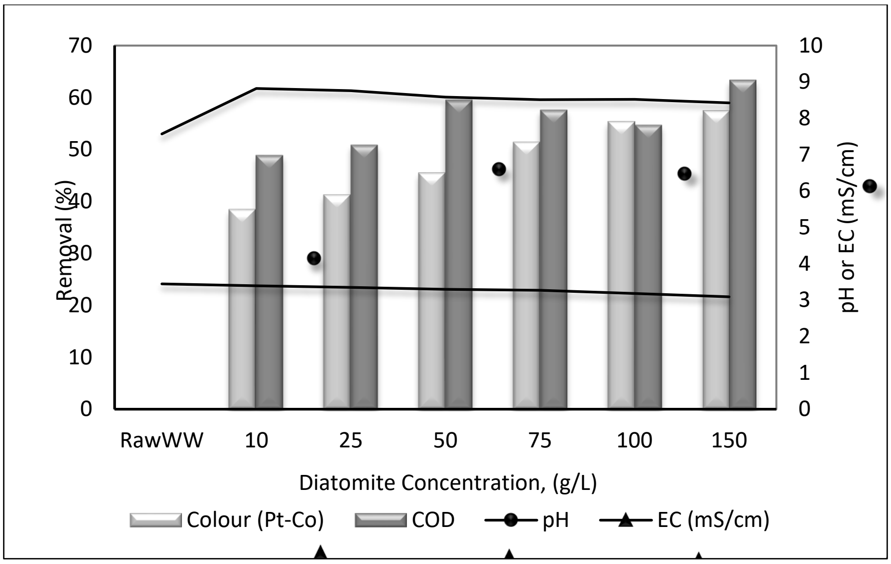

Figure 4. The effect of diatomite dosage on EC, pH, colour and COD removal

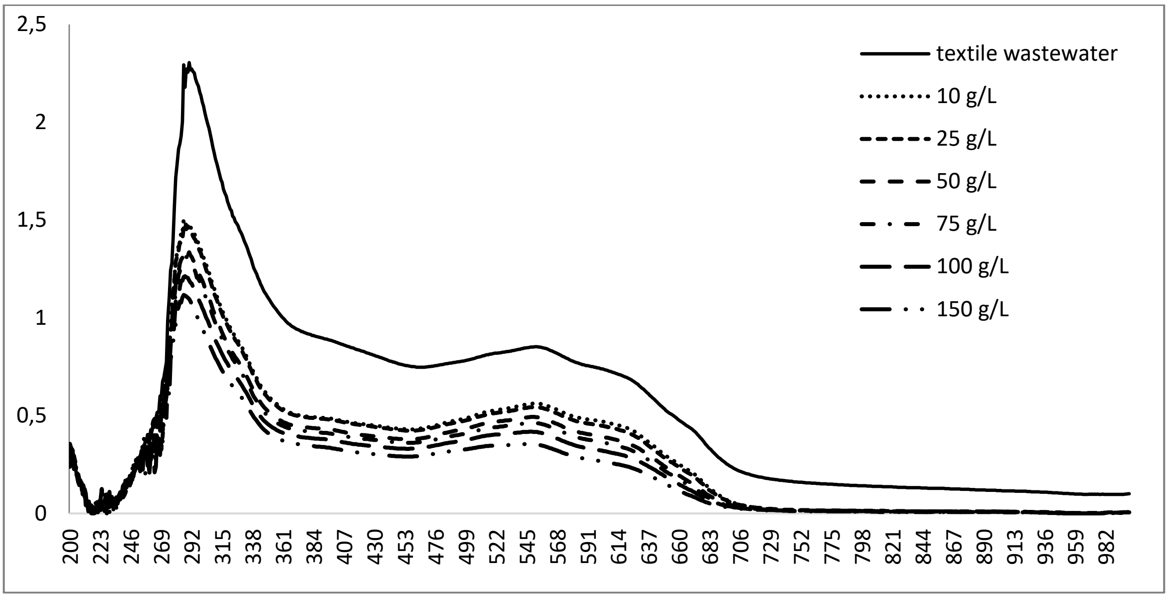

Figure 5. Spectra of dye before and after adsorption on diatomite

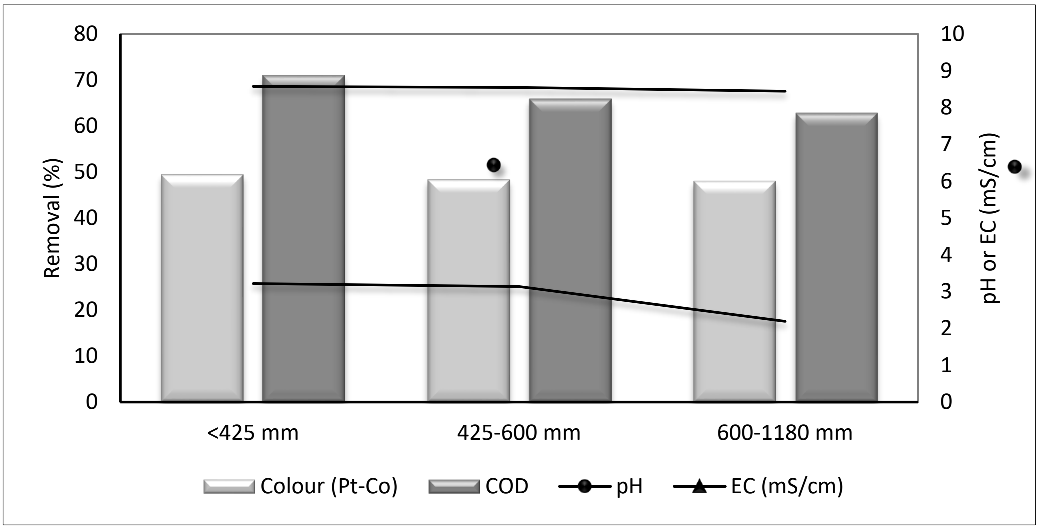

Figure 6. The effect of particle size on pH, EC, colour and COD removal

Effect of Thermal Treatment

It is assumed that thermal treatment causes desorption of adsorbed water in the crystal structure of the diatomite by formation of active hydroxyl groups. Generally, thermal treatment affects the type, distribution, content of hydrated species such as water, H-bonded and isolated silanol groups, and reactive sites for various surface reactions (Reza et al. 2015).

In order to investigate the effect of thermal treatment, adsorption experiments were performed with thermally pre-treated diatomite (<425 mm). It can be seen from Figure 7 that, the EC values of textile wastewater decreased for diatomite pre-treated at higher temperatures. The EC of textile wastewater dropped from 3.37 mS/cm to 3.09 mS/cm for 500 °C and to 1.68 mS/cm for 900 °C. These results imply that thermal treatment activates sorption sites on diatomite resulting in elevated ion sorption. The pH levels measured reflected a different trend for increased thermal pre-treatment temperatures. The pH of textile wastewater dropped from 7.49 to 7.02 for 500 °C and increased to 7.83 for 900 °C.

Considering the results for the removal of colour and COD, it can be stated that thermal pre-treatments had insignificant influence on the sorption of textile dyes and organic constituents. Changes in the removal of colour and COD were only ±4% and ±5%, respectively (Figure 7). In general, it can be concluded that the thermal pre-treatment increased the affinity of diatomite towards ionic constituents rather than dyes and organic constituents present in the textile wastewater.

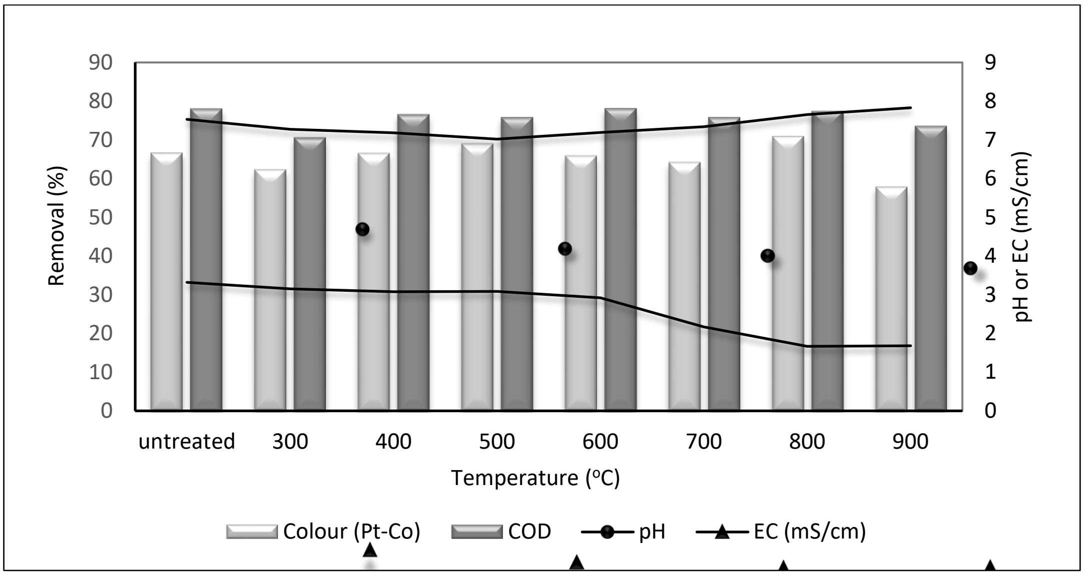

Figure 7. The effect of thermal treatment on EC, pH, colour and COD removal

3.4. Effect of Acid/Alkaline Treatment

Chemical treatment is widely used for purification of diatomite and alteration of its surface properties. Acid treatment is expected to reduce or remove the other oxides of diatomite in proportion to SiO_2 and to increase its surface area and adsorption capacity. The acid activators used for modification of diatomite include hydrochloric acid, nitric acid, sulfuric acid, sulfuric acid/H_2O_2 and phosphorous acid. The alkaline activators include sodium hydroxide, potassium hydroxide and sodium carbonate. These activators are used for purification diatomite, removal of impurities and chemically formation of finer pores (Reza et al. 2015).

In order to improve the performance of adsorbent, diatomite was treated with 2 M H_2SO_4 or NaOH solutions. These pre-treatments presented different effects on colour and COD removals. Acid treatments seem to have increased the colour removal efficiency from approximately 50% to 88%, whereas COD removal efficiencies decreased from about 65% to 23% (Figure 8). On the contrary, alkaline treatments seem to have an opposite influence on colour. NaOH treatments caused to an increase in colour, implying that some constituents have been released during the interaction of textile wastewater and diatomite. The COD removal efficiency, on the other hand, decreased to approximately 40%. Thus, both treatments did not increase the COD removal efficiency.

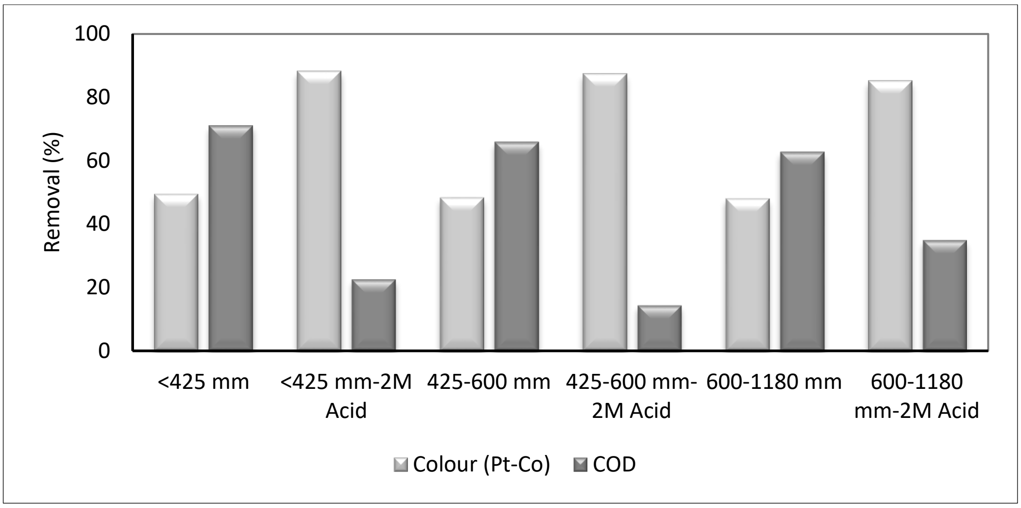

Figure 8. The effect of acid treatment on colour and COD removal

Adsorption Kinetics

Kinetic studies are important to analyse the controlling mechanism of adsorption process. The kinetic parameters provide information about mechanism and rate of adsorption process. Pseudo-second-order model was found to fit well the experiment data. The pseudo-second order kinetic plots obtained for colour and COD removal are presented in Figure 9 and the kinetic parameters are given in Table 2. The conformity of data to pseudo-second order kinetic model suggested that the chemisorption is the dominant mechanism controlling the rate of the adsorption process. Similar results were observed in previous studies (Kehinde & Aziz, 2016).

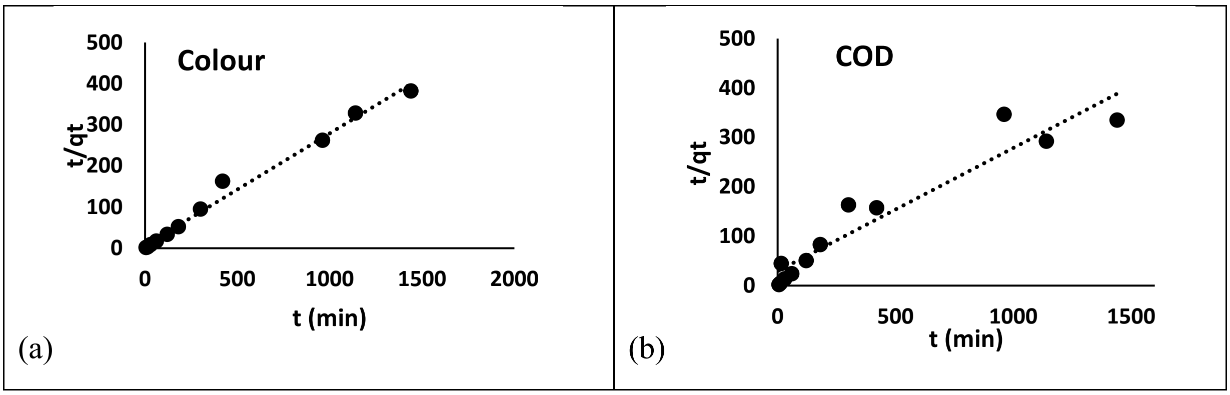

Figure 9. The plots of the pseudo second-order kinetics (a) Colour, (b) COD

Table 2. Parameters of the pseudo-second order model

	qe (cal) mg/g	**k (min^{-1})**	**R^2**
COD (mg/L)	4.011	0.0021	0.9141
Colour (Pt-Co)	3.664	0.0119	0.9883

Conclusion

In this study the adsorption performance of natural diatomite for the removal of colour and COD from real textile wastewater has been investigated. The effect of time, adsorbent dosage, particle size on colour and COD removals and medium EC and pH were analysed. Contact time has an insignificant effect on EC and colour removal, while significant effect on COD removal. Diatomite concentration, on the other hand, seems to have reduced the medium EC and increased the colour and COD removals. Particle size has been found to influence colour and COD removals differently; as smaller particle sizes seem to increase COD removal; bigger sizes seem to increase colour removal. Thermal pre-treatment was found to mainly influence EC by revealing half levels. Acid and alkaline treatments of diatomite, on the other hand, did not change the adsorbent performance to the desired levels. Overall it can be concluded that natural diatomite was effective in the treatment of raw textile wastewater, removing mainly dyes and organic compounds and inorganic ions at a lower degree.

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