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Reduction of oil, COD and turbidity of Kermanshah oil refinery effluent using modified nano-zeolite by bismuth and iron

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ABSTRACT

In this paper, modified nano-zeolite by bismuth and iron (Bi/Fe-zeolite) was used to reduce oil, chemical oxygen demand (COD) and turbidity (TUR) of Kermanshah refinery effluent. At first, Bi/Fe-zeolite was synthesized and characterized using scanning electron microscopy, Fourier transform infrared spectroscopy and transmission electron microscopy analysis. The effect of experimental parameters such as pH, contact time, temperature and initial concentration on reduction of oil, COD and TUR was studied. According to the results, the optimum reduction was carried out using 2 mg/L of Bi/Fe-zeolite at 25°C and pH of 7, after 30 min of contact time.

Keywords: Nano-adsorbent; Effluent; Zeolite; COD; Bismuth; Iron

1. Introduction

Oil refining inevitably leads to production of a large volume of oily wastewaters. Wastewater disposal is a significant environmental challenge in the oil industry and the effluent exiting from these industries must be treated before being discharged to the environment.

Various treatment technologies have been used for the reduction of chemical oxygen demand (COD), which is a major contaminant in petroleum refinery and industrial wastewaters. These techniques include filtration, ion-exchange, coagulation/flocculation, reverse osmosis and electrodialysis. Adsorption provides an attractive alternative treatment, especially if the adsorbent is inexpensive and readily available. Adsorption of COD has been previously studied to evaluate the overall adsorption behavior in wastewaters [1]. The use of activated carbon (AC), as an absorbent, has proven to be effective in a wide range of applications, including the removal of both organic and inorganic pollutants from wastewater [2].

Ahmad et al. [3] have conducted researches on three various adsorbents, AC, bentonite and chitosan, for removing oil from wastewater. Among these three adsorbents, chitosan has been the most efficient adsorbent in solutions with pH of 4–5 and in a 30-min period time and has been able to remove 99% of oil from the wastewater [3]. The adsorption of palm oil mill effluent (POME) using montmorillonite clay has been investigated by Said et al. [4]. The results indicated that the optimum conditions for mixing speed of the stirrer, contact time, dosage of adsorbent, concentration of POME and pH were 300 rpm, 90 min, 5 g/L, 25% POME and 7, respectively. Liu et al. [5] have reviewed the new method for the synthesis of nano-structures of boehmite and their conversion process to aluminum oxide nano-structures for removing Congo Red (CR) dye. Their adsorption experiments showed that the adsorption capacity of C-Al_2O_3 nano-rods for removing the CR dye is better than other existing C-Al_2O_3 nano-structures and commercial alumina (Al_2O_3). Their results also indicated that the adsorption follows the Langmuir isotherm model and the pseudo-second-order kinetic equation [5]. The traditional technologies based on adsorption, frequently involving the use of AC for the removal of organic contaminants in

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water. However, it is well known that regeneration of active carbon is complicated and expensive [6–9]. Many researchers have focused on various materials that are able to remove organic pollutants from water [10–24].

One of the important class of hydrated aluminosilicates is zeolites. They own cage-like structures with internal and external surface areas of up to several hundred square meters per gram. An important property of these materials is the ability to be easily regenerated while keeping their initial properties. Zeolites are a group of crystallized hydrated aluminosilicates with fine pores containing balanced cations from earth alkaline metals group (Na^+, K^+, Mg^{2+} and Ca^{2+}), which can absorb and release water reversibly without major change in their structure and exchange some of their cations. The wide use of synthetic and natural zeolites as adsorbents for removal of phenolic compounds from water have been reported [25–28].

Bimetallic nano-particles have attracted enormous attention in the past decade. They provide exciting opportunities for developing novel catalysts with unique or improved activities [29]. In addition, bimetallic catalysts have been prepared using heavy post-transition elements such as bismuth, lead or thallium with transition elements such as Pd or Pt for the selective organic reaction such as oxidation of alcohols into aldehydes and carboxylic acids and catalytic oxidation of glucose [30]. The promoting role of other post-transition elements such as Te or transition metals for reactions has also been investigated [31]. In the present work, Bi/Fe-zeolite was prepared through iron and bismuth precipitation on nano-zeolite. The characterization of prepared sample was accomplished using Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Finally, the prepared modified zeolite performance was examined in reduction of COD, oil and turbidity (TUR) from Kermanshah petroleum refinery effluent.

2. Materials and methods

2.1. Materials

All chemicals were used of analytical grade or with the highest purity available. All solutions were prepared with double-distilled deionized water. All other materials including $C_8H_5KO_4$, $CHCl_3$, $FeCl_3$, $BiNO_3.3H_2O$, HgO_4S, $K_2Cr_2O_7$, H_2SO_4, NaOH and zeolite ($MA/(AlO_2),(SiO_2).nH_2O$) were purchased from Merck (Germany). The effluent samples were obtained from Kermanshah Oil Refinery (Kermanshah, Iran) and used as received. According to the raw effluent analysis the COD content was 30 mg/L, TUR was 14.2 NTU and oil concentration was 2 mg/L.

2.2. Instruments

UV–Vis spectroscopy was carried out on a Cary 100 UV–Vis spectrophotometer (Varian, USA) at room temperature (25°C). FTIR spectra were prepared on a Bruker spectrophotometer pressed into KBr pellets. TEM was carried out on a Philips CM30 – 200 kV, FESEM images were obtained using a Hitachi S-4160 field emission scanning electron microscope. A Metrohm 692 pH meter (Herisau, Switzerland) and SEM (zeiss-TEM-em10) was used for pH measurements and determination of nano-particles size. A reactor Model 45600 (Hach Co., USA) and turbidimeter Model 2100P (Hach) were used for measurement of COD and TUR, respectively.

2.3. Preparation of nano-zeolite

To prepare nano-zeolite, certain amount (about 2 g) of this material was placed in electric furnace at temperature 700°C for 3 h. Then, it was cooled up to room temperature [32,33].

2.4. Preparation of modified nano-zeolite

To prepare the modified Bi/Fe-zeolite, certain amount (about 2 g) of zeolite was placed to one beaker, and 25 wt% of zeolite, $FeCl_3$ and $BiNO_3$ was added to it, which was stirred for 5 h at room temperature so that the uniform solution was formed.

The solution was placed in electric furnace at 700°C for 5 h and then cooled to room temperature, after rinsing with distilled water the nano-particles have been isolated using centrifugation.

2.5. Method

In this study, different experiments were performed in order to investigate the oil, COD and TUR reduction by the synthesized nano-zeolite and at the next step the Bi/Fe-zeolite has been investigated. In order to perform the experiments, given the type of the experiment and the study, a specific amount of the modified nano-zeolite has been added to 50 mL of effluent samples with various pH amounts. Then, the solution was stirred for a certain amount of time. The resulting solution was poured into a test tube and placed in centrifuge at 8,000 rpm for 10 min so that adsorbents would remain at the bottom of the test tube. Finally, the COD, oil and TUR amounts of obtained solution were measured.

3. Results and discussion

3.1. Investigation of absorbents' structure using FTIR

The FTIR spectra of zeolite and Bi/Fe-zeolite are shown in Figs. 1 and 2, respectively. The peak in the region of 1,673 cm^{-1} corresponds to O–H bending vibration. The FTIR spectrum of nano-zeolite shows a peak in the ranges of 500–900 cm^{-1}. This strong vibration is assigned to the T–O–T (T = Al or Si) asymmetric stretching vibration. The sharp band at 460.65 cm^{-1} can be assigned to the T–O bending mode [34–36]. The located band at 3,483 cm^{-1} for zeolite corresponds to the bridging OH groups in Al–OH–Si and is attributed to the location of hydrogen atoms on different oxygen atoms of zeolite framework [37]. Fig. 2 also shows that Bi/Fe-zeolite spectra are similar to the zeolite spectra in the spectral regions 700–4,000 cm^{-1}. However, the peak at 574.81 cm^{-1} can be attributed to stretching mode of Fe–O band [38] and the Bi–O trend peak at 1,128.39 cm^{-1} [39] which is an indication of the presence of bismuth and iron in the structure.

3.2. Investigating the structure of adsorbents using SEM and TEM

SEM images shows that powders with particles size less than 100 nm which can be recognized as a separated particle or in the form of larger agglomerates (Fig. 3). Moreover most

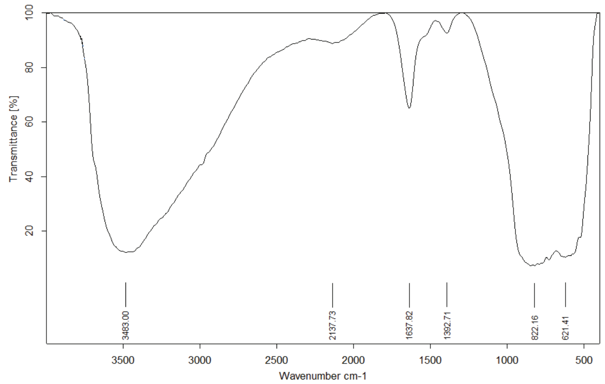


Fig. 1. FTIR spectrum of zeolite.

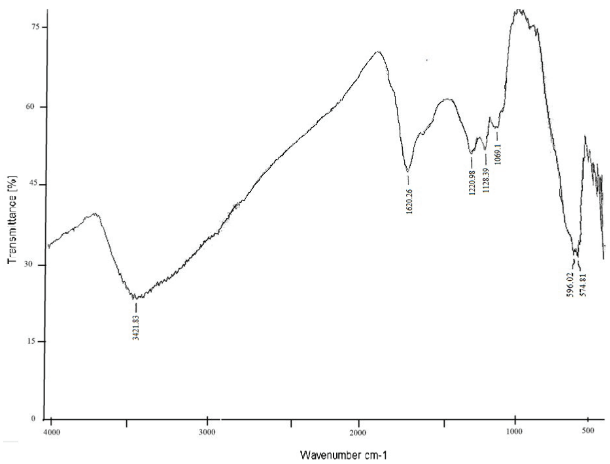


Fig. 2. FTIR spectrum of Bi/Fe-zeolite.

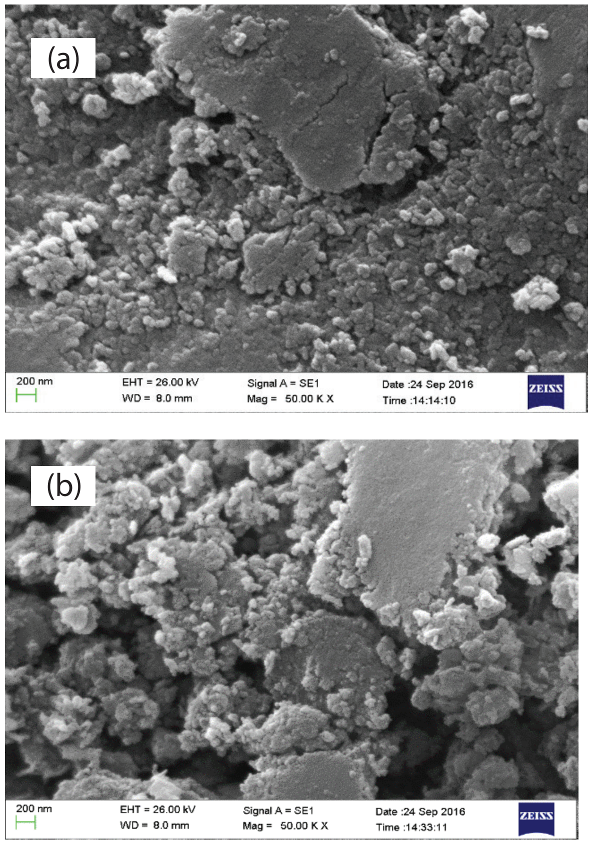


Fig. 3. SEM image of zeolite (A) and Bi/Fe-zeolite (B).

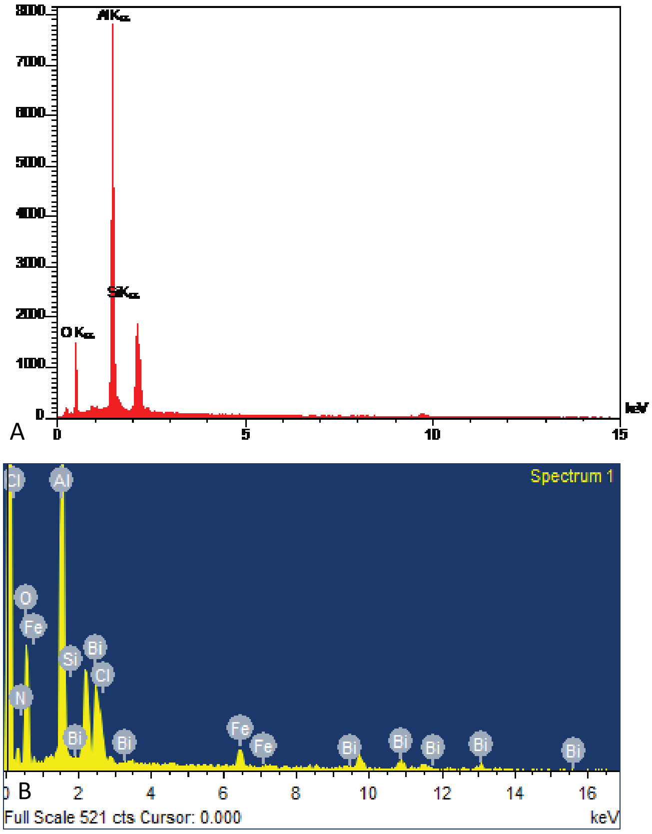
particles have lost their initial layered shape and converted into spherical, elliptical or irregular shapes. Also, some crystals with sharp edges and clean surfaces were observed; which are about 100 nm in size.

The elemental analysis (EDX) image of the zeolite and Bi/Fe-zeolite has been shown in Fig. 4. The spectrum EDX indicates the presence of Al, oxygen and Si in the zeolite structure (Fig. 4(A)). The EDX for Bi/Fe-zeolite (Fig. 4(B)) proves that iron has been entered onto the zeolite structure in the FeO-loaded sample. By comparing the EDX images associated with the Bi/Fe-zeolite and zeolite adsorbent, it becomes clear that the surface of the adsorbent has been covered with iron and bismuth and the SEM images show that the number of active sites on the surface of the modified adsorbent has increased. Also, TEM images (Fig. 5) show that the size of the composing substances is smaller than 60 nm [36].

3.3. The effect of various parameters on the behavior of zeolite nano-adsorbent in the reduction of COD, oil and TUR

3.3.1. The effect of the adsorbent dosage

To study the effect of adsorbent dosage on the adsorption efficiency, 50 mL of the sample solution with different amounts of nano-adsorbent (from 0.001 to 1 g) with the pH of 7 was prepared which was stirred for 10 min at 30°C and then the amounts of oil, TUR and COD were measured. The obtained results have been presented in Figs. 6 and 7. By taking the obtained results into consideration, it becomes clear that the modified zeolite is way more efficient than unmodified zeolite in reducing COD and TUR. By comparing the results, it becomes clear that by using unmodified zeolite, COD and TUR have increased; in such a way that with 0.01 g of adsorbent, there would be 1.5 mg/L of COD and 0.13 NTU of TUR and with 1 g of adsorbent, there would be 14 mg/L of COD and 1.9 NTU of TUR. However, when Bi/Fe-zeolite adsorbent is used, it is quite different. When 0.001 g of the modified adsorbent is used, there would be 1 ppm of COD and by using 0.01 g of this adsorbent, there would be no COD in the solution (COD = 0 ppm). However, increasing the amount of modified adsorbent had increased this parameter; in such a way that when 0.01 g of the Bi/Fe-zeolite is applied, there would be 0.1 NTU of TUR and when 1 g of this adsorbent is used, there would be 0.39 NTU of TUR. The results also show that the reduction of COD and TUR by the Bi/Fe-zeolite is more efficient than unmodified zeolite. In this case, it may be due to better oxidizing ability of modified zeolite after increasing metal ions with high electron-accepting effect, which in turn causes the better activity in COD reduction by modified zeolite. Reduction in TUR may be due to the presence of negative ions (organic and inorganic) in the real wastewater sample with high concentration, which had been bonded to positive sites of metal ions on the surface of modified zeolite. Therefore, the optimal amount of the adsorbent to be used for these experiments is 10 mg. Continuing the



Elements	Weight%	Attomic%
O K	34.39	35.30
Al K	70.17	60.22
Si K	5.44	4.48
Totals	100.00	

Elements	Weight%	Atomic%
N K	1.56	2.84
O K	36.84	58.48
Al K	35.31	33.25
Si K	0.22	0.2
Cl K	1.91	1.36
Fe K	2.83	1.28
Bi M	2.33	2.59
Totals	100.00	

Fig. 4. EDX image of zeolite (A) and Bi/Fe-zeolite (B).

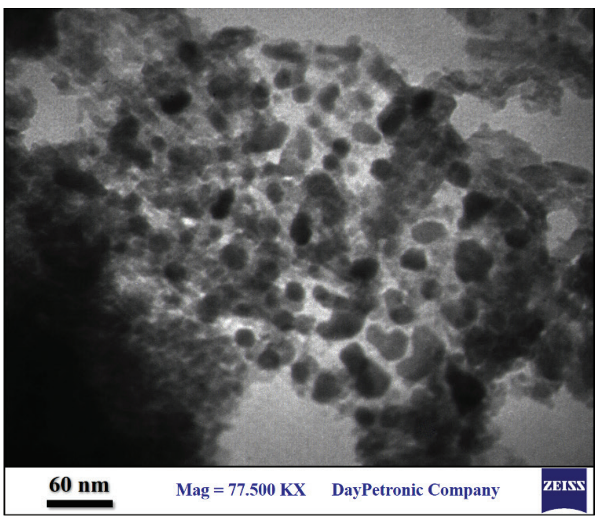


Fig. 5. TEM photograph of Bi/Fe-zeolite.

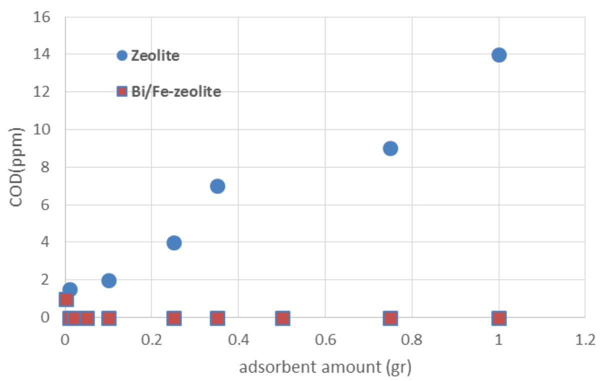


Fig. 6. Effect of adsorbent amount on COD.

modified adsorbent (Bi/Fe-zeolite) will be examined in order to obtain optimal operating conditions.

3.3.2. The effect of pH

The pH of point of zero charge of the adsorbent, pH_{PZC}, was 8 [40]. In low pH ($pH < pH_{PZC}$), the adsorbent has positive charge and high amounts of protons present in solution compete with positive ions for occupying the active sites of the adsorbent, both decrease the complexation of ions with adsorbent. By increasing the pH ($pH \geq pH_{PZC}$), removal extent tend to increase, so the best ions removal was obtained at pH = 8 and thereafter no significant increase was observed [41].

In order to review pH, 10 mg of the Bi/Fe-zeolite adsorbent was added to 50 mL of the effluent sample at 30°C and was stirred for 10 min, pH of the solutions was increased from 3 to 11 and the amounts of oil, COD and TUR were

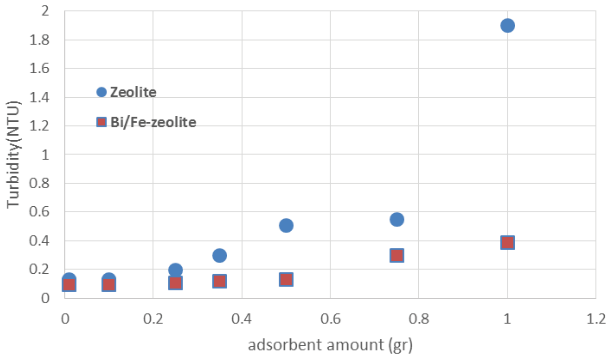


Fig. 7. Effect of adsorbent amount on TUR.

measured. As it can be seen in Fig. 8, the best result for oil and COD has been obtained at pH of 7. The amounts of oil and COD in this pH were equal to zero. As pH increased, the amount of TUR also started to increase. As the results show, the minimum amount of TUR was carried out in an acidic solution. At pH of 3, the amount of TUR was equal to 0.2 which then increased to 0.3 as pH of 7 and then raised to 1 at pH of 11. It seems that the high concentration of negative ions existing in the real wastewater sample is in competition with negative hydroxide ions by increasing pH which in turn reduces the TUR removal efficiency. Therefore, it can be concluded that the optimal operational pH is 7.

3.3.3. The effect of temperature

In the respect of reviewing the effect of temperature on the efficiency of adsorption, 10 mg of the Bi/Fe-zeolite adsorbent was added to 50 mL of the effluent sample at pH of 7 and was stirred for 10 min.

Oil, COD and TUR reduction efficiency was reviewed at different temperatures from 30°C to 60°C, 10-min centrifuge, a 10-min contact time and different amounts of Bi/Fe-zeolite adsorbent. The obtained results have been presented in Fig. 9, which is clear that at temperatures higher than 30°C, COD and oil reduction has not been positively affected. Thus, 30°C was determined as the optimal temperature due to increase in the mobility of ions by increasing temperature, which yields to the less adsorption efficiency [42].

3.3.4. The effect of contact time

For these experiments, 10 mg of the Bi/Fe-zeolite adsorbent was added to 50 mL of the effluent sample at pH of 7. These experiments were done in 5–60 min of contact time at 30°C. The results are presented in Fig. 10, from which it is clear that increasing time led to the COD and oil reduction which were reduced to zero at 30 min of contact time. In 15 min of contact time, the amounts of COD and oil parameters are equal to 1 and 6 mg/L, respectively, which shows that the adsorbent has a natural high capacity for adsorption. Increasing the stirring time was led to increase in TUR. Therefore, by taking into consideration that the other parameters, COD and oil, have been reduced to 0 in 30 min, it has been determined as the optimal contact time.

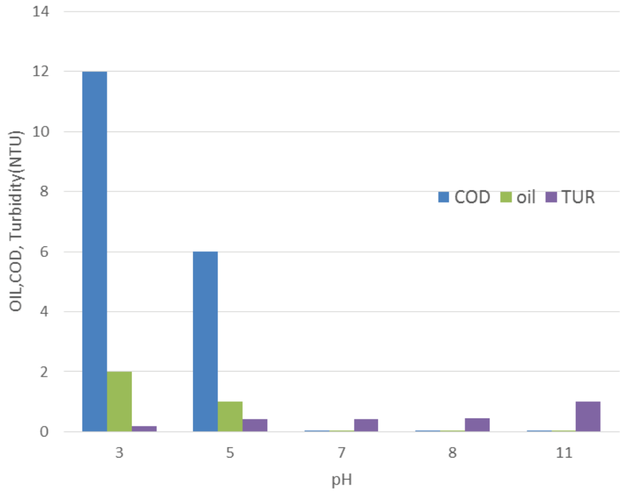


Fig. 8. Effect of pH on COD, oil and TUR for Bi/Fe-zeolite adsorbent.

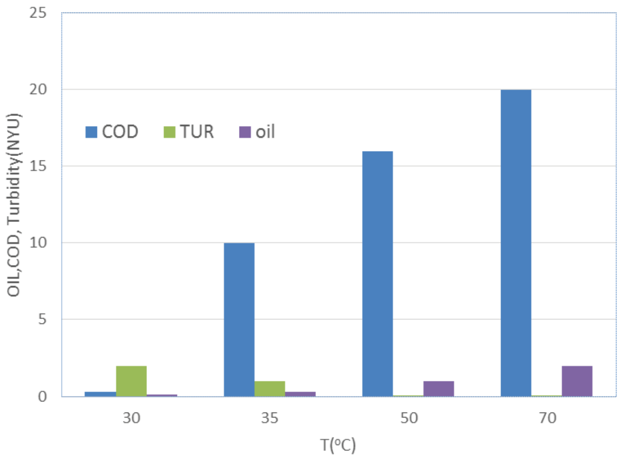


Fig. 9. Effect of temperature on COD, oil and TUR for Bi/Fe-zeolite adsorbent.

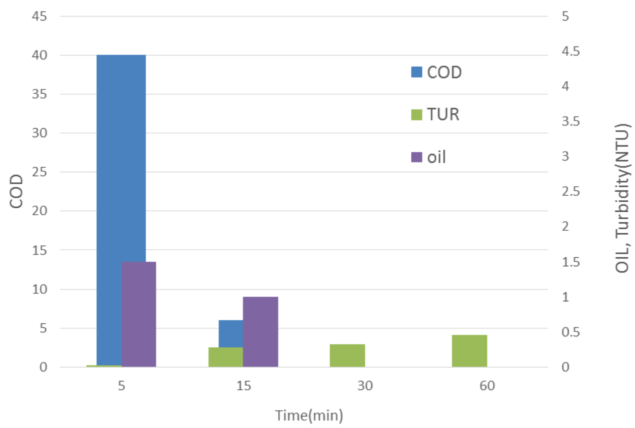


Fig. 10 Effect of time on COD, oil and TUR for Bi/Fe-zeolite adsorbent.

4. Conclusion

In this research, the modified Bi/Fe-zeolite nano-adsorbent was synthesized and used for reduction of COD, oil and TUR which are present in the Kermanshah petroleum refinery effluent. The morphology and structure of the synthesized nano-adsorbent were characterized by FTIR, SEM, EDX and TEM. The effect of operational parameters such as pH, contact time, adsorbent dosage and temperature was investigated. The minimum adsorbent required to achieve the maximum reduction efficiency for COD and TUR at the optimum contact time was 2 mg/L at 30°C and pH of 7. The Bi/Fe-zeolite nano-adsorbent is able to successfully remove the oil, COD and TUR from the petroleum effluents in moderate conditions which can be an efficient candidate for pollutions removal and control of them.

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