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Adsorption of methanol from methanol–water mixture by activated carbon and its regeneration using photo-oxidation process

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ABSTRACT

Activated carbon (AC) has been used as an adsorbent for centuries as a result of its ability to remove a large variety of compounds from contaminated waters. The objective of this study was to investigate the removal of methanol by adsorption and the use of advanced oxidation process for the regeneration of the exhausted AC as an alternative to thermal, biological, and chemical methods that are currently applied. Several experimental tests were carried out to examine the ability of AC for adsorbing methanol from methanol–water mixture. The results show fast saturation of the AC and short breaking time, especially for solutions consisting of methanol above 3% vol. However, adsorption capacity of exhausted AC with methanol, after washing, showed an improvement in its adsorption capacity over that of fresh AC. This improvement may be due to that methanol may harsh the surface of AC causing an increase in the sizes of pores and cavities. Large cavities were micrograph using scanning electron microscope (SEM). After saturation, AC was regenerated using the photocatalytic process, the adsorption capacity of AC was fully restored. The results showed that the titanium dioxide with the aid of UV light can easily regenerate the AC by oxidizing the organic compounds adsorbed on the surface of AC. It was observed that the increase of UV light intensity had a positive effect on adsorption capacity. However, the increases of TiO_2 concentrations had a limited effect on the adsorption capacity of the AC.

Keywords: Activated carbon; Photocatalytic; Methanol; Regeneration

1. Introduction

There are several processes related to the production and uses of methanol which is directly responsible for methanol released into the soil and groundwater. Also, methanol plants produce large volumes of water containing less than 10% methanol during the start-up and shut-down operations. Such wastewater may be a significant source of contaminations to the environment. However, methanol released near drinking water supply would have a negative impact on the quality of the water. There currently exist several treatments for the removal of methanol from water such as air stripping, activated carbon (AC), advanced oxidation, membrane filtration, or biologically activated filters [1,2]. However, some studies have reported that the AC may be suitable for removal of low concentration methanol from wastewater [3].

Many countries around the world have taken precautions to prevent the risks resulting due to rapid industrial progress, especially within the chemical and petrochemical industries. In general, this has been linked to environmental problems contributing to the effect of global warming. The Sultanate of Oman embraces many chemical and petrochemical projects,

including the manufacturing of methanol such as that exists in regional cities of Sohar and Salalah. These industries are major water consumers and therefore cause large water pollution. Methanol as a contaminant is harmful to the biodiversity of the local environment.

Various methods have been proposed to treat the contaminated water with organic compounds. The most common method of treatment of contaminated water is the use of AC due to its large surface area of adsorption, fast adsorption kinetics, and costeffectiveness. The unique adsorption characteristics of AC depend on the specific surface area, pore structure, and surface functional groups [4–9]. However, depending on the adsorption capacity, AC becomes saturated after being used and, thus, needs to be regenerated and reused [10]. There are several well-established methods for the regeneration of spent AC that can be classified into three broad groups: thermal, chemical, and biological regeneration [11–19].

AC is widely used to remove organic pollutants from water, but, depending on its adsorption capacity, it increasingly becomes saturated over time. If AC need to be reused, it must therefore be regenerated. There are many methods have been applied on a small and large industrial scale such as thermal, chemical, microwave, biological, and the advanced oxidation process (AOP). One of the most versatile methods of regenerating AC is by thermal treatment in a normal industrial atmosphere. Also, the use of AOP for the regeneration of spent AC has gained greater attention among industry and researches, and thus, regeneration and the reuse of spent AC become decisive to ensure adsorption is most economical and environmentally acceptable method for the elimination of organic compounds [20].

Recently, the electrochemical regeneration of saturated AC has been investigated using SnO_2/Ti anode [21]. Further research has demonstrated the use of continuous adsorption and electrochemical regeneration of AC using an air-lift reactor [22]. A third similar electrochemical regeneration has been applied on Zealots and the removal of ammonia [23]. In addition, electrochemical regeneration has been applied for drinking water treatment applications, three different samples of A were chosen as follows: fresh, field spent, and field thermally reactivated [24].

AOP technology is proposed as a viable alternative to thermal and other regeneration methods as a photo-catalytic oxidation process in which photo-catalyst promotes destruction of organic compounds when exposed to UV light with aid of TiO_2. The use of AOP presents new possibilities for the regeneration of the AC [20,25–29].

Kurniawan [20] investigated the treatment of recalcitrant compounds from leachate using fresh AC and a combined AC with advanced oxidation process (AOP) including ozone, H_2O_2 and TiO_2. He concluded that H_2O_2 and treated AC had demonstrated better capabilities than that conducted using TiO_2. Also, his results showed an improved effectiveness for the removal of refractory compounds, especially with reference to ozone. Yong [25,26] explored the synthesis of TiO_2/AC composite in treatment methanol gas emitted from pulp and paper industries. He demonstrated that the methanol gas adsorption capacity for fresh AC and TiO_2/AC composite was similar, especially in dry conditions. He concluded that the adsorption of methanol on carbon could not be transferred to the TiO_2 photo-catalyst for the degradation process. He, also, reported that the adsorption process was limited at high level of humidity. Research conducted by Yu et al. [27] indicated treatment of wastewater contaminated with azo dye using carbon nano-tube mixed with TiO_2, was achievable. Carpio et al. [28] used TiO_2 nano-crystals supported on AC. The AOP has been recognized for photo-catalytic degradation of phenol. He concluded only 20 ppm of phenol was removed. Al-Dawery [29] demonstrated that the ability of TiO_2 for regeneration of AC increased by increasing the intensity of UV light.

The photo-treatment time must be as short as possible in order to avoid high electricity consumption. There are some factors that may significantly influence the degradation process, such as pH, temperature, solar light intensity, catalyst, and pollutant concentrations. These factors should be carefully optimized in order to ensure efficiency of treatment process [30].

The AOP has been recognized as an efficient alternative compared to conventional technologies, mainly phase separation (adsorption processes, stripping techniques) and other methods which destroy the liquid contaminants (chemical oxidation/reduction) [31–34].

The main objective of this research was to remove methanol from waste water using adsorption and to regenerate the exhausted AC with methanol using photo-catalytic process. The photo-catalytic regeneration is ascribed to both desorption from AC and photo-catalytic degradation on TiO_2. The proposed project was carried out in two different sets of experiments at the laboratories of University of Nizwa. The first experiment was primarily concerned with the methanol adsorption by AC; while the second set of experiments were focused on the regeneration of AC using titanium dioxide and UV as economical and feasible process. To assess the level of regeneration, the exhausted AC was also subjected to two other different solutions: Tartrazine dye solution and ferric chloride solution.

2. Methodology and procedures

2.1. Methanol adsorption

The granular AC particles (density 400 kg/m^3) of diameter 0.0015 m were supplied by the Haya Company in Sultanate of Oman. Two different methanol–water mixtures (5% and 10% vol methanol) were prepared and used as an adsorbent. The experimental setup consisted of five liter glass vessel feed and an adsorption glass column of 5 cm I.D and 1.2 m height. The column was filled to 100 cm in height with AC. The methanol solution was fed to the column via a peristaltic pump at a flow rate 3.75 L/h. The effluent liquid stream from the adsorption section was collected in a five liter plastic bottle. The schematic diagram of the process is shown in Fig. 1. Samples were taken every 15 min from the effluent solution and then were analyzed for methanol content.

Methanol concentrations in the effluent were analyzed using a method proposed by Wood and Siddiqui [35] in which methanol is oxidized to formaldehyde with potassium permanganate, followed by condensation with 2,4-pentanedione to yield the colored product 3,5-diacetyl-1,4-dihydro-2,6-dimethylpyridine. The optical density was then measured using UV–visspectrophotometer.

2.2. Regeneration process of AC using TiO_2 and UV light

Here, an experimental apparatus was designed and many tests were conducted in order to study the regeneration process of the spent AC using TiO_2 and UV light. Different parameters were considered such as: TiO_2 concentration, contact time, methanol concentration, intensity of UV light, and dye concentration.

The selected photo- catalyst was the titanium dioxide TiO_2 (P25, Degussa AG, Germany) with a surface area of 50 m^2/g and a primary particle size of 20 nm. Degussa P25, a commercially produced form of titanium dioxide and reference catalyst composed of both phases 80% anatase and 20% rutile [33].

Experiments were performed in a (26.7 × 13.5 × 6.5 cm) transparent glass flat vessel as a photo-reactor. The photo-reactor was connected by set of tubes, pump, and beaker systematically as shown in Fig. 2. During operation, liquid height in the reactor was about 1.25 cm and UV lamps were placed 10 cm above the liquid surface of the vessel and both vessel and lamps were covered with aluminum tin foil to reflect UV light optimizing maximum light intensity. The UV radiation source was UV lamp (2 x 6 W) offering light intensity around the two lamps 0.53 mW/cm^2 and around one lamp 0.29 mW/cm^2 at a wavelength of 365 nm.

For each test, sample of spent AC was placed in the photo-reactor, and experimental tests were carried out using one liter of TiO_2 solution of different concentrations: 100, 200, and 300 ppm. The solution was circulated at a flow rate of 0.8 L/min. The reactor was then exposed to the UV light for 3 h in order to provide the suitable energy level that is required to excite the TiO_2 particles

2.3. Adsorption capacity tests

In order to examine the adsorption capacity of the spent and regenerated AC, three different types of activated carbons were chosen as follows: fresh AC, spent AC, and regenerated AC using TiO_2. In addition, two solutions were chosen as an adsorbent: Tartrazine dye solution and ferric solution

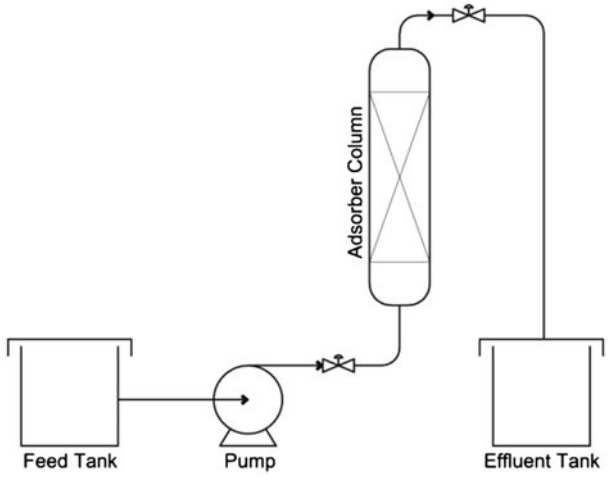

Fig. 1. Schematic diagram of the experimental setup for methanol adsorption.

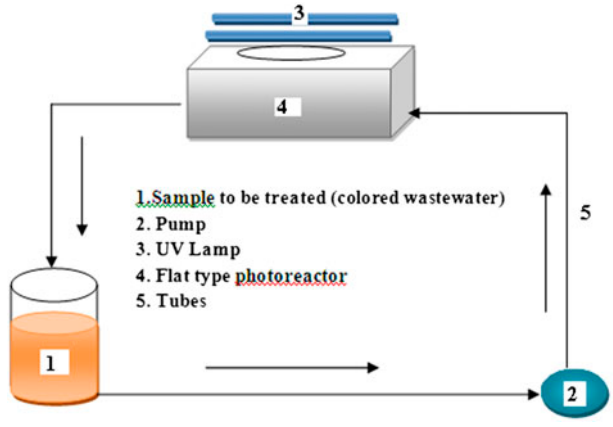

Fig. 2. Schematic diagram of photo-catalytic process.

($Fe_2Cl_3.6H_2O$). The amount of dye and Fe^{3+} adsorbed per unit mass was calculated using the following formula:

$$q_e = \frac{(C_i - C_e)V}{m} \quad (1)$$

where C_i and C_e are the initial and equilibrium concentrations of adsorbed material (mg/l), q_e is the equilibrium amount adsorbed (mg/g), m is the mass of AC, V is the volume of dye solution (l).

For dye adsorption, three different dye concentrations (Tartrazine) were used: 4, 7, and 15 ppm. Then, samples of each type of AC were placed in a 40 ml of each dye solutions and kept on an orbital shaker at constant temperature of 25˚C for a period of 24 h. After that, dye concentrations were measured using UV–Vis spectrophotometer (BioMate5 from Thermoscientific).

For ferric adsorption, three different ferric concentrations ($Fe_2Cl_3.6H_2O$) were used; 366, 183, and 95.2 ppm. Then, samples of each types of AC were each placed in a 50 ml of each ferric aqueous solutions and kept on an orbital shaker at constant temperature of 25˚C for a period of 24 h. The ferric concentrations were measured using an atomic absorption instrument (S4 AA, Thermo Electron Corp) at a wavelength of 228.8 nm.

3. Result and discussion

3.1. Adsorption of methanol

AC has been used to remove methanol from the methanol–water mixture, for this purpose, tests were carried out using two mixtures with a methanol concentration of 5% and 2% separately, the results are shown in Fig. 3. It can be seen that the average estimation of the break point of the adsorption process is about 100 min for both tests: 2% and 5% methanol contents. The fast saturation of the AC reflects its positive adsorption capacity; however, such fast saturation would not be suitable for the treatment of industrial solutions with high methanol content in respect to operational costs and the needs of frequent regeneration. The reason of hindering methanol adsorption may be referred to the formation of hydrogen bond between water and adsorbed methanol, consequently filling the pores of AC and resulting less space for adsorption.

Scanning electron microscope is widely used to study the morphology of adsorbents. SEM was used in order to observe the micrographs of fresh and the exhausted AC. Scanning for fresh AC and exhausted

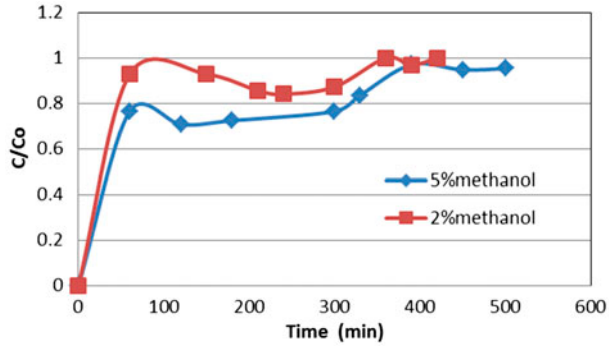

Fig. 3. Time profile of methanol output concentration from GAC.

sample from the adsorption column are shown respectively in Figs. 4 and 5. Comparisons between these images indicate a rough structure on the surface and the presence of many pores on the fresh AC, which is favorable for adsorption compared to that of the exhausted sample.

3.2. Regeneration process of spent AC with methanol

For purpose of examining the adsorption capacities of regenerated AC samples, firstly, four samples of AC were selected: fresh AC, spent AC (treated with methanol), two samples of regenerated AC using two different concentrations of TiO_2; 100 and 300 ppm. The analysis of these samples was performed using SEM and EDX techniques.

All samples were placed in the 366 ppm ferric solutions for 24 h on an orbital shaker. The SEM micrograph shown in Fig. 6 indicates (a) is for fresh AC; (b) is for spent AC; (c) is for regenerated AC using 100 ppm TiO_2, and (d) is for regenerated AC using 300 ppm TiO_2. From these micrographs, it can be observed that TiO_2 is placed on the top of the surface of the AC. It can, also be seen that the methanol had harsh the surface of AC causing larger pores and cavities which increased the adsorption surface area of the AC.

The EDX data of the average of three regions are shown in Table 1. It can be observed that the larger amount of adsorbed Fe is by the spent AC and by the regenerated AC compared to that adsorbed by fresh AC. This observation indicated that the surface area and cavities of the spent AC had increased due to the effect of methanol molecule on the surface of AC. In addition, it can be observed that the regenerated AC use TiO_2 regained it adsorption capacity. However, the use of 100 ppm TiO_2 outperformed the concentrated solution of the higher level 300 ppm TiO_2 as a

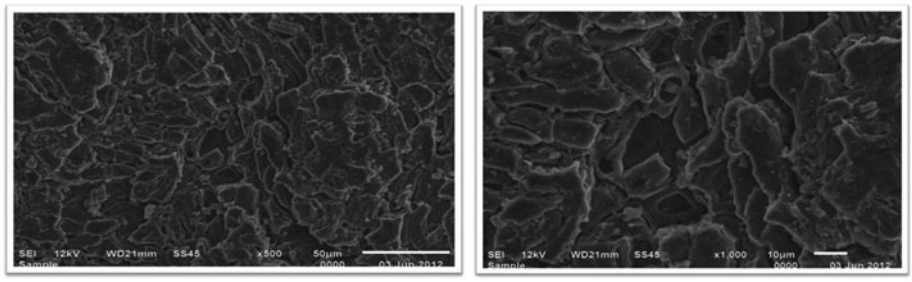

Fig. 4. SEM micrograph of fresh AC.

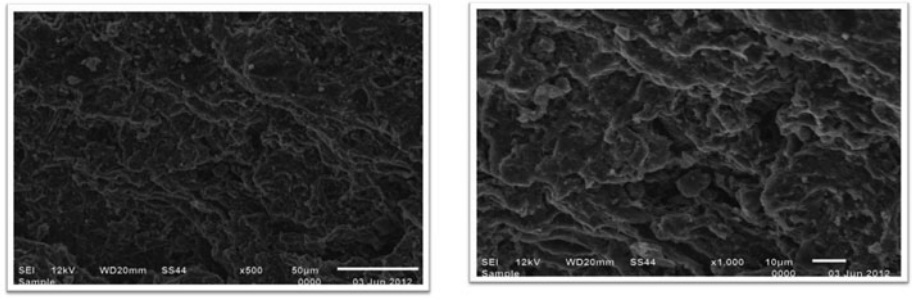

Fig. 5. SEM micrograph of exhausted AC.

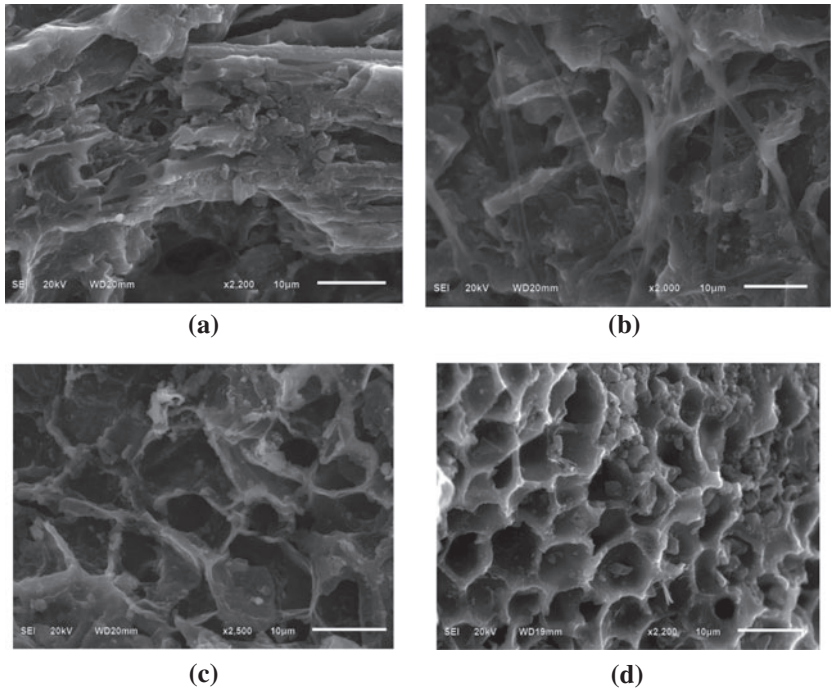

Fig. 6. SEM Micrographs of AC (a) Fresh AC, (b) Spent AC, (c) Regenerated AC using 100 ppm TiO_2, and (d) Regenerated AC using 300 ppm TiO_2.

Table 1
EDX data of Fe^{3+} that adsorbed on treated AC with methanol and regenerated with different concentrations of TiO_2

AC	Fe mass%	Ti mass%
Fresh	1.02	–
Spent with methanol	3.44	–
Generated using 100 ppm TiO_2	1.23	0.17
Generated using 300 ppm TiO_2	1.11	0.15

result of increase turbidity that reduced the UV light intensity that is required for the oxidation process.

A second test was performed for testing the adsorption capacities of AC samples using two different concentrations of Fe^{3+}: 95.3 ppm as low concentration and 183 ppm as high concentration. The results are presented in Fig. 7 that indicates AC–Ti is for regenerated AC with different concentration of TiO_2 (100, 200, and 300 ppm): AC is for Fresh AC and AC–ME is for spent AC with methanol. This figure shows that the larger amount of adsorbed Fe is by the spent AC and by the regenerated AC compared to that adsorbed by fresh AC. This observation indicated that the surface area and cavities of the spent AC had increased due to the effect of methanol molecular on the surface of AC. In addition, it can be observed that the regenerated AC use TiO_2 regained its adsorption capacity.

pH value of the solution has been raised from 7.8 to 8.3 during photo-catalytic process; this slight changes in the pH would not be considered to an impact on the regeneration and organic degradation processes.

A third test was performed using three different concentrations of dye; 4 ppm as low concentration; 7 ppm as medium concentration, and 15 ppm as high concentration onto the AC samples. The results are presented in Fig. 8 that indicates AC–Ti is for regenerated AC with 100 ppm TiO_2; AC is for Fresh AC and AC–ME is for spent AC with methanol. Similarly, this figure shows that the larger amount of adsorbed Dye is by the spent AC and by the regenerated AC compared to that adsorbed by fresh AC. This observation, also, indicated that the surface area and cavities of the spent AC had increased due to the effect of methanol molecular on the surface of AC. In addition, it can be observed that the higher the concentration of dye the higher the adsorption occurred.

3.3. Regeneration process of spent AC with tartrazine dye

Similar tests were also performed using the dye as an adsorbent instead of methanol solution for fresh AC. Firstly, 2.5 g of AC was placed in solution of 15 ppm of dye for period of 24 h. The AC sample was washed and dried, and then three samples of 500 mg each were regenerated using 100 ppm TiO_2 and different time exposures to UV light.

For adsorption test, the selected samples of AC were placed in the 366 ppm ferric solution for period of 24 h on an orbital shaker. The results of the EDX data are presented in Table 2. These results indicated the ability of the photo-catalytic process for regenerating the spent AC. Also, it can be seen the longer the time of exposure to UV light improved the regeneration process based on the amount of Fe^{3+} that had been adsorbed.

In order to enhance the regenerating of spent AC using titanium dioxide illuminated with UV light, additional tests were conducted using 100 ppm TiO_2 solution and two different UV illuminations: 6 and 12 W separately. After regeneration, test was performed for testing the adsorption capacities of AC samples using two different concentrations of Fe^{3+}; 95.3 ppm as low concentration and 183 ppm as high concentration.

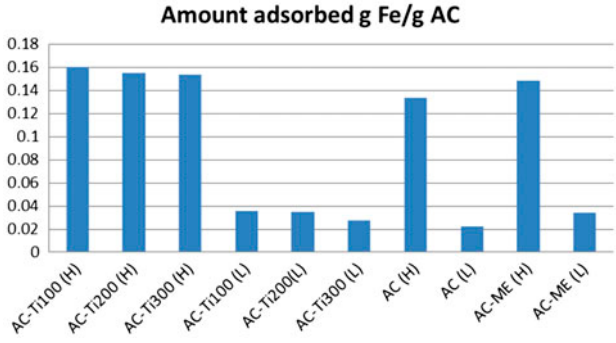

Fig. 7 Fe^{3+} adsorption on AC: regenerated (AC–Ti); spent (AC–ME); and fresh AC. Ferric concentration: L = 95.3 ppm and H = 183 ppm.

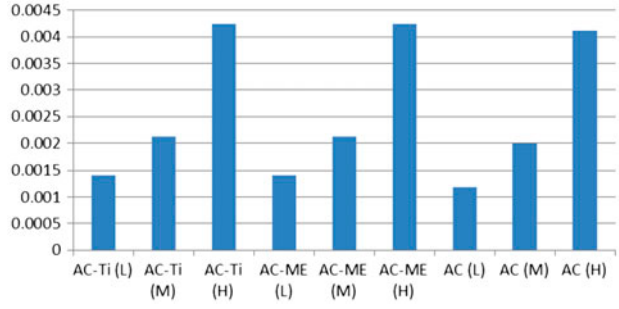

Fig. 8. Dye adsorption on AC: regenerated (AC–Ti); spent (AC–ME); and fresh AC. Dye concentration: L = 4 ppm; M = 7 ppm; and H = 15 ppm.

Table 2
EDX data of Fe^{3+} that adsorbed on treated AC with dye and different time of regeneration

	Exposure to UV light = 1 h	Exposure to UV light = 2 h	Exposure to UV light = 3 h	Fresh AC
Fe mass%	0.81	2.95	4.46	0.8
Ti	0.99	1.56	1.13	–

The results are shown in Figs. 9 and 10. It can be observed that there is an improvement in adsorption capacity in the regenerated AC compared to that adsorbed using fresh AC. These tests clearly indicated support the notion of using approved that photo-oxidation process for regeneration process. Also, it can be seen that the increased intensity of UV light improved the regeneration of AC and thus improved its adsorption capacity.

3.4. Effect of methanol concentration on the adsorption capacity of AC

Additional tests were considered in order to observe the effects of methanol concentration on adsorption capacity of fresh AC and spent AC samples. Samples of AC were placed in different concentrations of methanol solutions (10%, 20%, and 100% vol) for 24 h and then, adsorption capacity had been examined using both dye and ferric solutions. The used dye solutions were 4, 7, and 15 ppm while the ferric solutions were 183 and 95.3 ppm. The results are presented in Figs. 11 and 12 that indicate AC–ME10 is for AC treated with 10% methanol; AC–ME10 is for AC treated with 20% methanol; and AC–ME10 is for AC treated with 100% methanol. It can be seen that the adsorption capacity of AC decreases with the

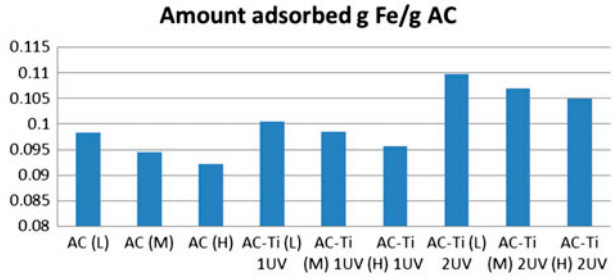

Fig. 9. Fe^{3+} adsorption on AC using 183 ppm ferric concentration: AC treated with dye and regenerated AC–Ti; illuminated (1 UV lamp); (2 UV lamp); dye concentration; L = 4 ppm; M = 7 ppm; and H = 15 ppm.

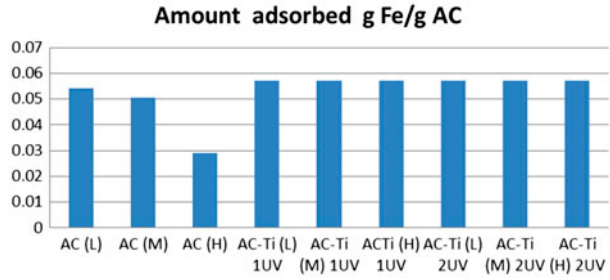

Fig. 10. Fe^{3+} adsorption on AC using 95.3 ppm ferric concentration: AC treated with dye and regenerated AC–Ti; illuminated (1 UV lamp); (2 UV lamp); dye concentration; L = 4 ppm; M = 7 ppm; and H = 15 ppm.

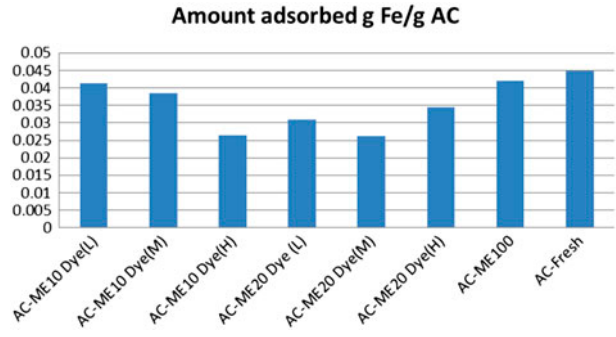

Fig. 11. Fe^{3+} adsorption of 183 ppm ferric concentration on AC treated with different methanol concentrations: AC–ME10 (10%); AC–ME20 (20%); AC–ME100 (100%); dye concentration; L = 4 ppm; M = 7 ppm; and H = 15 ppm.

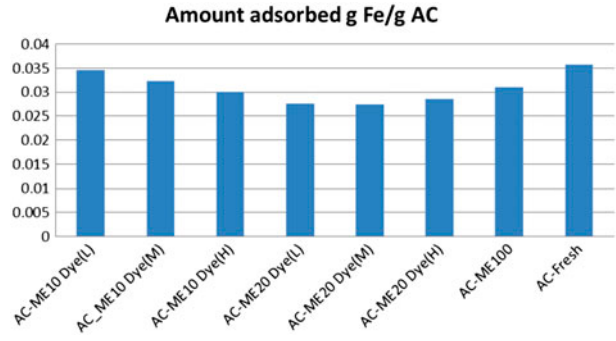

Fig. 12. Fe^{3+} adsorption of 95.3 ppm ferric concentration on AC treated with different methanol concentrations: AC–ME10 (10%); AC–ME20 (20%); AC–ME100 (100%); dye concentration; L = 4 ppm; M = 7 ppm; and H = 15 ppm.

increase of methanol concentrations. While, at the same time, it can be observed at the higher the dye concentration, the lower the adsorption capacity had occurred. The explanation of this observation can be refer to: the lower adsorption capacity of Fe^{3+} is due to large amount of dye that have been adsorbed on the AC that was treated with higher concentrations of methanol, and thus, less available surface area for adsorption capacity available to be used by the ferric solutions. This test again supports the idea that the methanol solution harsh the surface of AC causing larger size of pore and cavities to form, thus increasing the adsorption capacity of AC.

4. Conclusion

The obtained results showed a significant adsorption capacity of AC to methanol, but with fast saturation and short breaking time. Such fast saturation is not suitable for the treatment of industrial solutions with high methanol content in respect to the need of frequent regeneration. The reason of hindering methanol adsorption may be referred to the formation of hydrogen bond between water and adsorbed methanol, consequently filling the pores of AC and resulting in less space for adsorption.

However, the results showed that the treated AC with methanol solution had harsh the surface area of the AC causing an increase in the size of the pores that created more space onto the AC surface and improved adsorption.

The use of the photo-catalytic process for regeneration of the spent AC showed positive results and improved in the adsorption capacity of AC after regeneration. Also, it was observed that there was an improvement of adsorption capacity of both spent AC and regenerated AC compared to that of fresh AC.

The data obtained showed that increase UV light intensity improved the rate of degradation of organic compound on surface of the AC and thus increased the adsorption capacity.

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