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A NOVEL APPROACH FOR WATER TREATMENT BY USING ACTIVATED CARBON: APRICOT KERNEL SHELL

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Aktif Karbon Kullanarak Su Arıtımında Yeni Bir Yaklaşım: Kayısı Çekirdek Kabuğu

Öz

Endüstrinin hızlı bir şekilde büyümesi ile birlikte çevre kirliliğinin artması ve küresel ısınmanın sebep olduğu anormal iklim değişiklikleri su kaynaklarının azalmasına sebep olmuştur. Bu durum ise son 40 yıldır içme su kaynaklarının korunması ve temizlenmesine yönelik artan bilim ve araştırmalara sebep olmuştur. Bunun sonucunda su arıtılması ile ilgili biyolojik arıtma ve oksidasyon teknikleri gibi pek çok değişik teknolojiler ve araştırmalar yapılmaktadır. Bu çalışmada metilen mavisi (MB) içeren suyun renk giderimi aktif karbon kullanılarak gerçekleştirilmiştir. Kayısı çekirdeğinden elde edilen aktif karbon dünyanın en yüksek yüzey alanlarından birine sahiptir. UV-Vis spektrofotometre ile yapılan analiz sonucunda yaklaşık %95 boya giderimi ilk yarım saat içerisinde gerçekleştirilmiştir. Ayrıca yaptığımız aktif karbon ve UV ışığı altında TiO_2 nanoparçacıkları kullanılarak elde edilen renk giderim sonuçlarını karşılaştırdığımızda aktif karbonun çok daha iyi sonuçlar verdiği gözlemlenmiştir. Bu sonuçlar neticesinde dünya kayısı üretiminde ilk sırada olan ülkemizin, ekonomik değeri yok denecek kadar az olan kayısı çekirdek kabuğunun günümüzün en önemli problemlerinden biri olan temiz suyun eldesi konusunda büyük bir potansiyele sahip olacağı öngörülmektedir.

Anahtar Kelimeler: *Su arıtımı, aktif karbon, titanyum dioksit (TiO_2), metilen mavisi*

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A Novel Approach for Water Treatment by Using Activated Carbon: Apricot Kernel Shell

Abstract

The rapid growth of industry with increasing environmental pollution and abnormal climate changes caused by global warming leading to reduce water resources. It has encouraged strengthening the science and research to protect and clean drinking water resources since the last 40 years. As a result, many different technologies and researches such as biological treatment and oxidation techniques related to water treatment are being carried out. In this study, the color removal of water containing methylene blue (MB) by using activated carbon was performed. The activated carbon, which was obtained from the apricot kernel shell, has one of the world's highest surface areas. As a result of the analysis with UV-Vis spectrophotometer, approximately 95% dye removal was obtained within the first half hour. We have also observed that the apricot kernel activated shell gives much better results when we compare the color removal results obtained using TiO_2 nanoparticles under UV light. It can be concluded that our country, which is the first in the world for apricot production, can supply the apricot kernel shell with a very low cost can have a great potential to treat water which is one of the most important problems of our lives.

Keywords: *Water treatment, activated carbon, titanium dioxide (TiO_2), methylene blue,*

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1. Introduction

Universal clean water access is very important and is the most essential component for the life. The lack access to fresh and clean water can lead many problems including malnutrition, sickness, and death (Avci et al., 2013; Montgomery and Elimelech, 2007; Shannon et al., 2008). Moreover, it is becoming more and more important for the future years due to population growth, climate changes, expansion of agricultural and industrial activities with enhancing the living standards (Zimmerman et al., 2008; Kim et al., 2010). Nowadays, disproportionate incidence of environmental contamination is one of the important reason for the water shortage. In general, contamination is raised by developing and industrialized countries via release of organic dyes, distillates, heavy metal ions, and micropollutants into water supplies (Kaur et al., 2008; Avci et al., 2017). In particular, the training of people in this field with the application and enforcement of laws related to these subjects are the primary precautions. The two main strategies in this regard are foreground (Legrini et al., 1993): (1) treatment of contaminated drinking, underground and surface waters; (2) treatment of wastewaters containing biocidal or nondegradable pollutants in the nature.

Especially in recent years, many different technologies and researches on water treatment have been carried out (Lee and Park, 2013). These can be categorized as biological purification, coagulation & sedimentation techniques, Fenton oxidation purification and advanced oxidation techniques. Biological treatment utilizes microbial metabolism, while coagulation and sedimentation techniques are based on solving the solid substances in the form of suspension by clustering and precipitating with inorganic coagulants such as iron and aluminum. On the other hand, the Fenton oxidation treatment method is based on the disintegration of organic substances with hydroxyl radicals produced by using Fenton compounds, which have strong oxidizing properties.

Photodegradation of environmental pollutants by using photocatalyst is one of the popular removing strategies (Tahir and Amin, 2015). TiO_2 as a photocatalyst is one of the most used water treatment materials due to the extensive properties such as having high efficiency, low cost, chemical and optical stability with demonstrating harmless property, dissolvable character in water, also does not produce pollution and need low energy (Farbod and Jafarpoor, 2012).

Methylene blue is a cationic dye and widely used as a traditional dye for wool, silk, and cotton. Consuming water which contains methylene blue may cause vomiting, nausea, diarrhea and the burn effect of eyes (El-Sharkawy et al., 2007; Lang, 2009). Recently, different techniques have been used for the removal of the dyes from the wastewater. However, the most of the treatment techniques are comparatively expensive and complicated. It is possible to remove the pollutants in the water by adsorption to a suitable solid surface. As adsorbents, porous solids which generally have a high surface area are preferred. Activated carbon is one the most commonly used adsorbent because it has high adsorption capacity for many different substances. Therefore, activated carbon is widely applied for removal of colored pollutions from the wastewater, treatment of discharged gaseous effluents from industry, purification and treatment of gases, separation of mixtures, and food processing industry (Basso et al., 2002; Küçükgül, 2004; Saheed et al., 2017). In the last decades, activated carbon has been applied to clean aqueous pollutants by removing silver, copper and nickel salts (Adhoum and Monser, 2002; Deveci et al., 2006; Depci, 2012). Activated carbon has more efficient adsorbent due to high degree of surface reactivity, variable characteristics of surface chemistry, large surface area that can reach 3000 m^2/g and sophisticated porosity development (Rajalekshmi et al., 2016).

Almost all carbon containing materials can be used to produce activated carbon. They must be found in nature or as industrial waste, and their prices must be low. Up to the present, activated carbon has been produced by using bagasse, cassava peel, date pits, fruit stones and nutshells, rice husks, olive stones, and jute fiber (Yalçın and Sevinc, 2000; Sivakumar et al., 2001; Tsai et al., 2001; Girgis and El-Hendawy, 2002; Aygün et al., 2003; El-Sheikh et al., 2004; Senthilkumaar et al., 2005). Recently, Renugadevi et al. reported that obtained activated carbon from fruits of Mimusops elengi could adsorbed 99.1% methylene blue after 180 min treatment (Renugadevi et al., 2010).

In this study, activated carbon which was obtained by using a lignocellulosic material of apricot kernel shell to remove methylene blue in the contaminated water is aimed. Turkey, which is the first country in the world for fresh and dried apricot production, has great potential for the both in terms of species and production areas. Hence, apricot kernel shell has low-cost and can be found abundantly in Turkey (Depci et al., 2014). Activated carbon was evaluated based on adsorption performance of methylene blue and reusability capacity. In addition, the performance of activated carbon was compared to TiO_2 photocatalyst which is a common method under UV light for the ability of removal of the dye molecules.

2. Materials and Methods

2.1. Materials

In this study, activated carbon was provided from Dr. Önal research group at İnönü University, Malatya, Turkey. This material has been obtained from waste apricot kernel shell as shown in Figure 1a. As seen in Figure 1b, it has highly developed homogeneous and uniform pore sizes and shape with controlled microporosity structures to control of the properties and the functionality. In general, the activated carbon was prepared by using the appropriate amount of apricot kernel shell which was carbonized at 800 ^oC for 1 hour. In the chemical activation process of the carbonized specimens, the sample was dried at 105 ^oC by mixing with KOH in different proportions values by weight. In the activation process; impregnated specimens were placed in steel tubs and the heat treatment was applied in a tubular reactor at 800 ^oC maximum temperature for 1 hour at a heating rate of 10 ^oC/min at a flow rate of 100 mL / min under N_2. After the activation process the samples were cooled in the N_2 atmosphere. After the addition of diluted HCL, it was washed with hot distilled water. The samples obtained were classified depending on the KOH ratio (Önal et al, 2010). After the optimization process, it is claimed that the material has the highest surface area within its category that can reach 3120 m^2/g with sophisticated homogeneous porosity distribution (Kayısı, 2013). Figure 1b displays image of the apricot kernel shell activated porosity taken by scanning electron microscope. In present study, Aeroxide P25 TiO_2 (composed of 75% anatase and 25% rutile) with 21 nm primary particle size was bought from Sigma-Aldrich with molecular weight of 79.87 g/mol. It was used as a photo-excitation of semiconductor to remove the dye molecules. Methylene blue as frequently used was chosen as model pollution due to its rapidly react in the presence of the oxygen (Tabbara and Jamal, 2012) with having stock solution of $1.5*10^{-5}$ mol/L. Methylene blue was purchased from A.D.R Group with molecular weight of 319.85 g/mol.

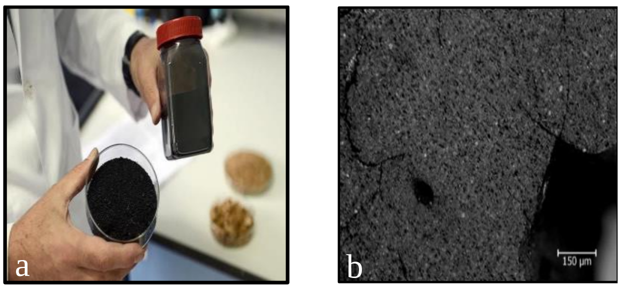

Figure 1. Produced activated carbon from apricot kernel shell (a), and a microscope image (b).

2.2. Dye Calibration Curve

To determine the concentration of methylene blue dye solution, a JENWAY-6105 UV/Vis device was used. Methylene blue solutions with concentrations of 5, 2.5, 1.25 and 0.75 ppm were prepared to obtain calibration curve to measure the unknown concentration. Figure 3a displays calibration curve of methylene blue. The maximum wavelength absorption of methylene blue was measured at 665 nm as demonstrated in the literature (Basavaiah and Kumar, 2007).

2.3. Adsorption Process of Activated Carbon

In order to evaluate the trend of methylene blue adsorption by the prepared adsorbent at different times (30 min, 60 min, and 90 min), 0.1 g of activated carbon was contacted with 30 ml methylene blue solution (5 ppm) and mixed in a magnetic stirrer (SCILOGEX MS/H280) at 25 °C and 400 rpm under the sunlight. Then, 4.5 ml of the solution was taken and centrifuged (BENCH-TOP-NF200) for 5 minutes at 2500 rpm. Moreover, activated carbons were dried under the room temperature for 48 hours after adsorption process. The activated carbons again were used for methylene blue adsorption at 25 °C in order to find out the reusability capacity. The rate of adsorption the methylene blue concentration was analyzed and monitored by UV-Vis spectrophotometry at 665 nm wavelength.

2.4. Photocatalytic Degradation Process

The water treatment was carried out at concentration of 5 ppm MB with adding 0.2 g TiO_2 powder into beaker under room temperature. In addition, the experiments were performed inside a chamber, which covered with aluminum foil. Two UV–A lamps (PL-S 9W/10/2P, Philips) were installed into chamber with 13 cm above the beaker. The solution containing the dye and TiO_2 nanopowder were continuously mixed by stirring in order to improve the interaction for the photocatalyst degradation. At specific time intervals (30 min, 60 min, and 90 min), 4.5 mL of solutions were taken and transferred to a cuvette for the analysis. The amount of the dye was measured at 665 nm by employing UV-Vis spectroscopy.

3. Result and Discussion

3.1. Adsorption Analysis of Activated Carbon

In general, activated carbon has microspores (pore size <2 nm) over 95% of the total surface area (El-Geundi, 1997). Hence, activated carbons extensively apply for the water treatment. Table 1 shows the effect of contact time on the removal of methylene blue by the activated carbon obtained from apricot kernel shell. According to the Table 1, interestingly the adsorption of dye has been increased with the time passing. The most adsorption has been observed in the first 30 min during contact time between the adsorbent and the adsorbate. For the complete removal, the process was continued till 90 min with demonstrating a lower slope. In order to determine reusability capacity and performance of the activated, the experiments were repeated three times by using the same activated carbons. After each trial the activated carbons were dried about 48 hours under the room temperature. In the first treatment, the colored water was exposed by the activated carbon for the adsorption process for 30 min, 60 min, and 90 min. It demonstrated about 94.75 %, 98.12 %, and 99.25 % color removal, respectively. Also, Figure 2 shows apparent images of the colored water after 30 min, 60 min, and 90 min from left to right. The second treatments show color removal of 95.13%, 98.50%, and 99.62% for 30 min, 60 min, and 90 min, respectively. At the final trial, the percentage adsorptions were 92.50 at 30 min, 98.50 at 60 min, and 99.25 at 90 min. Even if it is strongly believed that the cycle of reusability of activated carbon which was obtained by using apricot kernel shell is higher due to a very high surface area, the experiment was terminated after the third trial.

On the hand, the adsorption capacity of the activated carbon started to decrease about 92% at the end of 30 min after the third cleaning cycle, while it maintained its almost all performance at the end of 90 min after all cycles.

Table 1. Reusability capacity of activated carbon (% Removal of Methylene Blue)

Treatment	after 30 min	after 60 min	after 90 min
The first cycle	94.75	98.12	99.25
The second cycle	95.13	98.50	99.62
The third cycle	92.50	98.50	99.25

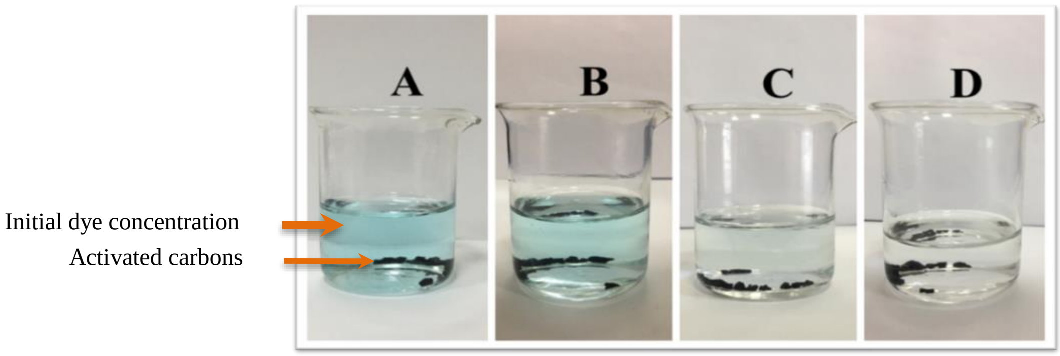

Figure 2. Images of A) Initial dye of apparent methylene blue, B) after 30 min, C) 60 min, and D) 90 min treatment.

3.2. Photocatalytic Degradation Analysis

The photocatalytic reaction takes place because of presence of N-dealkylation of dyes containing auxochromic alkylamine groups in methylene blue. It is expected at final photocatalytic reaction, methylene blue degrades into H_2O, CO_2 and other inorganic molecules (Zhang et al., 2001). Figure 3b displays the percentage degradation versus time for methylene blue at predetermined different time intervals. As seen in Figure we can observe that degradation of methylene blue increases with time passing from 30 to 90 min. In the other words, photonic efficiency is decreased with high initial dye concentration (Dai et al., 2013). Percentage photodegradation of methylene blue by UV-A/TiO_2 process during 30 min, 60 min, and 90 min was 74.53%, 88.01%, and 94.75%, respectively. The photocatalytic degradation process results suggest that the combination of TiO_2 nanopowders and UV-A lamp with 9 watts can degrade methylene blue about 94.75 % after 90 min process time.

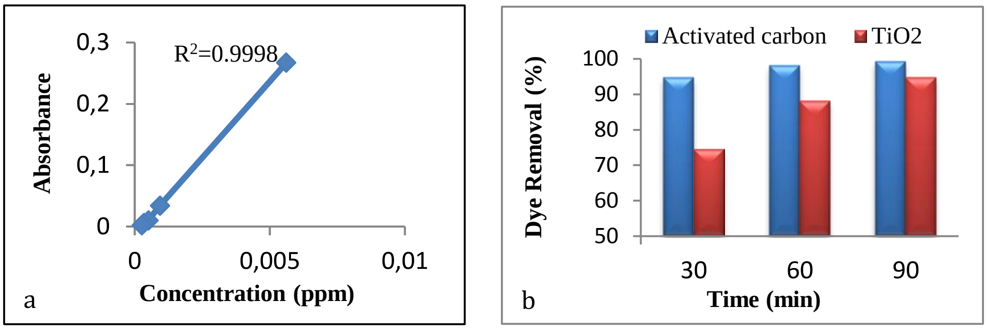

Figure 3. a) Methylene blue calibration curve, b) percentage removal of methylene blue versus time for activated carbon and TiO_2, respectively.

Figure 3b displays the comparison of percent degradation and adsorption of methylene blue by using TiO_2, and activated carbon, respectively. It is clearly seen activated carbon removed almost all dye molecules in the first 30 min, however TiO_2 under UV light in the chamber needed about 90 min to demonstrate the similar performance. During the all experiment of 30, 60, and 90 min, activated carbon demonstrated higher performance than TiO_2. Specifically, there is a clear difference at the end of 30 min 74.53% for TiO_2 versus 94.75 % for activated carbon. Furthermore, activated carbon does not require any special chamber or equipment and TiO_2 can only be activated by UV light. Hence, activated carbon appears to give great advantages over TiO_2/UV process.

4. Conclusion

In this research, almost 100% of the water was cleaned in about half an hour with using only activated carbon obtained from the apricot kernel shell. It demonstrated that the use of activated carbon which has low-cost abundantly found in Turkey can have a great potential to clean the wastewater.

Summary of such additional results are indicated below:

- Activated carbon was much more efficient than TiO_2-UV photocatalytic process in the first half hour that is important for the saving time and reducing the cost. It is most probably due to having high specific surface area and pore volumes of the activated carbon that play an important role in high adsorption capacity for the pollutant species at short time. In general, the adsorption capacity of an activated carbon depends on several factors such as the nature of the adsorbent and the adsorbate, the solution conditions, and etc.
- As demonstrated in the experiments, the reusability capacity of activated carbon gives advantages over TiO_2-UV due to deactivation of the photocatalyst. The surface area of the activated carbon obtained from the apricot kernel shell is much higher than the other raw materials such as coconut, almond, nut kernel shell, walnut shell, corn cob, olive kernel, rice stem, which causes to obtain high performance and reusability for the water treatment. As a result, more economical and more effective water treatment is foreseen.
- On the other hand, activated carbon produced from the apricot kernel shell can be used in the purification of gas and refining, separation of mixtures and purification processes in food industry.

As a result, more economical and more effective water cleaning and treatment is foreseen.

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Conflict of Interest

No conflict of interest was declared by the authors.

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