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REDUCTION DYE IN PAINT AND CONSTRUCTION CHEMICALS WASTEWATER BY USING MICROWAVE RADIATION METHOD

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ABSTRACT

In this study, a novel process, microwave (MW) radiation, was used for the removal of dye from wastewater of paint and construction chemicals producing factory in Turkey. This process was the combination of MW irradiation, MW adsorbent (as catalyst), coagulant and oxidant. The activated carbon prepared from olive-waste cake by chemical activation was investigated as an MW adsorbent. Aluminum sulfate and hydrogen peroxide were used as coagulant and oxidant, respectively. The effects of radiation time, adsorbent dosage, coagulant and oxidant on the dye removal were investigated. The surface area and micropore volume of activated carbon was 1418 m^2/g and 0.197 cm^3/g, respectively. The presence of hydrogen peroxide showed no effect on dye removal. It has been demonstrated that the color can be effectively removed from wastewater by using activated carbon and aluminum sulphate in combination with microwave radiation. Experiments were also performed for the use of only coagulant (aluminum sulphate) and it was observed that the dye was well removed from the wastewater when the amount of coagulant was more than 0.1 g / 100 mL. Results suggest that the activated carbon obtained from olive-waste cake has potential in remediation of dye contaminated waters.

KEYWORDS:
Olive-waste cake, Activated carbon, Coagulant, Wastewater, Microwave radiation

INTRODUCTION

Wastewater containing paint and construction chemicals is very harmful to the environment due to high concentration of organic and inorganic pollutants [1]. The direct discharge of this wastewater into the environment causes various undesirable changes, affecting its ecological status [2]. For instance, the paint and construction chemicals in the wastewater deteriorates the quality of the water and gradually causes a decrease in clean water resources. The discharge of dyes into receiving waters is one of the major causes of water pollution. Even small quantities of dyes color the water body due to their synthetic origin and complex chemical structure [3]. Dyes in water limit the photochemical and biological activities of aquatic life by weakening the permeability of sunlight [4]. Excessive phosphate anions in wastewater disrupt the quality of the water and cause a gradual decrease in clean water resources. Therefore, the removal of dyes from wastewater is of great interest from environmental point of view [5].

Different adsorbents have been used for removal of dyes. Commercial activated carbon could have been a preferable adsorbent for the removal of organic pollutants from wastewater, however its widespread use is restricted due to high associated costs [6]. In this respect, many researchers have investigated low cost and efficiently activated carbon production from industrial and agricultural wastes [7-9].

Activated carbon can be prepared by physical and chemical activation methods. The former involves primary carbonization of the raw material followed by controlled gasification at higher temperatures in a stream of an oxidizing gas (steam, CO_2, air or a mixture) [10]. Chemical activation, on the other hand, involves impregnation of the precursor by a solution of the chemical ($ZnCl_2$, Na_2CO_3, K_2CO_3, KOH, NaOH, H_3PO_4 etc.), followed by the heat treatment that influences the carbonization process and leads to generation of porosity which becomes accessible when the chemical is removed by washing [11].

Microwave (MW) has gained increasing attention in industrial processes and wastewater treatment [12-15]. MW radiation exhibits higher heating rates, reduced activation energies, increased reaction rates, improved energy efficiency and reduced equipment size. The energy of one mole of photon from MW at a frequency range of 1-100 GHz is equal to 0.4-40 J. However, the energy of MW is insufficient to disrupt the chemical bonds of many organic compounds. Therefore, MW has been combined with catalysts, coagulants and oxidants for increasing the treatment efficiency [16].

The food industries produce large amounts of solid waste that can cause environmental pollution.

Olive oil is the most produced food in Mediterranean countries. In this industry, different amounts of products are produced according to the production method. Depending on the olive oil production method used in each country, there are different types of wastes, most of which involve one type of residue or another [17]. The main olive oil producers are Spain (36%), Italy (27%), Greece (15%), Tunisia and Syria (6%), and Turkey (4%). Turkey is 6th in olive production in the world. In Turkey, a great quantity of olive-waste cake is annualy generated as a waste in the industrial production of olive oil [18]. Therefore, this study has focused on the production of activated carbon from olive-waste cake by chemical activation with $ZnCl_2$.

The aim of this study was to investigate the effect of MW radiation on dye removal in wastewater containing paint and construction chemicals by using activated carbon as adsorbent. For this purpose, activated carbon was produced from olive-waste cake by chemical activation. The resultant carbons, coagulant and oxidant were used to remove dye from wastewater by MW radiation. The effects of radiation time, dosage of adsorbent, coagulant and oxidant on the removal were investigated.

MATERIALS AND METHODS

Materials. The wastewater containing dye was collected from a factory producing dyes and construction chemicals in Eskişehir, Turkey. The displayed wastewater color value is greater than 500 Pt/Co. In this case, the wastewater had very high color and suspended solids. The samples were refrigerated at 4 °C prior to performing subsequent experiments. Olive-waste cake provided by the HISAR Olive Ind. Inc. (Manisa, Turkey) was first air dried, then crushed and finally sized. The fraction of particle sizes between 1 and 2 mm was chosen for subsequent studies. Aluminum sulfate and hydrogen peroxide were used as coagulant and oxidant, respectively. The chemicals used in this study were analytical grade, and obtained from Merck. The color value was measured using a HACH DR/2000 spectrophotometer in units of point color (Pt/Co). A domestic microwave oven (750 W, 2450 MHz, Vestel) with different power setting was used as MW source.

Preparation of Activated Carbon In this study, chemical activation of olive-waste cake was performed using zinc chloride ($ZnCl_2$) with an impregnation ($ZnCl_2$:olive-waste cake) ratio of 3:1. About 10 g of the impregnated sample was placed on a ceramic crucible in the tubular reactor (Protherm PTF 12) and heated up to the final activation temperature (800 °C) under the nitrogen flow (≈200 cm^3/min) at heating rate of 10 °C/min and held for 2 h at this final temperature. The resulting solids after carbonization were boiled at about 90 °C with 100 mL of 1 N HCl solution for 30 min to leach out the activating agent, filtered and rinsed by warm distilled water several times until the pH value was reached to 6-7. Finally, they were dried at 105±3 °C.

Characterization of Olive-Waste Cake and Activated Carbon Proximate analyses of olive-waste cake were determined according to the ISO R 771, ISO R 749 and ASTM E 872. Content of ash, moisture and volatile matter of activated carbon were determined according to the ASTM D 2866, ASTM D 2867 and ASTM D 5832, respectively. Fixed carbon content was determined by difference. To determine the surface area of olive-waste cake and activated carbon, the nitrogen adsorption-desorption isotherms at 77 K were measured by an automated adsorption instrument, Micromeritics Instruments, Tristar II 3020. The surface area was determined from nitrogen adsorption data by using Micromeritics Instruments software. Adsorption data were obtained over the relative pressure, P/P0, range from 10-5 to 1. The sample was degassed at 300 °C under vacuum for 5 hours. The apparent surface area of nitrogen was calculated by using the BET (Brunauer–Emmett–Teller) equation within the 0.01-0.2 relative pressure range.

TABLE 1
Characteristics of the olive-waste cake and activated carbon

Surface properties	Olive-waste cake	Activated carbon
BET surface area ($m^2\ g^{-1}$)	n.d.	1418
Micropore area ($m^2\ g^{-1}$)	n.d.	1025
Total pore volume ($cm^3\ g^{-1}$)	n.d.	0.410
Micropore volume ($cm^3\ g^{-1}$)	n.d.	0.197
Average pore diameter (nm)	n.d.	1.16
Moisture content (wt.%)	4.66	2.24
Proximate analysis (wt.%)		
Ash	3.56	0.22
Volatile Matter	76.08	14.91
Fixed carbon*	20.36	82.63

* By difference n.d: not detected

Microwave Study A fixed amount of adsorbent, coagulant and oxidant and 100 mL of wastewater were mixed in capped volumetric glass flasks and radiated by MW (336 W). In order to achieve the maximum removal of dye by MW radiation, the operation conditions were optimized using five factors including dosage of adsorbent (0.01-0.1 g/100mL wastewater), dosage of coagulant (0.01-0.1 g/100mL wastewater), dosage of oxidant (0.1-0.3 mL/100mL wastewater), and radiation time (0.5 and 2 minute). All the samples were filtered and the colour values in the supernatant were measured at 455 nm using a UV spectrophotometer (Hach DR-2000).

RESULTS

Characterization of Activated Carbon The results of proximate and surface properties of the olive-waste cake and activated carbon were given in Table 1. The olive-waste cake contained 3.56 wt.% ash, 76.08 wt.% volatile matter and 20.36 wt% fixed carbon.

The acceptable ash content of the olive-waste cake indicated that it was a suitable raw material for activated carbon production. Ultimate analyses results showed that there was an increase in the carbon content after activation process as we expected. However, the amount of volatile matter ash content was greatly decreased. This is due to the release of volatiles during carbonization that results in the elimination of non-carbon species and enrichment of carbon [19]. The porosity has a strong effect on the adsorption properties of the activated carbon. The specific surface area of activated carbon was 1418 m2 /g and the most of the material (28%) consisted of micropores. The activated carbon produced from olive-waste cake contained both micropores and mesopores but the mesopore volume was larger than the micropore volume.

Effect of Dosages of Adsorbent, Coagulant and Oxidant The effects of adsorbent, coagulant and oxidant dosage on dye removal were investigated by addition of different amounts of adsorbent, coagulant and oxidant into 100 mL of wastewater. The impacts of adding different doses of adsorbent varied from 0.01 to 0.1 g/100 mL in combination with a constant coagulant dose (0.05 g/100 mL) and oxidant dose (0.3 mL/100 mL) at an initial pH value of 7.8. In the experiments made without carbon, the color was never removed. Very good color removal results were obtained in all carbon doses. Adsorban surface absorbs MW and speed up the degradation process. The impacts of adding different doses of coagulant varied from 0.01 to 0.1 g/100 mL in combination with a constant activated carbon dose (0.075 g/100 mL) and oxidant dose (0.3 mL/100 mL) at an initial pH value of 7.8. It was observed that there was no color removal in experiments with a coagulant dosage of up to 0.05 g/100 mL. Very good color removal was observed for coagulant doses greater than 0.05 g/100 mL. Al^{+3} helped to neutralize the negative charge on the particles, which led to an increase in the amounts of flocs. The impacts of adding different doses of oxidant varied from 0.1 to 0.3 mL/100 mL in combination with a constant activated carbon dose (0.075 g/100 mL) and coagulant dose (0.075 g/100 mL) at an initial pH value of 7.8. No effect was observed on the color removal of the oxidant material. The pH of the treated wastewater was found to be in the appropriate range between 6 and 8 in all experiments. In the case of coagulant alone application, good results were obtained when the amount of coagulant was greater than 0.1g/100 mL. However, the final pH values were obtained between 3.5-4.5. The results were shown in Table 2, Table 3, Table 4 and Table 5. Figure 1 showed the untreated wastewater and treated wastewater. The color value of the treated wastewater shown in Figure 1 was approximately 100 Pt / Co.

FIGURE 1
Wastewater and treated sample image

TABLE 2
Effect of adsorbent dosage on dye removal (2 min, 336 W)

Activated Carbon (g/100 mL)	Aluminium sulfate (g/100 mL)	Hydrogen peroxide (mL/100mL)	pH	Color (Pt/Co)
0	0.05	0.3	8.24	>500
0.01	0.05	0.3	7.74	71
0.025	0.05	0.3	7.4	135
0.05	0.05	0.3	8.0	164
0.075	0.05	0.3	7.28	90
0.1	0.05	0.3	8.0	73

TABLE 3
Effect of coagulant dosage on dye removal (2 min, 336 W)

Activated Carbon (g/100 mL)	Aluminium sulfate (g/100 mL)	Hydrogen peroxide (mL/100mL)	pH	Color (Pt/Co)
0.075	0	0.3	8.3	>500
0.075	0.01	0.3	8.2	>500
0.075	0.03	0.3	8.06	>500
0.075	0.05	0.3	7.5	126
0.075	0.075	0.3	7.4	25
0.075	0.1	0.3	5.6	26

TABLE 4
Effect of oxidant dosage on dye removal (2 min, 336 W)

Activated Carbon (g/100 mL)	Aluminium sulfate (g/100 mL)	Hydrogen peroxide (mL/100mL)	pH	Color (Pt/Co)
0.075	0.075	0	6.6	18
0.075	0.075	0.1	7.05	39
0.075	0.075	0.2	7.24	60
0.075	0.075	0.3	7.4	25

TABLE 5
Effect of coagulant dosage on dye removal in the absence of adsorbent and oxidant (2 min, 336 W)

Aluminium sulfate (g/100 mL)	pH	Color (Pt/Co)
0.1	4.66	60
0.2	3.68	12
0.3	3.94	21
0.4	3.87	11
0.5	3.81	25
0.6	3.54	36

TABLE 6
Effect of radiation time on dye removal (336 W)

0.075g of adsorbent and 0.075 g coagulant into 100 mL of wastewater.		0.2 g coagulant into 100 mL of wastewater.	
Radiation time (min)	Color (Pt/Co)	Radiation time (min)	Color (Pt/Co)
0.5	60	0.5	40
1	25	1	39
2	18	2	12

Effect of Radiation Time The effect of the radiation time on dye removal was investigated by addition of 0.075g of adsorbent and 0.075 g coagulant into 100 mL of wastewater. In addition, the effect of the radiation time under conditions of 0.2 g coagulant was investigated. Table 6 showed the effect of MW irradiation time on dye removal. It was found that the maximum removal of the dye achieved 12 Pt/Co at low power by 2 min.

CONCLUSIONS

This study demonstrated the feasibility of olive-waste cake as a promising precursor for the production of activated carbon with a noticeable adsorption capacity for removal of dye. MW technology reduces the reaction time, decreases the activation energy, improves the reaction rate, reduces the equipment size and waste, and increases the yield and purity of products. Greater removal of dye was achieved by 2 min of MW radiation using 0.075g of activated carbon and 0.075g of coagulant. If adsorbent is not used, a large amount of color can be removed by using 0.2 g of coagulant alone. Thus, MW radiation can be considered as an alternative technique for the removal of dye in wastewater containing paint and construction chemicals.

REFERENCES

[1] Nasr, F.A., Doma, H.S., Abdel-Halim, H.S., El-Shafai, S.A. (2007) Chemical industry wastewater treatment. Environmentalist. 27, 275–286.
[2] Verma, A.K., Dash, R.R., Bhunia, P. (2012) A review on chemical coagulation/flocculation technologies for removal of colour from textile wastewaters. J. Environmental Management. 93, 154-168.
[3] Ghaedi, M., Mosallanejad, N. (2014) Study of competitive adsorption of malachitegreen and sunset yellow dyes on cadmium hydroxide nanowires loaded onactivated carbon. J. Ind. Eng. Chem. 20, 1085–1096.
[4] Goscianska, J., Marciniak, M., Pietrzak, R. (2014) Mesoporous carbons modified withlanthanum(III) chloride for methyl orange adsorption. Chem. Eng. J. 247, 258–264.
[5] Djilania, C., Zaghdoudi, R., Djazi, F., Bouchekima, B., Lallam, A., Modarressi, A. and Rogalski, M. (2015) Adsorption of dyes on activated carbon prepared from apricot stones and commercial activated carbon. Journal of the Taiwan Institute of Chemical Engineers. 53, 112–121.
[6] Chen, B. and Chen, Z. (2009) Sorption of naphthalene and 1-naphthol by biochars of orange peels with different pyrolytic temperatures. Chemosphere. 76, 127- 133.
[7] Angin, D. (2014) Production and characterization of activated carbon from sour cherry stones by zinc chloride. Fuel. 115, 804-811.
[8] Fernandez, M.E., Nunell, G.V., Bonellia, P.R., Cukierman, A.L. (2014) Activated carbon developed from orange peels: Batch and dynamic competitive adsorption of basic dyes. Ind. Crop. Product. 62, 437-445.
[9] Foo, K.Y. and Hameed, B.H. (2012) A rapid regeneration of methylene blue dye-loaded activated carbons with microwave heating. J. Anal. Appl. Pyrol. 98, 123-128.
[10] El-Hendawy, A.N.A., Samra, S.E. and Girgis, B.S. (2001) Adsorption characteristics of activated carbons obtained from corncobs. Colloids Surf. 180, 209–221.
[11] Nakagawa, Y., Sabio, M.M. and Reinoso, F.R. (2007) Modification of the porous structure along the preparation of activated carbon monoliths with H3PO4 and ZnCl2. Micropor. Mesopor. Mater. 103, 29–34.
[12] Lai, T.L., Lee, C.C., Wu, K.S., Shu, Y.Y., Wang, C.B. (2006) Microwave-enhanced catalytic degradation of phenol over nickel oxide. Applied Catalysis. 68, 147-153.
[13] Lin, L., Yuan, S., Chen, J., Xu, Z., Lu, X. (2009) Removal of ammonia nitrogen in wastewater by microwave radiation. Journal of Hazardous Materials. 161, 1063-1068.
[14] Wu, G., Yuan, S., Ai, Z., Xie, O., Li, X., Lu, X. (2005) Degradation of Various Chlorophenols by Electrochemical, Electro-Fenton, Microwave Assisted Photolytic and Microwave Assisted Photocatalytic Methods. Fresen. Environ. Bull. 14 (8), 704-710.
[15] Wang, N., Wang, P. (2016) Study and application status of microwave in organic wastewater treatment- a review. Chemical Engineering Journal. 283, 193-214.
[16] Remya, N. and Lin, J.G. (2011) Current status of microwave application in wastewater treatment- a review. Chemical Engineering Journal. 166, 797-813.
[17] Fernández-Bolaños, J., Rodríguez, G., Rodríguez, R., Guillén, R., Jiménez, A. (2006) Potential use of olive by-products, Extraction of interesting organic compounds from olive oil waste. Gras. Aceit. 57, 95–106.
[18] Erses, A.S., Yay, H.V., Oral, T.T., Onay, O. (2012) Yenigün, A study on olive oil mill wastewater management in Turkey: A questionnaire and experimental approach. Resour. Conserv. Recyc. 60, 64– 71.
[19] Aygün, A., Yenisoy-Karakaş, S., Duman, I. (2003) Production of granular activated carbon from fruit stones and nutshells and evaluation of their physical, chemical and adsorption properties. Micropor. Mesopor. Mat. 66, 189–195.

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