ADSORPTION OF METHYLENE BLUE FROM TEXTILE WASTEWATER WITH PYROLYZED WALNUT SHELL

Scientific paper,
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ABSTRACT: *Discharge of colored wastewater, especially textile applications, into receiving environments can cause serious environmental problems. Conventional methods are not preferred because they are not successful in the treatment of colored wastewater or are not economical. Among different techniques, adsorption is gaining importance in pollutant removal from wastewater due to its low operating cost and ease of use. The use of agricultural wastes as low-cost adsorbents in the removal of dyestuffs from wastewater after applying various activation processes is of interest.*
The aim of this study is to evaluate the adsorption performance of methylene blue (MB) dye, which is used in textile, from aqueous solutions with walnut shell (WAC), an agricultural waste that has been pyrolyzed and activated with phosphoric acid. In the study, in batch experiments were carried out at fixed adsorbent dose (0.1 g/200 mL), constant temperature (20 ^{0}C), different pH values (4, 6, 7, 9, 11), different contact times (0, 5, 15, 30, 60, 90 and 120 minutes), different initial dyestuff amounts (2, 4, 6, 8 and 10 mg/L) and at different adsorbent doses (0.05, 0.1, 0.2, 0.5 and 1 g/ 200 mL) was carried out. Moreover; the effect of ionic strength on the color removal efficiency from the dye solution was evaluated by adding different salt doses (500, 1000, 1500, 2000 and 2500 mg/L NaCl). By increasing the pH value of the dye solution from 4 to 11, the color removal efficiency by WAC was determined as 65% at 90 minutes for pH:9, 4 mg/L MB concentration and 0.1 g/200 mL adsorbent dose. Optimum pH values were determined as 9 for WAC. In all experiments, adsorption increased with increasing contact time, and removal efficiency decreased with the increase in dye concentration. The color removal efficiency increased slightly with increasing ionic strength. While 38% removal efficiency was achieved with 2000 mg/L NaCl application in 90 minutes, the removal efficiency decreased to 30% with 2500 mg/L NaCl application.

Keywords: *Textile wastewater, methylene blue, color removal, walnut, adsorption, activated carbon.*

ADSORPCIJA METILENSKE PLAVOSTI IZ TEKSTILNIH OTPADNIH VODA SA PIROLIZOVANOM LJUSKOM ORAHA

APSTRAKT: *Ispuštanje obojene otpadne vode, posebno tekstilnih aplikacija, u prijemno okruženje može izazvati ozbiljne probleme životne sredine. Konvencionalne metode nisu poželjne jer nisu uspešne u tretmanu obojenih otpadnih voda ili nisu ekonomične. Među različitim tehnikama, adsorpcija dobija na značaju u uklanjanju zagađivača iz otpadnih voda zbog niskih operativnih troškova i lakoće upotrebe. Interesantna je upotreba poljoprivrednog otpada kao jeftinih adsorbenata u uklanjanju boja iz otpadnih voda nakon primene različitih procesa aktivacije.*
Cilj ovog istraživanja je da se proceni sposobnost adsorpcije boje metilen plavo (MB), koja se koristi u tekstilu, iz vodenih rastvora sa ljuskom oraha (VAC), poljoprivrednog otpada koji je pirolizovan i aktiviran fosfornom kiselinom. U studiji su serijski eksperimenti izvođeni pri fiksnoj dozi adsorbenta (0,1 g/200 mL), konstantnoj temperaturi (20 ^{0}C), različitim pH vrednostima (4, 6, 7, 9, 11), različitim kontaktnim vremenima (0, 5, 15, 30, 60, 90 i 120 minuta), različite početne količine boje (2, 4, 6, 8 i 10 mg/L) i različite doze adsorbenta (0,05, 0,1, 0,2, 0,5 i 1 g / 200 mL). Štaviše; Efekat jonske snage na efikasnost uklanjanja boje iz rastvora boje je procenjen dodavanjem različitih doza soli (500, 1000, 1500, 2000 i 2500 mg/L NaCl). Povećanjem pH vrednosti rastvora boje sa 4 na 11, efikasnost uklanjanja boje pomoću VAC-a je određena kao 65% na 90 minuta za pH:9, 4 mg/L MB koncentracije i 0,1 g/200 mL doze adsorbenta. Optimalne pH vrednosti su određene kao 9 za VAC. U svim eksperimentima, adsorpcija se povećava sa povećanjem vremena kontakta, a efikasnost uklanjanja opada sa povećanjem koncentracije boje. Efikasnost uklanjanja boje blago se povećala sa povećanjem jonske snage. Dok je efikasnost uklanjanja od 38% postignuta primenom 2000 mg/L NaCl za 90 minuta, efikasnost uklanjanja je smanjena na 30% sa primenom 2500 mg/L NaCl.

Ključne reči: *Tekstilna otpadna voda, metilen plavo, uklanjanje boje, orah, adsorpcija, aktivni ugalj*

1. INTRODUCTION

Textile wastewater is intensely colored and direct discharge of this wastewater into the receiving environment can cause many environmental problems such as decreased light transmittance, aesthetic deterioration, and negative effects of life in the aquatic environment. Traditional methods for treating textile wastewater mostly rely on organic carbon removal. Traditional treatment methods used to treat wastewater of industries that produce colored wastewater, such as the textile industry; coagulation flocculation, biological treatment, oxidation etc. However, activated sludge systems are mostly preferred. However, these treatment systems are not effective in removing color from wastewater containing dyestuffs that resist biological parasites and oxidation. Coagulation-flocculation, advanced oxidation processes (as H_2O_2 + Fe^{+2}), membrane processes and

electrochemical methods are effective in color removal. However, these methods have disadvantages such as high cost and high amount of sludge formation [1].
The most preferred method for color removal is adsorption, and activated carbon in granular or powder form is generally used as an adsorbent. However, commercial activated carbon costs are also quite high. For this reason, research is being carried out on the production of adsorbents with high adsorption capacity using materials such as different agricultural wastes (walnut shells, almond shells, olive seeds, rice husks, etc.) as an alternative to commercial activated carbon [2]. Active carbon from agricultural wastes is used. The most important reason for choosing carbon production is that it provides both environmental and economic benefits. Generally, for the production of activated carbon, the carbonization and activation process of the material is applied by oxygen-free combustion with inert gas flow (such as N_2) in an oxygen-free environment below 800 ^{0}C. During the carbonization process, non-carbonic elements turn into volatile gases and are removed. The structure formed by the remaining carbon atoms is disordered. In this way, gaps are created between them. Thanks to these gaps, it can show good adsorbent properties. The quality parameters that show the effect of the carbonized material on the adsorption efficiency are affected by the heating rate in the pyrolysis application, the final temperature, the holding time at the final temperature, and the structure and physical properties of the raw material [3].
In this study, the use of walnut shells, which are produced in large quantities around the world due to their easy adaptation to different climates, as an adsorbent in color removal was investigated. For this purpose, the biochar obtained from pyrolyzed walnut shell was activated using phosphoric acid and Methylene Blue (MB) adsorption was evaluated by taking into account the effect of pH, contact time, initial concentration and ionic strength.

2. MATERIAL AND METHOD

2.1. Preparation of adsorbent

In this study, walnut shells used as feed for the pyrolysis unit were obtained from local markets. Walnut shells were chopped into pieces with a diameter of 2-3 cm and subjected to pyrolysis with nitrogen gas at 600 °C for 2 hours. The pyrolysis process was carried out in a down-flow, fixed bed and throatless type pyrolysis unit. The pyrolysis unit was operated at a speed of 200 kg/m^{2}h. The resulting biochar was sieved to be smaller than 1 mm. Biochar obtained from walnut shells was activated with phosphoric acid. For this, biochar with H_3PO_4 (85 %) at a ratio of 1:3 (w:w) in an oven at 105 ◦C for 12 h. The resulting activated adsorbent was washed with distilled water and dried in an oven at 105 °C and labeled as WAC [4].

2.2. Analytics

The dye concentration in the samples collected after the adsorption process was measured at a wavelength corresponding to the maximum absorbance (λmax 670 nm) using a Thermospectronic AquaMate brand spectrometer. Accordingly, as a result of measurements made at different wavelengths (400 nm–700 nm), 670 nm was the wavelength that gave the highest adsorbance.

2.3. Dye adsorption

Methylene blue (MB) is a cationic dye and has numerous uses in the textile and paper industry. MB used as adsorbate was supplied as Merck brand. A 20 mg/L stock solution was prepared and used in dilutions (2-10 mg/L) for adsorption studies. In the study, in batch experiments, fixed adsorbent dose (m=0.1 g/200 mL), constant temperature (20 ^{0}C), different pH (4, 6, 7, 9, 11), different contact time (0, 5, 15, 30, 60, 90 and 120 minutes), at different initial dyestuff amounts (Co=2, 4, 6, 8 and 10 mg/L) and at different adsorbent doses (m=0.05, 0.1, 0.2, 0.5 and 1 g/200 mL) was carried out. Moreover; The effect of ionic strength on the color removal efficiency from the dye solution was evaluated by adding different doses of salt (500, 1000, 1500, 2000 and 2500 mg NaCl /L). The collected samples were centrifuged at 3500 rpm for 5 minutes, and then color measurement will be carried out in a spectrophotometer.

3. RESULTS AND DISCUSSION

3.1. Effect of pH

The pH value of the solution significantly affects the adsorption of the dye molecule. The reason for this is that it affects the binding units on the surface of the dye molecule and the adsorbent. Since the chemistry of the dye molecule and adsorbent in aqueous solutions is affected by the pH value of the solution, the effect of pH was first examined in studies on the removal of MB from aqueous media with WAC. It has been evaluated at different pH values such as pH 4, 6, 7, 9 and 11.

pHpzc is an important parameter to explain the adsorption mechanism and determine the optimum pH value. The pHpzc value for WAC was determined as 5.8±0.2. If the pH value of the adsorbent is above the pHpzc value, the adsorbent becomes negatively charged. Therefore, when the adsorbent surface is negatively charged, the cation adsorption ability will increase due to the effect of electrostatic attraction. At pH values below this value, the pH of the solution tends to increase. Color removal efficiencies for WAC depending on pH change are shown in Figure 1.

The pH effect on MB adsorption with WAC was evaluated for 4, 6 (original pH), 7, 9 and 11 (Co = 4 mg/L and m=0.1 g/200mL adsorbent dose). An increase in removal efficiency was determined with an increase in the pH value of the solution. While the removal efficiency was 27% at pH:4, the removal efficiency reached 65% at pH:9. In case of pH: 11, the removal efficiency (61%) tended to decrease. Since MB is a cationic dye, it can be stated that electrostatic attraction and ion exchange may be effective in the adsorption mechanism. The maximum removal efficiency was obtained at pH:9. In subsequent evaluations, pH 9 value was taken as a referenc

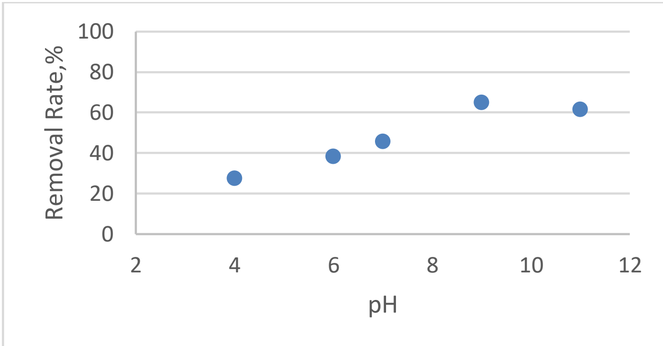

Figure 1: Effect of pH on removal rate (t=90 min, Co=4 mg/L, m=0.1 g/200mL)

3.2. Effect of initial dye concentration

Removal efficiencies in MB adsorption with WAC at different initial dye concentrations, 0.1 g/200 mL adsorbent dose and constant pH (pH:9) conditions at a contact time of 90 minutes are shown in Figure 2. Removal efficiencies decreased due to increasing MB concentration. At the end of 90 min, the removal efficiency obtained for 2 mg/L MB was 67%, while the removal efficiency was determined as 13% at 10 mg/L MB concentration.

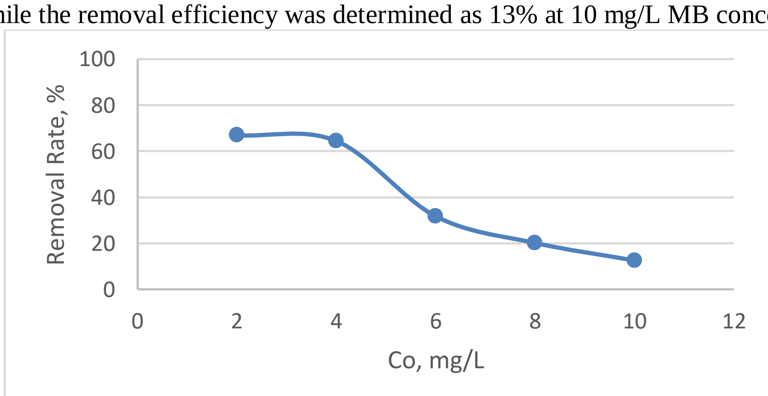

Figure 2: Effect of initial dye concentration (t=90 min, m=0.1 g/200mL, pH:9)

Removal efficiencies decreased with the increase in initial MB concentration. This can be expressed as the required driving force above the mass transfer resistance of MB being provided by the initial MB concentration [5].With the increase in Co, the removal efficiency decreased as the binding areas on the WAC surface were filled by MB. At low Co values, MB could bind to effective sites on the WAC surface, and a high adsorption rate could be achieved. With the increase in MB concentration, the areas that can be adsorbed on the WAC surface decrease [6].

3.3. Effect of Contact Time

The change in removal efficiency depending on contact time in MB adsorption experiments with WAC within 4 mg/L initial dye concentration, 0.1 g/200 mL adsorbent dose, 120 min contact time is shown in Figure 3. According to Figure 3, adsorption was rapid and removal efficiency increased with the increase in contact time. It was assumed that the equilibrium state was reached in 90 min. The optimum contact time was accepted as 90 min.

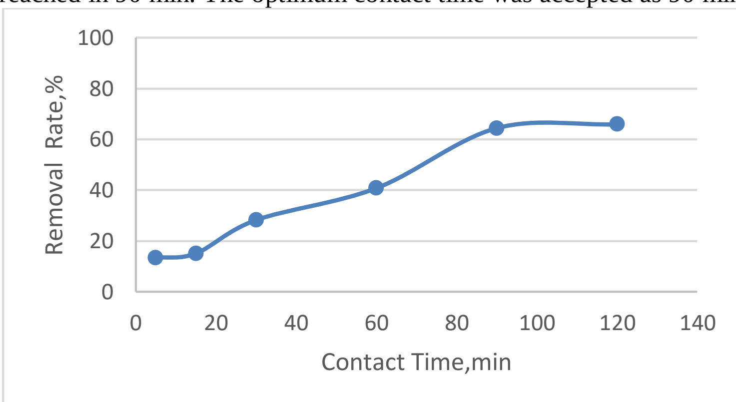

Figure 3: Effect of contact time (m=0.1 g/ 200mL, pH:9, Co=4 mg/L)

3.4. Effect of adsorbent dosage

Adsorbent dose is also an important parameter in determining adsorption efficiency in adsorption applications. The change in removal efficiencies depending on different adsorbent doses in case of Co=4 mg/L, pH:9 and 90 min contact time is shown in Figure 4. As seen in Figure 4, dye removal efficiencies increased from 26% to 92% by increasing the adsorbent dose from 0.05 g/200 mL to 1 g/200 mL. This situation can be explained by the increase in dye-binding areas on the adsorbent surface

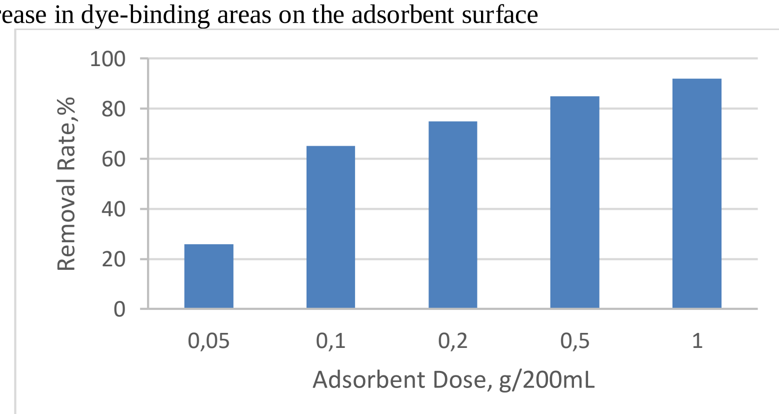

Figure 4: Effect of adsorbent dose (t= 90 min, Co= 4 mg/L, pH:9)

3.5. Effect of ionic strength

The effect of ionic strength on dyestuff adsorption with WAC was realized by adding 500, 1000, 1500, 2000 and 2500 mg/L NaCl into the dyestuff solution. The removal efficiencies obtained for different NaCl concentrations in the case of pH: 9, 0.1 g/ 200 mL adsorbent dose and Co=4 mg/L are shown in Figure 5. While the removal efficiency was 65% in the absence of NaCl, the removal efficiency decreased to 18% in the presence of 500 mg/L NaCl. Accordingly, an increase in MB removal efficiency was observed with the increase in ionic strength.

A removal efficiency of 38% was achieved with the application of 2000 mg/L NaCl, but the maximum removal efficiency decreased slightly (30%) with the application of 2500 mg/L NaCl. Industrial wastewater may contain high concentrations of salt as well as dyestuffs, and salt concentration may affect adsorption. In typical dyeing processes, salt can accelerate or slow down dye adsorption. Various studies have evaluated the effect of salt concentration during dye adsorption [7-8]. In general, a decrease in adsorption capacity is observed with an increase in ionic strength. The reason for this is the electrostatic interaction between the adsorbent surface and the adsorbed substance [7]. The change in ionic strength with the addition of electrolyte can affect the potential interfaces on the adsorption surface of the electrolyte ions and compete for the sorption areas between the electrolyte ions and the adsorbed ions.

In this study, a decrease in removal efficiency was determined by increasing the ionic strength in the solution. However, with the increase in NaCl concentration, removal efficiencies tended to increase. The presence of NaCl in solution can cause two opposite effects. One of these is that it can shield the electrostatic interaction between dye molecules and adsorbent. MB adsorption capacity may decrease with the increase in NaCl concentration. Another is that salt positively affects adsorption by facilitating the dissociation of dye molecules into their protons.

According to the results obtained, the dye removal efficiency increased until 2000 mg/L NaCl, but the removal efficiency tended to decrease again when it was 2500 mg/L NaCl. It can be said that this situation arises from the decomposition of the dyestuff under the influence of salt. Similar results were obtained in some studies evaluating the effect of NaCl on the adsorption of various dyestuffs [8-9].

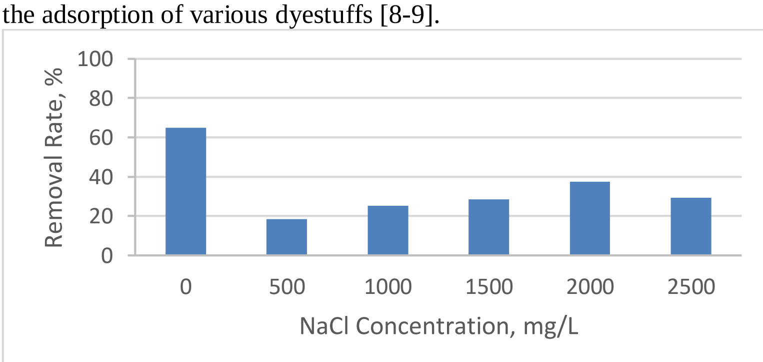

Figure 5: Effect of ionic strength (t=90 min, Co=4 mg/L, pH:9, m=0.1 g/200mL)

4. CONCLUSION

In this study, activated carbon (WAC), obtained by activating the biochar obtained as a result of applying pyrolysis to walnut shells, which is an agricultural waste, with phosphoric acid, was used to remove MB by adsorption. The results of the study are summarized as follows;

- The maximum removal efficiency with WAC was determined as 65% (t=90 min, pH:9, Co=4 mg/L MB and m=0.1 g/200 mL adsorbent dose)
- Optimum pH values are 9 for WAC.
- In all experiments, adsorption increased with increasing contact time, and removal efficiency decreased with the increase in dye concentration.
- While the removal efficiency was 65% in the absence of NaCl, the removal efficiency decreased to 18% in the presence of 500 mg/L NaCl. The dye removal efficiency increased until 2000 mg/L NaCl, but at 2500 mg/L NaCl, the removal efficiency tended to decrease again. It can be stated that the salt concentration affects both the shielding of the electrostatic interaction between the dye molecules and the adsorbent and the fact that the salt facilitates the dissociation of the dye molecules into protons.

As a result, the use of WAC in the removal of MB dyestuff, which is widely used in the textile industry, by adsorption process has been evaluated, and kinetics and isotherm calculations continue in the other part of the study. Additionally, the physical and chemical properties of the adsorbent used will also be determined. The fact that WAC, which will be used instead of commercial activated carbon in color removal from textile industry wastewater, is produced from waste material, makes it economically and ecologically advantageous.

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