Adsorption of Crystal Violet on Activated Carbon Prepared from Coal Flotation Concentrate

Ramazan Aydogmus 1, Tolga Depci 1, Musa Sarikaya 1, Ali Riza Kul 2, Yunus Onal 3

1 Department of Mining Engineering, Inonu University, Malatya, Turkey
2 Department of Chemistry, Yuzuncu Yil University, Van, Turkey
3 Department of Chemical Engineering, Inonu University, Malatya, Turkey

E-mail: raay.tr@gmail.com

Abstract. The objective of this study is firstly to investigate the floatability properties of Zilan-Van coal after microwave irradiation and secondly to produce activated carbon from flotation concentrate in order to remove Crystal Violet (CV) from waste water. The flotation experiments showed that microwave heating at 0.9 kW power level for 60 sec exposure time enhanced the hydrophobicity and increased the flotation yield. The activated carbon with remarkable surface area (696 m²/g) was produced from the flotation concentrate and used to absorb CV from aqueous solution in a batch reactor at different temperature. The adsorption properties of CV onto the activated carbon are discussed in terms of the adsorption isotherms (Langmuir and Freundlich) and found that the experimental results best fitted by the Langmuir model.

1. Introduction

One of the main pollutant sources worldwide is dye-containing wastewater from textile and paper industries. Removal of dyes from wastewater is difficult since they resist breakdown by aerobic digestion, light, heat, and oxidizing agents [1]. Cationic Crystal Violet (CV) dye is extensively used not only in the textile and paper industries, but also in biology, dermatology, and veterinary applications [2]. This dye is toxic and even carcinogenic so it must be removed from discharge water.

Activated carbon is the most popular adsorbent, but production and regeneration is expensive, so considerable attention has been given to find low cost and easily available carbon sources, like local low-rank coal [3, 4]. In the present study, Zilan-Van coal, having high ash and moisture content, was selected as a carbon source to produce activated carbon. However, it is generally known that high surface area and low ash content are the most important properties for activated carbon. Therefore, the floatability properties of Zilan coal was investigated and activated carbon was produced from the flotation concentrate. Literature survey shows that microwave radiation pre-treatment is an effective method and improves the coal floatability and the microwave heating is an alternative to conventional heating methods and can eliminate moisture selectively without causing any oxidation at coal surface in a very short time [5]. In addition, the cationic dye adsorption capacities of the produced activated carbon from the flotation concentrate was investigated using crystalline violet.
2. Materials and methods

2.1. Coal sample
A coal sample was taken from Zilan, Van Turkey and the proximate analysis of the sample is shown in Table-1. High ash content ratio was explained by the elemental analysis, which were determined by XRF and showed that the coal had high content of SiO₂ (37.70 %), Al₂O₃ (7.80 %), Fe₂O₃ (4.49 %).

Table 1. Proximate analysis of coal sample

| Analysis       | As received, % | Dry basis, % | Analysis       | As received, % | Dry basis, % |
|----------------|---------------|--------------|----------------|---------------|--------------|
| Moisture       | 25.41         | -----        | Fixed carbon   | 17.26         | 48.10        |
| Ash            | 42.12         | 13.94        | Calorific value| 3005 kcal/kg  | 3106 kcal/kg |
| Volatile matter| 15.21         | 37.96        |                |               |              |

2.2. Flotation experiments
The experimental procedure was based on the study conducted by Ozbayoglu et al., [5]. The flotation experiments were carried out using oven-dried samples and home type microwave oven-treated samples. 50 g of the sample (-28 mesh) was used for each experiments and the condition time was taken as 2 min before addition of heptanol and then 1 min with heptanol. The froth was collected for 30 seconds from a 500 ml Denver cell with a 1,200 rpm impeller speed.

2.3. Preparation of activated carbon and adsorption experiment
The flotation concentrate of Zilan-Van coal, which was pre-treated with microwave oven, was used as a carbon source to obtain activated carbon. The coal concentrate was mixed with ZnCl₂ (the coal/ZnCl₂ weight ratio of 1:1) and the mixture was heated to an activation temperature of 500 ºC for 1 hour under N₂ flow (100 ml/min). The obtained activated carbon was rinsed with 0.5 N HCl then filtered and washed with distilled water and then dried. The surface areas of the coal and activated carbon were determined by a Tri Star 3000 surface analyzer. Crystal violet (CV) dye employed in the present study was supplied from MERCK (101458, CI = 42,555) and used as obtained without any further purification. Adsorption tests were conducted in stoppered Pyrex glass Erlenmeyer flasks with dye concentrations (50, 100, 200 and 300 mg/l) at 60 min at different temperature. In each test 0.1g activated carbon in 50 ml solution was shaken at 400 rpm. The dye concentration was determined by UV/VIS spectrometer. The amount of dye adsorbed on activated carbons was calculated by equation (1).

$$ q = \frac{C_o - C}{W} \times V $$

$C_o$ (mg/l) is the initial dye concentration and $C$ (mg/l) is unabsorbed dye concentration in solution at time $t$. $V$ (l) and $W$ (g) are the volume of the solution and the weight of the dry activated carbon, respectively.

3. Results and discussions
3.1. Flotation experiment results
Before the flotation experiments, the effect of duration time of microwave ration on the coal samples were investigated in terms of the weight loss and surface area. The weight loss of the coal increased from 2.45 wt % to 21.44 wt % while increasing the microwave radiation time from 30 sec to 150 sec. The sudden weight loss could be explained by different dissemination factors of coal ($\varepsilon'' : 0.25$) and water ($\varepsilon'' : 12$) inside the coal structure [6]. Therefore, microwave treatment heats the coal in a very short time. On the other hand, when the water was suddenly evaporated by microwave, the crack occurred on the coal structure, causing the increase in the surface area. The surface area was raised from 4.27 m²/g to 8.44 m²/g.
All microwave treated coal samples and oven dried coal samples were floated at the same condition using heptanol. The yield and ash content of the flotation concentrate are given in Table 2. As can be seen that flotation yield and ash content increased depending on the heptanol concentration, as expected. Comparison of the flotation yields and especially ash content showed that the concentrate of microwave-irradiated coal for 60 secs was much cleaner than the untreated coal and oven dried coal for 2 h. The overall results indicated that nearly same quality coal flotation concentrate could be obtained with microwave dried coal in a very short time (60 sec). The results are in a good agreement with the literature [5].

| Radiation duration time [sec] | 10^{-2} M | 5 \times 10^{-2} M | 10^{-1} M |
|-----------------------------|-----------|-------------------|-----------|
| wt. % | Ash % | wt. % | Ash % | wt. % | Ash % |
| 0   | 6.19 | 18.27 | 32.54 | 22.8 | 33.18 | 23.7 |
| 30  | 6.72 | 18.87 | 33.07 | 21.7 | 33.24 | 22.9 |
| 60  | 11.53 | 19.37 | 38.52 | 23 | 38.12 | 25.14 |
| 90  | 6.41 | 19.47 | 34.26 | 21.2 | 35.61 | 23.65 |
| 150 | 4.72 | 19.97 | 35.59 | 22 | 34.15 | 23.12 |

| Oven dried sample | 35.70 | 23.0 | 34.82 | 22.67 |

However, it must be said that high energy consumes with 60 sec microwave radiation in home type microwave. In order to decrease energy consumption, high power level, which decreased the duration time, should be used. The simple calculation is given as an example below.

\[
\frac{(0.90\text{kW} \times 1 \text{min} \times 1 \text{h} / 60 \text{min})}{50 \text{g}} \times 1000000 \frac{\text{g}}{\text{t}} = 300 \text{kws/}t
\]  

(2)

### 3.2. Characterization of the obtain activated carbon

The surface area and pore structure of the activated carbons produced from the raw coal and the flotation concentrate coal which was pre-treated by microwave irradiation for 60 min were identified by BET. The BET results are given in Table 3, showing that highest surface area and porosity were obtained from the concentrate of microwave pre-treated coal flotation.

| Source                  | \(S_{\text{BET}}\) (m\(^2\)/g) | \(S_{\text{mic}}\) (m\(^2\)/g) | \(S_{\text{mezo}}\) (m\(^2\)/g) | \(V_{\text{t}}\) (cm\(^3\)/g) | \(V_{\text{mic}}\) (cm\(^3\)/g) | \(D_{\text{p}}\) (nm) |
|-------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|------------------|
| Raw coal                | 403                           | 385                           | 211                           | 0.361                         | 0.295                         | 3.08             |
| Microwave treated coal  | 696                           | 558                           | 138                           | 0.59                          | 0.44                          | 2.27             |

### 3.3. Adsorption isotherms

The adsorption experiments were done for different temperature at 60 min and at natural pH of the starting CV solution of 5.8 due to the considering of the cost and simplicity. Adsorption isotherms are mathematical models which describe distribution of the solute among two phases, i.e., the liquid and the adsorbed phases. In the present study, results of the adsorption at different temperature were fitted
with the Langmuir and Freundlich models. Langmuir model [7] and Freundlich model [8] are used to quantify adsorption isotherms.

\[
\text{Langmuir, } \quad q_e = \frac{Q_0 b C_e}{1 + b C_e} \quad (3)
\]

\[
\text{Freundlich, } \quad q_e = k_f (C_e)^{1/n} \quad (4)
\]

\(C_e\) is the equilibrium concentration (mg/L), and \(q_e\) is the adsorption capacity (mg/g). The Langmuir constants are \(b\) (L/mg) and the theoretical monolayer capacity, \(Q_0\) (mg/g). The Freundlich constants are the rate constant \(k_f\) (L/g) and the dimensionless heterogeneity factor, \(1/n\).

Langmuir plots (\(C_e/q_e\) versus \(C_e\)) and Freundlich plots (\(\log q_e\) versus \(\log C_e\)) for CV adsorption at different temperatures are represented in figure 1.a and figure 1.b. The results showed that for all temperature, the Langmuir isotherm described the system better than the Freundlich isotherm, so just the Langmuir isotherm parameters calculated by applying the commonly accepted linear regression procedure to the linear representation of the isotherms, are summarized in Table 4.

![Figure 1. Adsorption isotherms plots of CV onto activated carbon at different temperatures a) Langmuir model, b) Freundlich model](image)

| Temp. (K) | Concentration (mg/L) | \(Q_0\) (mg/g) | \(b\) (L/mg) | \(R^2\) | \(Q_0\) (mg/g) | \(b\) (L/mg) | \(R^2\) |
|-----------|----------------------|--------------|--------------|---------|--------------|--------------|---------|
| 298       | 50                   | 50.44        | 0.15         | 0.98    | 49.14        | 0.16         | 0.95    |
|           | 100                  |              |              |         |              |              |         |
|           | 200                  |              |              |         |              |              |         |
|           | 300                  |              |              |         |              |              |         |
| 303       | 50                   | 51.5         | 0.16         | 0.97    | 52.3         | 0.124        | 0.96    |
|           | 100                  |              |              |         |              |              |         |
|           | 200                  |              |              |         |              |              |         |
|           | 300                  |              |              |         |              |              |         |
| 318       | 50                   | 54.26        | 0.15         | 0.99    | 53.24        | 0.18         | 0.98    |
|           | 100                  |              |              |         |              |              |         |
|           | 200                  |              |              |         |              |              |         |
|           | 300                  |              |              |         |              |              |         |
The similar results are presented in the literature [9, 10]. In addition, it can be understood from Table 4 the adsorption capacity ($Q_0$) increased while increasing the temperature, indicating the endothermic process. It may be concluded that raise in temperature accelerates transportation of dye molecules from solution to the adsorbent surface [4].

4. Conclusions

The emphasis of the current research was to investigate the effect of pre-treatment of microwave radiation on the coal flotation and to produce of activated carbon from the coal flotation concentrate for removing CV dye from solution. The conclusions were as follows:

- Microwave pre-treatment of coal before flotation increases the floatability and the yield of concentration, since the coal was dried in a very short time without causing any oxidation at coal surface.
- Activated carbon with remarkable surface area (696 m$^2$/g) with a well-developed pore structure could be produced from the local low-rank coal and the surface area increased for activated carbon which was produced from the coal flotation concentrate. This may contribute the evaluation of Zilan coal which is not suitable for domestic heating purposes.
- The obtained activated carbon can be used as a promising adsorbent to remove CV from aqueous solution. main conclusions of the study may be presented in a short Conclusions section, which may stand alone or form a subsection of a Discussion or Results and Discussion section.

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