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# Removal of Acid black 210 by adsorption on calcite

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**ABSTRACT**

In the aquatic environment, the presence of dyes is one of the major pollution problems. The main objective of the present study is to evaluate the efficiency of calcite in the treatment of colored waters. The removal of an acidic dye (Acid black 210) used in the tanning industry by adsorption on calcite is investigated. The used calcite was characterized by X-ray diffraction and thermogravimetric and differential thermal analysis. The removal of the dye was studied in function of pH, temperature, contact time and the initial concentration. The effect of foreign ions was also evaluated. Kinetic and equilibrium studies were carried using several models. The obtained results show that the Acid black uptake by calcite increases when pH decreases and temperature increases. The highest removal is obtained at pH < 7. The dye adsorption on calcite is rapid, equilibrium is achieved in less than one hour. The removal kinetics is well described by the second-order model. At pH 6, the maximum adsorption capacity calculated by the Langmuir equation is about 210 mg/g.

*Keywords:* Calcite; Acid black 210; Water treatment; Tanning industry

## 1. Introduction

The presence of very low concentrations of dyes in aqueous effluents is undesirable due to their chemical stability, weak biodegradability and toxicity. It was shown that they are very harmful to young guppies and they inhibit the growth of algae and small crustaceans [1]. The main sources of pollution by colored effluents are textile processes, the leather industry and tanning [2]. Many studies have been interested in dyes removal from wastewaters by various processes [3]. Adsorption is considered better than many other techniques in terms of flexibility, simplicity of design, low cost, ease of use with no harmful substances production. Activated carbon and clays are the main adsorbents that have been largely used in dyes removal [4–7]. In this study, we are interested in the use of calcite which is abundant in nature as an adsorbent material for the treatment of colored waters. Calcite was mainly used in the adsorption of heavy metals [8–12]. However, no study can be found about its use in dyes adsorption. The objective of this work is the removal of a triazoic acidic dye used in the tanning industry (Acid black 210) by adsorption on calcite. Acid black is a toxic dye. It can generate carcinogenic aromatic amines [13]. Several authors have already studied the removal of Acid black from water by various physicochemical methods such as coagulation–flocculation [14], nanofiltration [15], adsorption on exfoliated graphite [16] and organo-montmorillonite clay minerals [17] and by biological methods [18–20].

## 2. Material and methods

Acid black used in the present study was supplied by tannery manufactory. Its structure is presented in Fig. 1.

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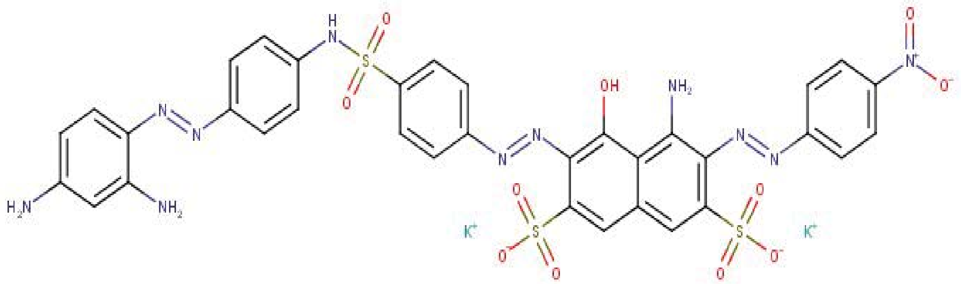

Fig. 1. Structure of Acid black 210.

*2.1. Calcite characterization*

Calcite used in the present study is a commercial product (Biochem Chemopharma, France). It was characterized by X-ray powder diffraction using a PERTE PANAYTICAL (Germany) diffractometer employing Cu-kα radiation and by thermal analysis using Setaram LABSYS TG (France). The pH of the zero point of charge (pHpzc) was determined by the drift method.

*2.2. Acid black sorption experiments*

Batch experiments were conducted for Acid black sorption on calcite. In each experiment, one parameter was changed. Prior to each adsorption experiment, pH was adjusted by adding HCl or NaOH to the suspensions formed by calcite and dye solutions. After agitation for the desired time, equilibrium pH was measured and the suspensions were centrifuged at 2,000 rpm for 15 min. Effects of pH, temperature, contact time, initial concentration and the presence of foreign ions were evaluated.

*2.3. Acid black analysis*

Acid black residual concentration was determined using the UV-1650PC Shimadzu spectrophotometer (Japan) by measuring the absorbance at 462 nm which is the more intense band in the UV/Visible spectrum (Fig. 2). The removed quantity was deduced from the difference between the initial and the remaining concentrations.

**3. Results and discussion**

*3.1. Calcite characterization*

The peaks observed in the X-ray diffraction spectrum confirm the calcite structure (Fig. 3). The measured pH of the zero point of charge ($pH_{PZC}$) is 8.5. This value is in agreement with those given by Kosmulski [21] for other calcite. The used calcite is thermally stable until 792°C and the endothermic peak observed at this temperature corresponds to decarbonization (Fig. 4).

*3.2. Acid black removal*

*3.2.1. Effects of pH and temperature*

Generally, pH is considered as an important parameter in controlling adsorption at solid–water interface. Acid black removal by calcite is maximal at pH < 7, then decreases when the pH increases (Fig. 5). At pH < 8.5, the positive charge of the calcite surface promotes the adsorption of the dye. However, at higher pH, the surface is negatively charged, favorizing the dye repulsion. The results obtained in this study show that the calcite use gives a larger pH range for Acid black removal than that obtained in the case of other acid dyes removal by bentonite [22].

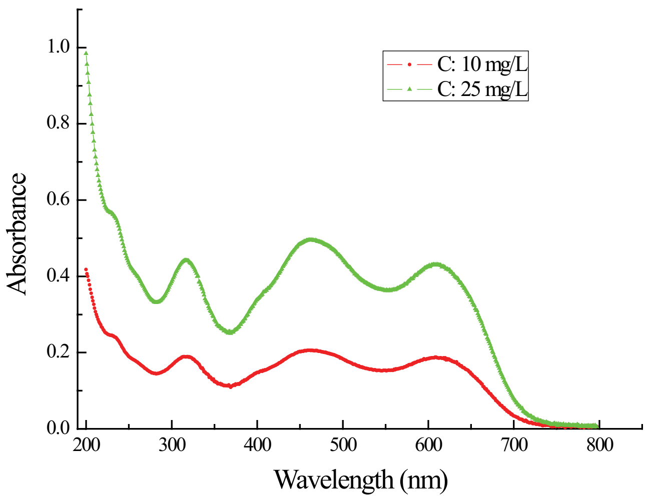


Fig. 2. UV-Visible spectra of Acid black 210.

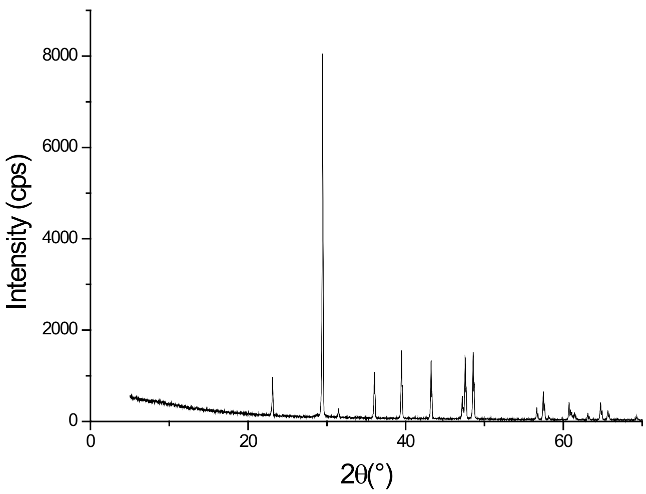


Fig. 3. X-ray diffraction spectrum of the raw calcite.

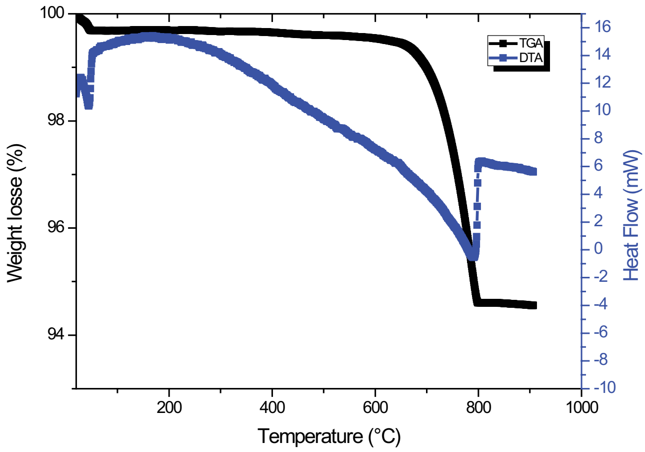


Fig. 4. Thermal analysis of the raw calcite.

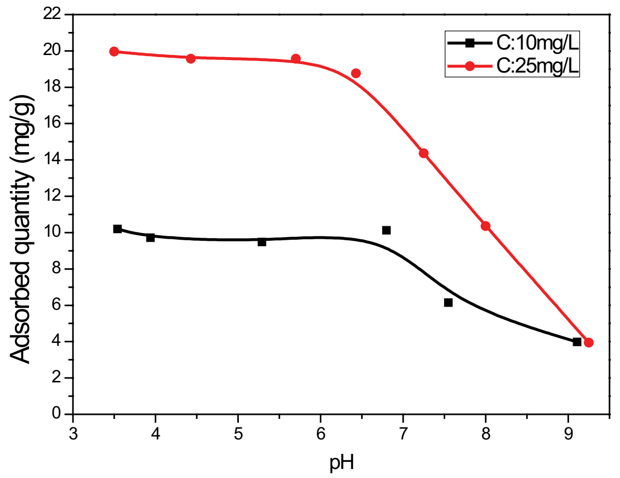


Fig. 5. Effect of pH on Acid black removal by calcite (calcite dose: 0.5 g/L; time: 1 h).

The increase in temperature implies a slight increase in Acid black removal by calcite (Fig. 6), suggesting an endothermic process.

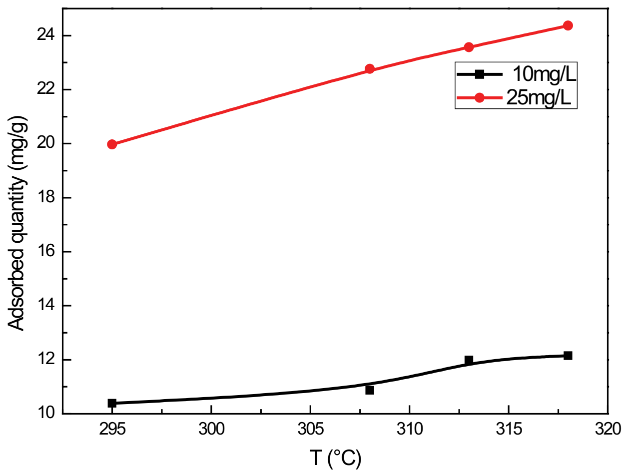


Fig. 6. Effect of temperature on Acid black removal by calcite (calcite dose: 0.5 g/L; pH: 6; time: 1 h).

### *3.3.2. Kinetics study*

Acid black removal by calcite increases rapidly with time during the first 30 min, then slows down to stabilize and reach equilibrium (Fig. 7). This evolution is identical to that obtained in the case of the removal of other acid dyes by the activated carbon [6]. To determine the kinetics parameters, different models were applied to the experimental data. The first-order model is ruled out, the equilibrium adsorbed quantity calculated by this equation is far from the experimental data. According to the calculated correlation coefficients (Table 1), at the lowest initial concentration used (10 mg/L), Acid black adsorption kinetics can be described by both the models second-order, Elovich and diffusion. However, when the concentration increases to 25 mg/L, the adsorption is not limited by diffusion and only the second-order model is suitable for describing the kinetics.

### *3.3.3. Equilibrium study*

The adsorption capacity increases with the increase of Acid black initial concentration to reach stability (Fig. 8). Consequently, the available active sites of the calcite are saturated. In order to model the experimental isotherm, Langmuir and Freundlich's equations were applied (Table 2). According to the calculated correlation coefficients, Acid black adsorption on calcite can be better described by the Freundlich model. The maximum adsorption capacity calculated by the Langmuir equation is about 210 mg/g at pH 6. This value

Table 1
Kinetic parameters of Acid black adsorption on calcite

| Model | First-order | Second-order | Elovich | Intraparticle diffusion | External diffusion |
|---|---|---|---|---|---|
| 10 mg/L | $R^2$: 0.960 | $R^2$: 0.999 | $R^2$: 0.981 | $R^2$: 0,979 | $R^2$: 0.960 |
| | $K$: 0.019 | $K$: 0.09 | $\alpha$: 9.03 | $K$: 0.16 | $K$: 4.05 |
| | $Q_e$: 1.15 | $Q_e$: 10.77 | $\beta$: 0.32 | | |
| 25 mg/L | $R^2$: 0.633 | $R^2$: 0.999 | $R^2$: 0.864 | $R^2$: 0.653 | $R^2$: 0.633 |
| | $K$: 0.018 | $K$: 0.29 | $\alpha$: 13.14 | $K$: 0.06 | $K$: 0.018 |
| | $Q_e$: 3.71 | $Q_e$: 20.63 | $\beta$: 1.83 | | |

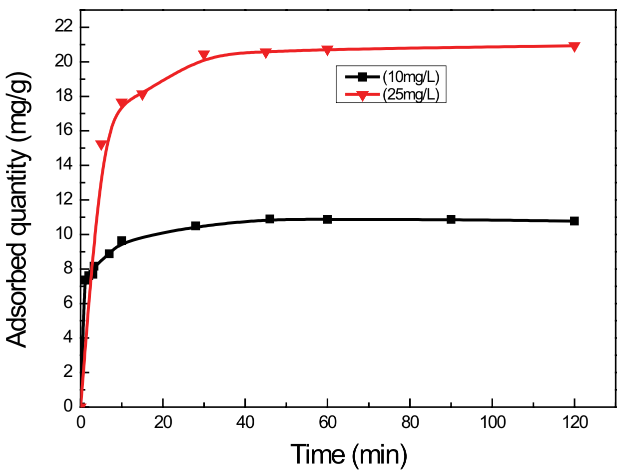


Fig. 7. Kinetics of Acid black removal by calcite (calcite dose: 0.5 g/L; pH: 6).

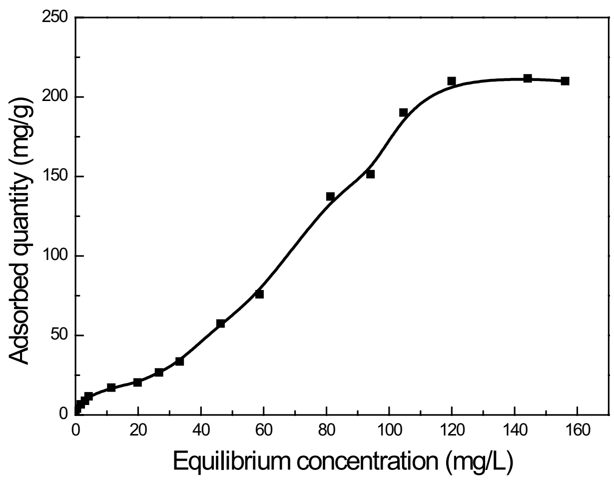


Fig. 8. Isotherm of Acid black adsorption on calcite (calcite dose: 0.5 g/L; pH: 6; time: 1 h).

is greater than those obtained in the case of the removal of other acidic dyes by clays and activated carbon (Table. 3).

### *3.3.4. Effect of foreign ions*

The presence of foreign ions has not an important effect on Acid black removal by calcite (Fig. 9). The presence of both $Na^+$ and $Cl^-$ has no effect. The increase of the dye removal observed in the presence of sulfate implies the absence of competition for the calcite adsorption sites. The slight decrease observed in the presence of $MgCl_2$ and $CaCl_2$ can be attributed to the interaction of the dye with $Mg^{2+}$ and $Ca^{2+}$ in solution.

## 4. Conclusion

The results of the present study, reveal that calcite can be successfully used in Acid black removal from water in a large pH range (pH < 7). The adsorption process is rapid and endothermic. The removal kinetics is well described by the second-order model and the experimental isotherm follows the Freundlich model. Sulfate and chloride anions do not compete with the dye for the adsorption surface sites. At pH 6, the maximum adsorption capacity of calcite for Acid black is about 210 mg/g.

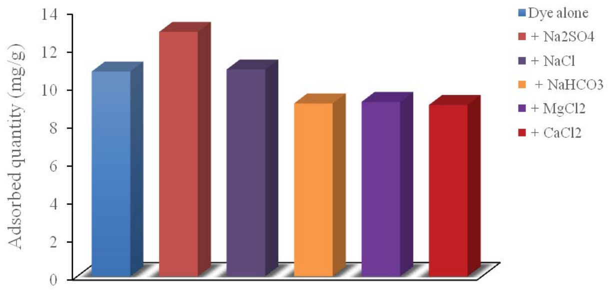


Fig. 9. Effect of foreign ions on Acid black adsorption on calcite ($C$: 10 mg/L; $C_{anions}$: 100 mg/L; calcite dose: 0.5 g/L; pH: 6; time: 1 h).

Table 2
Isotherm parameters of Acid black adsorption on calcite

| Model | Langmuir | Freundlich |
|---|---|---|
| Parameters | $R^2$: 0.868<br>$Q_{max}$: 210 (mg/g)<br>$K$: 0.26 | $R^2$: 0.915<br>$n$: 1.47<br>$K$: 4.23 |

Table 3
Adsorption capacities of clays and activated carbon for acidic dyes

| Adsorbent | Acidic dye | Adsorption capacity (mg/g) | References |
|---|---|---|---|
| Bentonite | Yellow bezanyl | 40.50 | [23] |
| | Red bezanyl | 39.11 | |
| | Green nylomine | 23.58 | |
| Kaolinite | Yellow bezanyl | 30.60 | [23] |
| | Red bezanyl | 29.22 | |
| | Green nylomine | 9.45 | |
| Activated carbon | Acid red 97 | 52.08 | [6] |
| | Acid orange 61 | 169.49 | |
| | Acid brown 425 | 222.22 | |
| Activated carbon | Methyl orange | 86.80 | [24] |

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