

# Synthesis, Characterization and Use of Supported Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> for the Removal of Reactive Blue 19 from Aqueous Solutions

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*In this study, systematic adsorption tests were carried out using Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> adsorbents of different compositions for removal of Reactive Blue 19 dye from aqueous solutions. The adsorbent was characterized by scanning electron microscopy, X-Ray powder diffraction, diffuse reflectance UV-visible spectroscopy and EDX analysis. The influences of several parameters such as pH, adsorbent concentration, adsorption time and dye concentration on the adsorption capacity of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were investigated. The obtained results indicate that the adsorption is strongly dependent on the solution pH. The maximum adsorption capacity of the Reactive blue 19 dye onto Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> takes place at around pH 2. The adsorption process is fast in the first minutes (95% from the amount of dye being removed after 6 minutes).*

**Keywords:** adsorption capacity, removal dye, SEM-EDX, X-ray diffraction

Vinyl sulfone dyes are a class of reactive dyes widely used for dyeing of cotton, silk and wool due to their bright colors and excellent colorfastness. They are involved in a proportion of 70-80 % in a nucleophilic addition reaction with these fibers while, up to 30% of the dye used in dyeing remain unbound from the fibers (the hydrolyzed dye) and is lost in the effluent. Extremely low concentrations of reactive dyes in residual waters affect not only the aesthetic nature but also inhibit sunlight penetration, reducing photosynthetic activity [1, 2]. In order to remove dyes from textile wastewaters various physical, chemical, biological treating methods have been investigated [3-8]. Many of these methods are relatively ineffective because most of the reactive dyes are highly water soluble, have complex structures and are stable to light, chemical and biological degradation. On the other hand, most commercial dyes are designed to resist to the chemical and biological degradation. In addition, an incomplete chemical oxidation or partial biodegradation can be environmentally detrimental because of the generation of toxic aromatic compounds. Therefore, the adsorption technique is the simplest process for removal of the dyes from the wastewaters. Different adsorbents are used for the removal of dyes from aqueous solutions such as activated carbon, magnesium oxide, grafted chitosan, modified bentonite, titanium oxide powder, alumina etc. [9-27].  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is one of the most promising support due to high surface area and good mechanical and thermal stability [28, 29].

In paper, the removal of Reactive Blue 19 dye from the aqueous solutions was investigated using Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> adsorbents of different cobalt concentrations. The effects of various parameters such as pH, adsorbent concentration, adsorption time and dye concentration on the adsorption capacity of Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were investigated.

## Experimental part

### Material and methods

The cobalt nitrate (Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were purchased from Sigma-Aldrich/Merck company. Commercial reactive dye Remazol Brilliante Blue R (C.I. Reactive Blue 19) was obtained from Dye Star Company and used without any further purification. The structure of the Remazol Brilliante Blue R (C.I. Reactive Blue 19) dye is shown in figure 1.

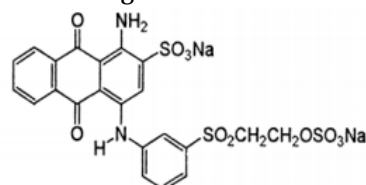


Fig.1. Chemical structure of Remazol Brilliante Blue R (C.I. Reactive Blue 19)

### Obtaining of the Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> nanostructures

Incipient wet impregnation followed by mild drying was used in order to obtain the adsorbents. The freshly calcined support was impregnated with Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O solution with concentration adequate to produce adsorbents with: 1 % Co (Co 1), 2 % Co (Co 2) and 5 % Co (Co 5). The samples were dried at 110 °C for 24 h and calcined at 550°C for 3 h.

### Characterization techniques

The wide angle X-ray diffraction patterns of the Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> nanostructures were recorded on a Philips X PERT MPD diffractometer in the 2 $\theta$  range of 10°-100°, at a scanning speed of 1°/min, using a nickel-filtered Cu K $\alpha$  radiation ( $\lambda$  = 0.15418 nm). Diffuse reflectance UV-visible (DR UV-Vis) spectra were recorded on a Shimadzu UV-2450 spectrometer equipped with an integrating sphere unit (ISR-2200). The spectra were collected in the range between 200-800 nm by using BaSO<sub>4</sub> as the reflectance standard. SEM-EDAX analysis of the Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>

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nanostructures was carried out with Quanta 200 (Fei) scanning electron microscope coupled with an energy dispersive X-ray analyzer.

### Adsorption studies

Adsorption experiments were performed using CarWin 50 UV-Vis spectrophotometer for different initial dye concentrations (30, 45, 60 and 75 mg/L) at various pH values (in the range 2 - 6) and different adsorbent loadings (10 - 30 mg/L). In all experiments the temperature was kept at 25°C and the stirring speed was 400 r.p.m. The equation obtained from the calibration curve was used for the estimation of the dye concentrations in the solution. The removal efficiency of the adsorbent was calculated by using the following formula:

$$\text{Dye removal (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where:  $C_0$  is the initial concentration of the dye solution (mg/L) and  $C_t$  is the concentration of dye at any time (g/L).

### Results and discussions

#### Characterization of $\text{Co}/\gamma\text{-Al}_2\text{O}_3$ used as adsorbent Wide angle X-ray diffraction I

XRD patterns for the  $\text{Co}/\gamma\text{-Al}_2\text{O}_3$  samples with different loadings of cobalt are shown in figure 2.

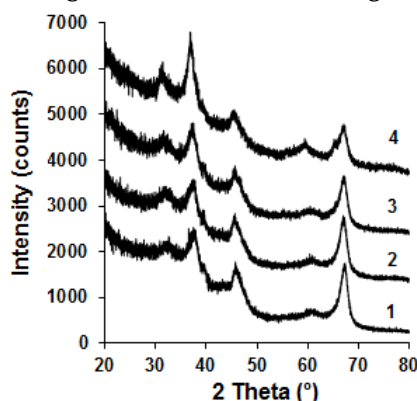


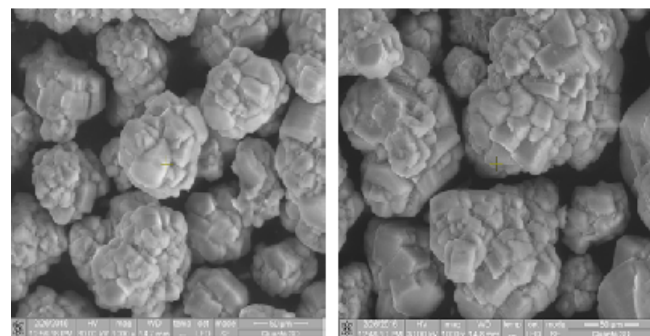
Fig 2. Diffractograms of the  $\gamma\text{-Al}_2\text{O}_3$  and  $\text{Co}/\gamma\text{-Al}_2\text{O}_3$  samples (1-  $\gamma\text{-Al}_2\text{O}_3$ ; 2- Co 1; 3 - Co 2; 4- Co 5)

Identification of the crystalline phases was performed by comparison to data from literature and those from the JCPDS data base [30, 31]. The diffraction peaks at  $2\theta = 37, 46$  and  $67^\circ$  might be attributed to gamma-alumina, while the ones at  $2\theta = 32, 37$  and  $60^\circ$  confirm the presence of  $\text{Co}_3\text{O}_4$ . It is noted that intensity of these peaks increases with the increase of the  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  amount used for obtaining  $\text{Co}/\gamma\text{-Al}_2\text{O}_3$  samples.

#### Scanning electron microscopy

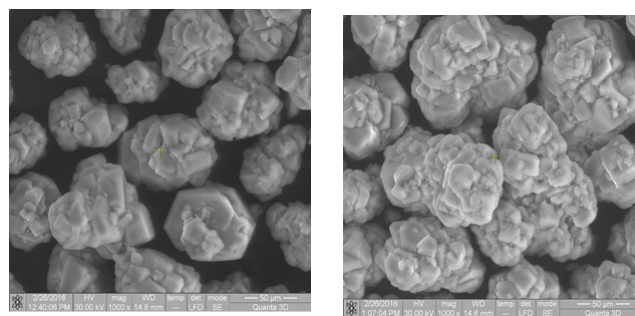
The surface morphology of the adsorbents was analyzed by scanning electron microscopy (fig. 3).

For the studied cobalt loadings it is observed that Co is uniformly integrated in the skeletal structure of  $\gamma\text{-Al}_2\text{O}_3$  and all the samples are in crystalline form.



a. 1% Co loading

b. 2% Co loading



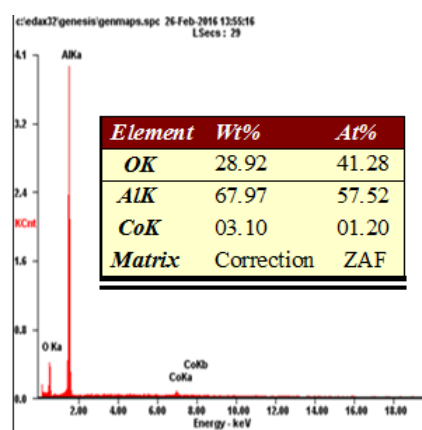
c. 5% Co loading

d.  $\gamma\text{-Al}_2\text{O}_3$

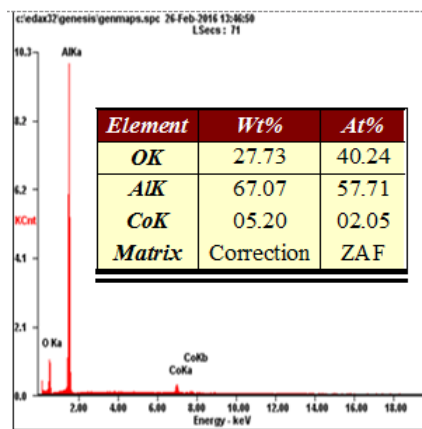
Fig.3. SEM image of the  $\text{Co}/\gamma\text{-Al}_2\text{O}_3$  and  $\gamma\text{-Al}_2\text{O}_3$  samples

#### Energy dispersive X-ray analysis (EDAX)

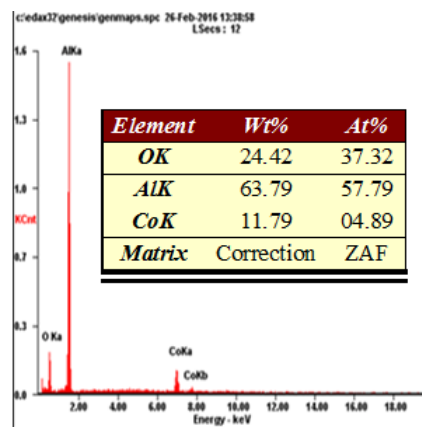
The chemical composition of the studied adsorbents was determined by EDX analyses (fig. 4).



a. 1% Co loading

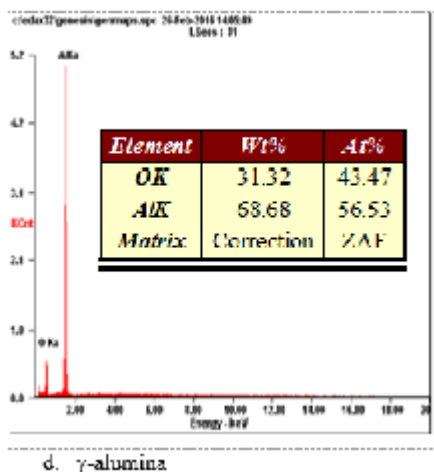


b. 2% Co loading



c. 5% Co loading

Fig. 4. Elemental analysis of the  $\text{Co}/\gamma\text{-Al}_2\text{O}_3$  and  $\gamma\text{-Al}_2\text{O}_3$  samples



d.  $\gamma$ -alumina

The elemental data and spectra obtained from the EDAX analysis confirm the presence of Co in the  $\text{Co}/\gamma\text{-Al}_2\text{O}_3$  samples.

### DR UV-Vis spectroscopy

As can be seen from figure 5, a band at 205 and a band at 250 nm for  $\text{Co}/\gamma\text{-Al}_2\text{O}_3$  are identified in the specimen of each sample due to  $\text{O}^{2-} \rightarrow \text{Co}^{2+}$  load transfer transitions.

The intense and broad absorption bands at 619 nm for Co1, 707 nm for Co2 and 747 nm for Co5 in the sample spectra indicate the presence of the cobalt ions in tetrahedral or octahedral coordinations [31].

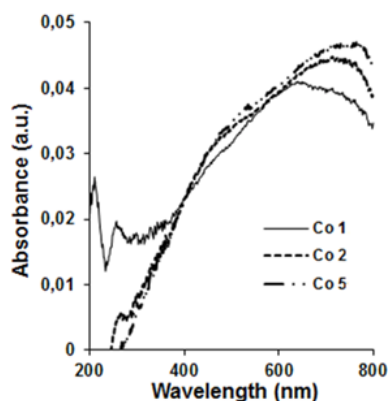


Fig. 5. DR-UV-vis spectra of  $\text{Co}/\gamma\text{-Al}_2\text{O}_3$  samples

### Adsorption studies

#### Effect of adsorbent concentration on dye removal

In order to investigate the effect of the adsorbent concentration on the amount of reactive dye removed from the aqueous solution a series of adsorption experiments was carried out with different adsorbent concentrations (from 0.2 to 0.8 g/L) at an initial dye concentration of 75 mg/L, pH of 2 and temperature of 25°C. The contact time was kept 15 min. The results are shown in figure 6.

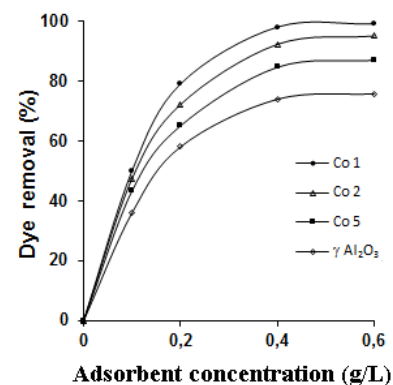


Fig. 6. Effect of adsorbent concentration on the removal of Reactive Blue 19 dye by  $\text{Co}/\gamma\text{-Al}_2\text{O}_3$  and  $\gamma\text{-Al}_2\text{O}_3$  (pH 2; 75 mg/L dye; temperature 25°C)

The percentage of uptaken dye onto  $\text{Co}/\gamma\text{-Al}_2\text{O}_3$  increases with the increase of the adsorbent dose due to the greater number of active sites available on the surface of the adsorbent.

#### Effect of pH

The pH is one of the most important factors that influence the sorption process of the dyes from aqueous solutions. The influence of pH on the sorption of Reactive Blue 19 dye onto  $\text{Co}/\gamma\text{-Al}_2\text{O}_3$  is shown in figure 7.

The plot shows that the adsorption of the anionic dye Reactive blue 19 decreased with the increase in pH. The higher adsorption capacity of the dye onto  $\text{Co}/\gamma\text{-Al}_2\text{O}_3$  at low pH values may be due to the neutralization of the negative charge and formation of a higher number of positive charges at the adsorbent surface which favors the uptake of the dye. The maximum adsorption capacity of the dye takes place around pH = 2; therefore this pH value was selected for all the further adsorption experiments.

Figures 6 and 7 show a slight decrease in the amount of dye adsorbed on  $\text{Co}/\gamma\text{-Al}_2\text{O}_3$  with the increase in the Co loading. This may be due to the increase in the size of cobalt oxide crystals, who leads to a decrease in the number of active centers.

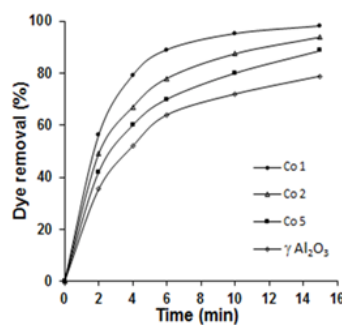
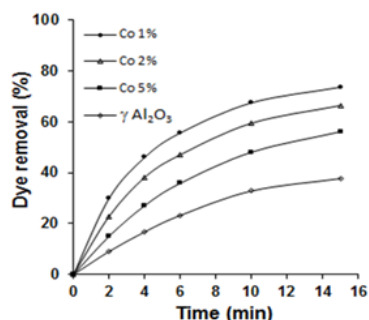
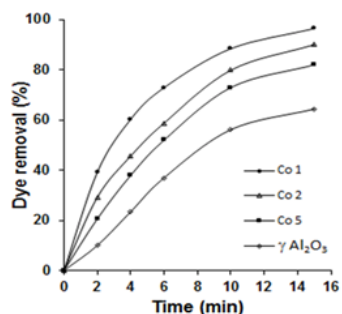


Fig. 7. The effect of pH on the removal of Reactive Blue 19 dye by  $\text{Co}/\gamma\text{-Al}_2\text{O}_3$  (75 mg/L dye; 0.4 g/L adsorbent; temperature 25°C).



#### Effect of the contact time and dye concentration

Different initial dye concentrations (30 - 75 mg/L) were used for adsorption studies (fig. 8) keeping constant the other parameters (pH, amount of adsorbent, dye concentration and contact time).

The amount of dye removed by adsorption decreases by increasing the dye concentration in the solution because for higher dye concentrations occurs saturation of the

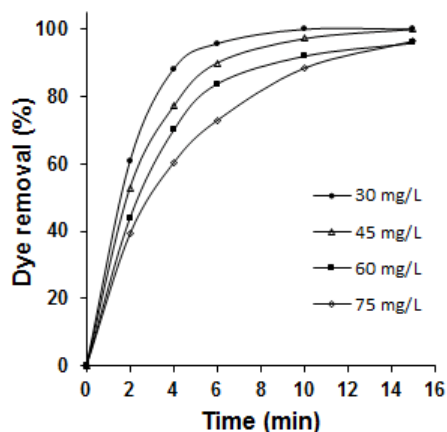


Fig.8. The effect of the initial dye concentration on the adsorption of Reactive Blue 19 dye on Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (pH 2; 0.4 g/L adsorbent; temperature 25°C).

surface of the adsorbent and respectively, a decrease in the number of the dye molecules adsorbed.

### Conclusions

Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> samples were obtained by treating gamma alumina with different concentrations of Co (NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O. EDX and SEM analyzes provide a good integration of Co in the skeletal structure of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The optimal working parameters were: contact time 15 min and pH = 2. The Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> samples showed a higher adsorption capacity of Reactive Blue 19 compared to the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> sample due to additional ionic interactions between Co cations and anionic dye. The highest adsorption capacity is presented by the Co1 sample (98% colorant removed in 15 min for initial dye concentration of 75 mg/L and temperature 25°C).

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