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## ACCEPTED MANUSCRIPT

### Azo dye adsorption on anthracite: a view of thermodynamics, kinetics and cosmotropic effects

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#### Abstract

The present paper presents anthracite – a low cost and naturally abundant coal – as a potential adsorbent of the azo dye Acid Yellow 42, evaluating parameters such as dye concentration, temperature and ionic strength. A thermodynamic and kinetic approach was also described. Interactions between the adsorbate and anthracite were described by isothermal titration as well. Anthracite was characterized by TGA / DTA, FT-IR, X-ray, TEM / EDS. The adsorption system anthracite-dye reached equilibrium in less than 10 min at room temperature, with a maximum adsorption capacity as high as 47 mg g<sup>-1</sup>. A multilayer pattern is observed according to the Freundlich adsorption model and the adsorption kinetics is best explained by the pseudo-second-order model. A chemisorption phenomenon drives the initial process, followed by a multi-layer physisorption phenomenon between dye molecules, with a prevalence of electrostatic interactions. The adsorption of acid yellow 42 onto anthracite is a spontaneous ( $\Delta_{ads}G^{\circ} = -11.68 \text{ kJ mol}^{-1}$ ) and endothermic ( $\Delta_{ads}H^{\circ} =$ 58.59 kJ mol<sup>-1</sup>) process, suggesting that the driving force to promote adsorption is the increase of the degree of freedom in the interface anthracite/solution ( $\Delta_{ads}S^\circ = 70.26$  kJ mol-<sup>1</sup>). The amount of AY immobilized at the surface of anthracite increased with the temperature rising, evidencing an endothermic process. Cations and anions influence the adsorption process, not obeying and following Hofmeister series, respectively. Ionic charge lead to increase Zeta potential. Therefore, anthracite highlights as a potential adsorbent material for azo dyes compared with other natural materials and some activated carbons. Keywords: Ionic Charge; Coal; Pigment; Hofmeister Series.

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