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Insights into the mechanism of cationic dye adsorption on activated charcoal: The importance of π - π interactions

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ABSTRACT

The mechanism and capacity of methylene green (MG5) adsorption onto commercial activated-charcoal (CAC, Norit RB4C) were investigated in batch experiments. The microporous CAC material was found to exhibit a large specific surface area (1026 m²/g) and high total pore (0.502 cm³/g) and micropore (0.347 cm³/g) volumes. The point of zero charge (9.81 ± 0.07) of CAC was determined by the “drift method” and found to be insignificantly dependent on the varying operation conditions. The dye adsorption process was low relative to the solution pH (2.0–10) and ionic strength (0–0.5 M). Kinetic studies indicated that the adsorption equilibrium was quickly reached based on low activation energy required for adsorption (E_a ; 4.12 kJ/mol). CAC can remove 53–64% of the MG5 concentration from solution within 1 min. The maximum adsorption capacities determined from Langmuir model at 10 °C, 30 °C, 40 °C, and 50 °C were 361 mg/g, 489 mg/g, 543 mg/g, and 581 mg/g, respectively. Desorption studies demonstrated that the MG5 adsorption was irreversible. The MG5 adsorption process was found to be spontaneous ($-\Delta G^\circ$), endothermic ($+\Delta H^\circ$), and increased the randomness ($+\Delta S^\circ$) in the system. Oxygenation of the CAC surface through a hydrothermal process with acrylic acid resulted in a decrease in MG5 adsorption and identified the importance of π - π interactions to the adsorption process. The analysis of Fourier transform infrared spectroscopy revealed that the aromatic C=C bonds decreased in intensity and upshifted after MG5 adsorption, which additionally confirms the significant contribution of π - π interactions. The combined results of our studies highly indicated that the primary mechanisms in MG5 adsorption were π - π interactions and pore filling, while hydrogen bonding and n- π interactions were minor contributors.

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1. Introduction

Activated carbon (AC) has been widely used in various applications and industries, including: air purification, (bio) gas purification, food ingredient and product purification, pharmaceuticals, the automobile industry, as a catalyst and catalyst carrier, gas and electrical energy

storage, water applications, and drinking water treatment. This is because the unique properties of AC: exceptionally large specific surface area, high pore volume, well-developed internal porous structure, relative chemical stability, durability, high thermal stability, and abundant surface functional groups. AC is used in water treatment as an effective adsorbent for the removal of various organic and inorganic contaminants (Radovic et al., 2001; Tran et al., 2017b).

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The presence of dyes and pigments in effluents is an enormous public health concern around the world because of their toxic, carcinogenic, mutagenic, and allergenic nature. It has been estimated that approximately 700,000 and 10,000 t of dye and pigment, respectively, are produced every year and approximately 10–15% of used dye is discharged into water streams annually (Gupta and Suhas, 2009; Raval et al., 2016). The colored effluents released into water environments have been receiving more attention recently due to the aesthetically displeasing (strong and persistent color) and environmentally adverse (oxygen deficiency) consequences of this action.

Dyes can be classified into different types based on the use: acidic (anionic), basic (cationic), dispersive, direct, reactive, solvent, sulfur, and vat (Gupta and Suhas, 2009). Methylene green (or basic green 5, MG5) is a cationic phenothiazine dye and heterocyclic aromatic compound that can be considered as a nitro derivative of methylene blue. MG5 shows considerable solubility in both polar organic media and water (Glusko et al., 2011).

It is difficult to decolor or treat dye-containing water and wastewater streams since dye molecules tend to show relatively strong recalcitrance and resistance to aerobic digestion as well as high stability to light, heat, and oxidizing agents (Crini, 2006). A wide variety of techniques have been employed in attempts to effectively remove dyes from spent textile dyeing wastewater: sedimentation, filtration, chemical treatment, oxidation, electrochemical methods, advanced oxidation processes, biological treatment, adsorption, and ion exchange (Gupta and Suhas, 2009). Adsorption is the most economically favorable of these techniques due to its relatively high removal efficiency, low operation costs, and feasibility for separating a wide range of pollutants from aquatic environments (Crini, 2006; Gupta and Suhas, 2009; Raval et al., 2016). Although AC has been used for removing dyes, there is limited understanding of the mechanism of dye adsorption onto microporous carbonaceous materials in literature. The objective of this study is to clarify which adsorption mechanisms control the adsorption of the cationic dye (MG5) onto activated carbon.

Commercial activated charcoal (CAC, Norit RB4C) with ~70% micropore volume was used in this study as a potential adsorbent for MG5. The point of zero charge (PZC) is an important and widely studied property in adsorption. Thus, we initially investigated the main factors affecting the PZC of CAC according to various operating parameters. Furthermore, we investigated the effects of solution pH, ionic strength, contact time, initial MG5 concentration, temperature, and the presence of desorption agents on the MG5 adsorption process. We compared the difference between MG5-loaded CAC and MG5-unloaded CAC using FTIR spectroscopy and BET specific surface area analysis, along with probing the adsorption kinetics, isotherms, and thermodynamics, and MG5 desorption, to identify the primary interactions in the adsorption process. Lastly, we suggest a simple and efficient method for identification of the dominant interactions in the adsorption process.

2. Materials and methods

2.1. Activated carbon preparation

Commercial activated charcoal (Norit RB4C) prepared by steam activation was purchased from Sigma–Aldrich. The CAC was ground and sieved to obtain particles in the size range 0.106–0.250 mm. These CAC particles were used as adsorbents without further modification or treatment.

2.2. Activated carbon properties

The CAC textural properties were analyzed using a Micromeritics ASAP 2020 sorptometer at 77 K. The CAC morphology was measured using scanning electron microscopy (SEM; Hitachi S-4800, Japan). The functional groups on the CAC surface were detected using Fourier transform infrared spectroscopy (FTIR; FT/IR-6600 JASCO); CAC particles were pelleted for FTIR measurements by mixing with KBr particles.

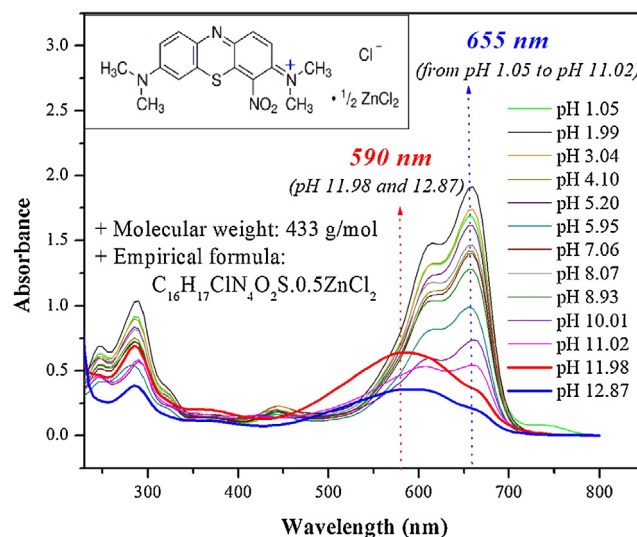


Fig. 1 – Ultraviolet visible absorption spectra showing the effect of pH of the MG5 solution λ_{\max} values (Data published in our recent work; Tran et al., 2017b).

All of solutions were prepared using distilled deionized water. The pH of CAC suspensions at the point of zero charge (pH_{PZC}) was determined using the common “drift method” (Kosmulski, 2009). The initial pH value (pH_i) of every known background electrolyte (i.e., NaCl, KNO_3 , NaNO_3 , or KCl) was adjusted from $\text{pH } 2.0 \pm 0.2$ to $\text{pH } 11 \pm 0.2$ by adding 1 M NaOH or 1 M HCl; 25 mL of this solution was then transferred to a series of Erlenmeyer flasks and a given mass of CAC was added to each flask. The flasks were securely sealed immediately and the suspensions were then spun at 150 rpm for a desired interval before the final pH value (pH_f) of the supernatant was recorded. The difference between pH_i and pH_f ($\Delta\text{pH} = \text{pH}_i - \text{pH}_f$) was plotted against pH_i , and the point of intersection of the resulting curve with pH_i was taken to be pH_{PZC} . The effect of CO_2 on the PZC was also examined.

2.3. Batch adsorption experiments

The effects of solution pH and ionic strength on dye adsorption capacity were investigated at various initial pH values (2.0–10.0) and NaCl salt concentrations (0–0.5 M), respectively. Studies on the adsorption kinetics were conducted using two different initial dye concentrations at 30 °C and 50 °C. The adsorption isotherm was investigated for MG5 concentrations of 50–1300 mg/L at different temperatures. Thermodynamic adsorption experiments were carried out at different temperatures (10–50 °C) and with various dye concentrations (50–1300 mg/L). The MG5-CAC mixture was shaken using an orbital-shaking incubator (S300R-Firstek) at a constant speed of 150 rpm. After predetermined intervals, the mixture was separated using a 0.45 μm glass-fiber filter. The MG5-laden CAC was rinsed with distilled deionized water, dried, and stored for further experiments (i.e., FTIR, BET analysis, and desorption). The MG5 concentration in solution was determined using ultraviolet visible spectrophotometry (Genesys 10 UV-Vis; Thermo Scientific) at the maximum absorbance wavelengths (Fig. 1). The maximum absorbance wavelength is approximately 655 nm at pH 1.05–11.02 (selected for this study) and 590 nm at pH 11.98–12.87 (Tran et al., 2017b). The

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