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# Adsorption of Reactive Blue BF-5G Dye onto Modified Bovine Bone Char

Celso Hissao Maeda[a], Lailson de Sousa[a], Alexandre Diório[a], Fabiano Bisinella Scheufele[b], Pedro Augusto Arroyo[a]

*[a] Department of Chemical Engineering, State University of Maringá, Maringá, Brazil*
*[b] Department of Chemical Engineering, Federal Technological University of Paraná, Toledo, Brazil*

## Abstract

Textile companies that engage in fabric dyeing processes often consume large quantities of water, Leading to a substantial volume of wastewater. In this context, it is crucial to remove the dye content of these effluents, and one effective and versatile technique that can be employed as a tertiary treatment is the adsorption process using bovine-derived activated carbon. Acid modifications were applied to the raw bone char to develop a new adsorbent with enhanced dye removal capacity. Characterization revealed a mesoporous structure with and average pore diameter of 94 Å, a specific surface area of 107 m²/g, and a negatively charged surface ($pH_{PZC}$ = 3.8). On the other hand, the modified bone chars exhibited an average pore diameter of 150 Å, a specific surface area ranging from 102 to 234 m²/g, and a $pH_{PZC}$ ranging from 6.4 to 7.3. Tests with modified chars were conducted to assess reactive blue BF-5G dye, showing that some modifications were more effective than others.

*Keywords: Adsorption; Azodye, Bovine bone char, Acid modification*.

## 1. Introduction

The primary characteristic of the textile industry is the pollution of large quantities of water during the dyeing process, which poses a real threat to the environment due to the discharge of untreated effluents [1]. In general, about 10-15% of all dyes used in the textile industry are discharged along with wastewater [2]. Among these, Reactive Blue BF-5G (C.I. Reactive Blue 203) is widely used in the dyeing of cotton fabric and is toxic to aquatic ecosystems due to its azo dye structure with toxic characteristics [3].

One of the wastewater treatment techniques that can be employed is adsorption, as it is considered effective in dye removal [4]. Various adsorbents can be used in the adsorption process, provided they have characteristics such as affinity with the adsorbate, mechanical and chemical stability, compatible textural properties, low cost, inertness, and the potential for regeneration. In this context, bovine bone char emerges as an interesting alternative for the removal of textile dyes from wastewater [5].

According to [6], mass transfer resistance was influenced by the electrostatic repulsion between the dye charges and the char surface, as well as by intraparticle diffusion resistance. In this context, the aim of this study was to use raw bone char and perform an acid modification on its surface to develop a new adsorbent with enhanced dye removal capacity.

## 2. Materials and Methods

Bovine bone char was used as the adsorbent, and Reactive Blue BF-5G dye served as the adsorbate. The $pH_{PZC}$ of the char was determined using the "11-point method" described by [7]. The textural properties of the char were analyzed using $N_2$ physisorption, applying the BET model, BJH method, and t-plot method [8], [9], [10]. Another important analysis related to the dye molecule is the pKa, which was obtained using the potentiometric method [11].

The pore size modification technique was based on Tessonier's method [12], which involves impregnating a quantity of acid solution ($HNO_3$) diluted in ethanol, equivalent to 2/3 of the total pore volume. A total of 11 bone char samples were modified as described in **Table 1**. The parameters evaluated included contact time, acid concentration, and the number of impregnation cycles. After acid impregnation, the char was washed and dried in an oven at 70 °C for approximately 12 h.

**Table 1**. Bone char samples and acid-modification parameters

| Sample | Properties | | |
|---|---|---|---|
| | *t (h) | $[HNO_3]$ (moL $L^{-1}$) | Cycles |
| 1 | 4 | 1.0 | 1 |
| 2 | 42 | 1.0 | 1 |
| 3 | 4 | 1.0 | 7 |
| 4 | 42 | 1.0 | 7 |
| 5 | 4 | 5.0 | 1 |
| 6 | 42 | 5.0 | 1 |
| 7 | 4 | 5.0 | 7 |
| 8 | 42 | 5.0 | 7 |
| 9 | 23 | 3.0 | 4 |
| 10 | 23 | 3.0 | 4 |
| 11 | 23 | 3.0 | 4 |
| 12 | *In natura* | 0 | 0 |

* Acid/bone contact time (h).

Adsorption kinetics experiments were conducted in duplicate with an initial concentration of 500 mg/L and agitation at 140 rpm. Erlenmeyer flasks containing 20 mL of dye solution and 0.1 g of bone char were placed in a thermostatic bath (Dubnoff Bath - Nova Ética) for periods ranging from 5 to 72 hours. Adsorption equilibrium experiments were carried out under the same conditions as the kinetics, but with initial concentrations ranging from 100 to 7000 mg/L.

## 3. Results and discussion

### 3.1 Characterization

As described by [13], the adsorption capacity of anionic dyes is reduced in solutions with pH values higher than the $pH_{PZC}$, as the adsorbent surface acquires a negative charge. Consequently, pH values above the $pH_{PZC}$ cause electrostatic repulsion between the negative charge generated on the adsorbent surface and the anionic group present in the dye. **Table 2** shows the $pH_{PZC}$ values for all bone char samples

**Table 2**. Value of $pH_{PZC}$ for the studied bone char samples.

| Samples | $pH_{PZC}$ |
|---|---|
| 1 | 7.34 |
| 2 | 6.90 |
| 3 | 7.18 |
| 4 | 6.95 |
| 5 | 6.66 |
| 6 | 6.42 |
| 7 | 7.06 |
| 8 | 7.01 |
| 9 | 6.66 |
| *In Natura* | 3.68 |

The raw bone char has a $pH_{PZC}$ of 3.68. Therefore, if the solution's pH is higher than the adsorbent's $pH_{PZC}$, the anionic Reactive Blue BF-5G dye will encounter difficulties in being adsorbed. Indeed, in the experiments conducted, the initial pH of the dye solution ranged from 5.6 to 6.2, and the final pH of the dye solution varied from 6.5 to 7.8. Thus, the dye solution pH was above the $pH_{PZC}$, resulting in high resistance due to electrostatic repulsion between the dye and the adsorbent surface. The acid treatment applied aimed to neutralize, to some extent, the surface charges of the bone char.

The nitrogen adsorption isotherm ($N_2$) is an important model for evaluating the porosity and specific surface area of a material. It was observed that there are no limits to adsorption at high relative pressures, as the amount adsorbed continuously increases with the increase of $P/P_0$, without reaching saturation. The adsorption curve differs from the desorption curve, indicating the presence of mesopores due to capillary condensation within the pores, which is characterized as hysteresis. Based on this, the isotherm can be classified as type IV, with H3-type hysteresis, suggesting the predominance of parallel plate-shaped pores.

The isotherm used to calculate the specific surface area was the BET model [8], which is well-suited for mesoporous materials. The obtained values for specific surface area, total pore volume, micropore volume, and average pore diameter are presented in **Table 3**.

In the study by [14], using bovine bone char, a specific surface area of 103 $m^2/g$ was found using the BET model, with a total pore volume and average pore diameter, obtained using the BJH model, of 0.284 $cm^3/g$ and 97 Å, respectively. Similarly, [6] found that the specific surface area of bone char was 109 $m^2/g$, with a total pore volume of 0.260 $cm^3/g$, a micropore volume of 0.0034 $cm^3/g$, and an average pore diameter of 94 Å. [13] also used bone char and obtained similar results using the same analysis methods, with a specific surface area of 107 $m^2/g$ and an average pore diameter of 94 Å. Therefore, the values from this analysis are consistent with those found in the literature for raw bone char. Among the adsorbents modified by acid treatment, samples 7, 8, and 9 showed an increase in specific surface area. However, the average pore diameter values decreased.

The determination of the dye's pKa was based on measuring pH changes with the addition of titrant (NaOH) to obtain a titration curve. The second derivative method allows for calculating the endpoint value from a titration curve (**Figure 1**).

The dye can be considered a diprotic acid with two dissociation constants: $pKa_1 = 4.6$ and $pKa_2 = 7.1$. Based on the dye's molecular structure, the $pKa_1$ and $pKa_2$ values likely correspond to the $-NH_2$ and -OH groups, respectively. However, this analysis could not identify the sulfonic acid group because this method analyzes a pH range from 2 to 12

**Table 3**. Bone char samples surface characterizations

| **Bone char sample** | **Specific surface area (BET) ($m^2/g$)** | **Average pore diameter (BJH) (Å)** | **Total volume of pores (single point) ($cm^3/g$)** | **Volume of micropores (t-plot) ($cm^3/g$)** |
|---|---|---|---|---|
| **1** | 135 | 98 | 0.338 | 0.0083 |
| **2** | 128 | 100 | 0.331 | 0.0077 |
| **3** | 150 | 91 | 0.364 | 0.0012 |
| **4** | 148 | 93 | 0.381 | 0.0015 |
| **5** | 136 | 96 | 0.338 | 0.0045 |
| **6** | 102 | 101 | 0.284 | 0.0033 |
| **7** | 234 | 65 | 0.388 | 0.0157 |
| **8** | 199 | 74 | 0.370 | 0.0130 |
| **9** | 172 | 90 | 0.398 | 0.0095 |
| *In natura* | 113 | 97 | 0.320 | 0.0052 |

For this reason, a literature search was carried out and, according to [15], sulphonic acids are strong acids and good proton dono.rs with a pKa = - 2.65, i.e. in solution these groups tend to remain in their anionic form (sulphonate) giving anionic character to the dye in solution.

The researchers found three different species in which the sulphonate groups were in the anionic form for the entire pH range studied (from 2 to 12). In this way, it can be assumed that the sulphonic acid group of the BF-5G blue reactive dye, even at a pH of 2, is in the anionic form in 4 places around its molecule.3.2 Adsorption experiments.

For this reason, a literature review was conducted, and according to [15], sulfonic acids are strong acids and good proton donors with a pKa of -2.65, meaning that in solution, these groups tend to remain in their anionic form (sulfonate), imparting an anionic character to the dye in solution. The researchers identified three different species in which the sulfonate groups were in the anionic form across the entire pH range studied (from 2 to 12). Thus, it can be assumed that the sulfonic acid group of Reactive Blue BF-5G dye, even at a pH of 2, remains in the anionic form at four sites around its molecule.

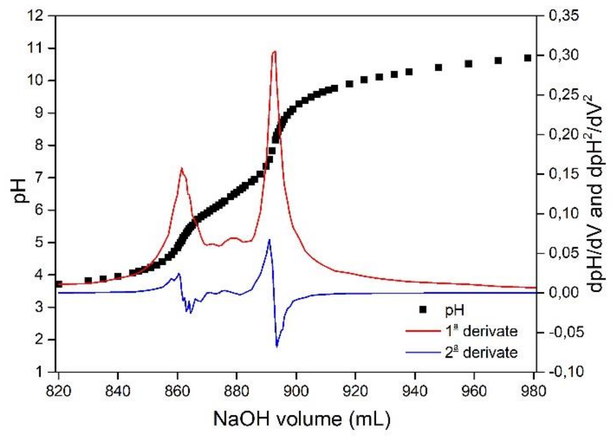

**Figure 1**. Trends of the 1st (—) e 2nd (—) derivate of dye titration with NaOH.

The final concentration used was 750 mg/L, which confirmed the trend observed at 500 mg/L, indicating that samples 7, 8, and 9 showed the greatest potential for dye removal.

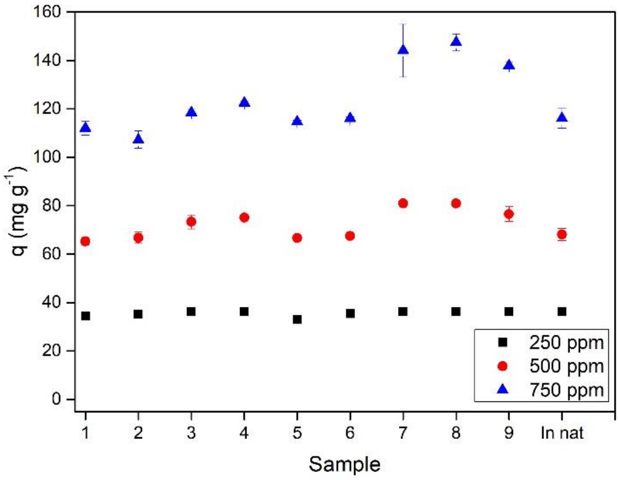

**Figure 2.** Adsorption experiments with nitric acid-modified bone char.

## 4. Conclusion

This study successfully enhanced the adsorption capacity of bone char through acid modification, resulting in modified chars with improved efficiency in dye removal, particularly at higher concentrations. The modifications increased the specific surface area and altered the pore structure, which contributed to better adsorption performance. The results confirm that acid-treated bone char is a promising adsorbent for effective removal of anionic dyes, making it a viable option for wastewater treatment applications in the textile industry.

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