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Application of pyridine-modified chitosan derivative for simultaneous adsorption of Cu(II) and oxyanions of Cr(VI) from aqueous solution

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Abstract

The bioadsorbent **C1**, which is a chitosan derivative prepared in a one-step synthesis, was successfully used to adsorb Cr(VI) and Cu(II) simultaneously. Here, for the first time the simultaneous adsorption of a cation and an anion was modeled using the Corsel model for kinetics and the Real Adsorbed Solution Theory model for equilibrium data. Batch studies of the adsorption of Cu(II) and Cr(VI) in single and binary aqueous solutions were performed as a function of initial solute concentration, contact time, and solution pH. Here, for the first time the simultaneous adsorption of a cation and an anion was modeled using the Corsel model for kinetics and Real Adsorbed Solution Theory model for equilibrium data. The maximum adsorption capacities of **C1** in single and binary aqueous solutions were 1.84 and 1.13 mmol g⁻¹ for Cu(II) and 3.86 and 0.98 mmol g⁻¹ for Cr(VI), respectively. The reuse of **C1** was investigated, with Cu(II) ions being almost completely desorbed and fully re-adsorbed. For Cr(VI), the desorption was incomplete resulting in a lower re-adsorption. Energy-dispersive X-ray spectroscopy was used for mapping the distributions of Cr(VI) and Cu(II) adsorbed on the **C1** surface in single and binary adsorption systems. Isothermal titration calorimetry experiments were performed for Cr(VI) and Cu(II) adsorption in single solutions. The thermodynamic parameters of adsorption showed that the adsorption of both metal ions was enthalpically driven, but entropically unfavorable.

Keywords: one-step synthesis; pyridine-2-carbaldehyde; copper; chromium; Real Adsorbed Solution Theory, Corsel model.

1. Introduction

Many environmental and public health problems are related to the contamination of water resources (Li et al., 2015; Purkayastha et al., 2014; Wu et al., 2018). Metals are often found as major contaminants of aquatic systems, and can be highly toxic to humans and animals (Teodoro et al., 2016; Uddin, 2017; Xin et al., 2017). The main causes of contamination of water by toxic metals include industrial activities such as the manufacture of batteries, textiles, paints, and pesticides, as well as petroleum refining and mining operations (O'Connell et al., 2008; Ramos et al., 2015). The toxic metals discharged by industries include cadmium, mercury, lead, chromium, copper, nickel, and zinc (Wan Ngah et al., 2011).

Copper is widely used in electrical materials, alloys, fungicides, and herbicides, and is associated with industrial wastes, mining activities, and power generation (Ayres et al., 2003). High concentrations of copper lead to health impacts including chronic or acute liver disease, neurological problems, and psychiatric disorders such as Wilson's disease (Mulligan and Bronstein, 2020). Chromium is used in stainless steel and alloys, chrome plating, leather tanning, dyes and pigments, and wood preservation (Morrison and Murphy, 2010). Cr(VI) is toxic and a well-known human carcinogenic. It causes damage to the immune, respiratory, gastrointestinal, reproductive, and hematological systems (Wilbur et al., 2012).

Cr(VI) and Cu(II) are common ions and generally coexist in wastewater, notably in discharges from the electroplating and tanning industries. For example, Sarkar et al. (2015) showed concern to analyze the concentrations chromium and copper in the Buriganga river (Bangladesh) due to the pollution caused by the tannery effluent. In addition to the tannery industry, copper is also emitted from the sewage pipe lines (Sarkar et al., 2015). Regarding this kind of waste, some works reported the use of photoreduction

(Yan et al., 2020) and adsorption on carbonized crofton weed (Chen et al., 2016) and hyacinth shoot powder (Sarkar et al., 2017) for simultaneous removal of Cr(VI) and Cu(II). Copper and chromium are also present in the formulation of chromated copper arsenate (CCA), a wood preservative to avoid attack by termites and fungi (ATSDR, 2011). CCA is no longer used for residential construction but it still used for industrial and commercial constructions (NPIC, 2014). Since CCA is a water-soluble substance, there is a concern about water and soil contamination by leaching from CCA-treated wood (ATSDR, 2011).

Inefficient treatment of effluents contaminated with toxic metals in wastewater treatment plants (WWTPs) can cause long-term risks to ecosystems and humans. Various techniques have been used for removal of toxic metals in WWTPs, such as chemical precipitation, flocculation and coagulation, oxidation/reduction, and nanofiltration (Mosa et al., 2016; Purkayastha et al., 2014; Teodoro et al., 2016). Adsorption may be used as a treatment or as a polishing technique in WWTPs, offering high efficiency and flexibility of operation (Li et al., 2018; Silva-Yumi et al., 2018; Xin et al., 2017). As a polishing technique, adsorption can be used to achieve drinking water standards. According to the WHO, the provisional guideline values for Cr and Cu in drinking water are 0.05 and 2.0 mg L⁻¹, respectively (WHO, 1996a, b).

The availability of cost-effective, highly efficient, and environmentally friendly adsorbents is extremely important for the feasibility of adsorption techniques applied to treat water and wastewater (Rahimi et al., 2018; Silva-Yumi et al., 2018; Teodoro et al., 2016). To this end, the use of adsorbents prepared from chemical modification of biopolymers has attracted attention in recent years (Almeida et al., 2016; De Gisi et al., 2016).

Polysaccharide-based biopolymers are a potential source of adsorbent materials. Polysaccharides are widely found in nature, have varied molecular structures, and present a wide range of physicochemical properties that can be exploited for different applications (Kurita, 2001). Among the many types of natural polysaccharides, cellulose and chitin are the most abundant (Ahmad et al., 2017; Almeida et al., 2016). Chitin is mainly isolated from shrimp or lobster carapaces, as well as from the cell walls of some fungi (De Gisi et al., 2016; Kurita, 2001). The partial deacetylation of chitin results in the formation of chitosan, a polyaminosaccharide with glucose-like structures (2-amino-2-deoxy- β -D-glucose and 2-acetamido-2-deoxy- β -D-glucose units) connected by $\beta(1\rightarrow4)$ linkages (Ahmad et al., 2017; Kyzas et al., 2017). The presence of hydroxyl and free amine groups in the chitosan structure provides excellent capacity of this material to act as a scavenger of metal ions, so it is a promising starting material for the synthesis of different adsorbents with improved properties (Divya and Jisha, 2018; Li et al., 2018; Wu et al., 2010). Several recent studies have discussed the development of low-cost adsorbents based on biopolymers such as chitosan, as an alternative to synthetic polymers (Ahmad et al., 2017; De Gisi et al., 2016).

The aim of the present study was to model the simultaneous adsorption of a cation and an anion using a versatile bioadsorbent. The present study is the first study to model the simultaneous adsorption of a cation and an anion using the Corsel model for kinetics and the Real Adsorbed Solution Theory (RAST) model for equilibrium data. These models provide a more in-depth analysis of the interactions involved in the simultaneous adsorption of Cu(II) and Cr(VI). It was employed a bioadsorbent, denoted **C1**, prepared by modification of chitosan with pyridine-2-carbaldehyde (Goncalves et al. (2018). The use of **C1** is relevant, because it was prepared using a one-step synthesis employing a

green solvent. **C1** was subsequently used to remove Cr(VI) and Cu(II) from single and binary aqueous solutions.

Reuse of the spent adsorbent was also investigated. Isothermal titration calorimetry was used to understand the differences between the adsorption of Cu(II) and oxyanions of Cr(VI) on **C1**, with determination of the adsorption thermodynamic parameters.

2. Material and methods

2.1. Material

Chitosan (medium molecular weight, cat. no. 448877), pyridine-2-carbaldehyde, CuSO₄·5H₂O, and sodium chloroacetate (98%) were purchased from Sigma-Aldrich. K₂Cr₂O₇, monochloroacetic acid (99%), CH₃COONa·3H₂O, Na₂CO₃, anhydrous CaCl₂, NaH₂PO₄, Na₂HPO₄, and ethylenediaminetetraacetic acid (EDTA) were purchased from Synth (Brazil). Glycine was purchased from Isofar (Brazil). Glacial acetic acid (99.5%) was purchased from Neon (Brazil). Ethyl alcohol (99.8%) was purchased from Dinâmica (Brazil). HCl (37 wt.% in H₂O) was purchased from Vetec (Brazil). Filter paper (quantitative, black ribbon, C-41, 12.5 cm diameter, 0.01% ash content, and grammage of 85 g m⁻²) was purchased from Unifil (Brazil).

The degree of acetylation (DA) of the chitosan was determined in a previous study of our research group (Goncalves et al., 2018), using quantitative solid-state ¹³C nuclear magnetic resonance (SS ¹³C NMR) spectroscopy. The estimated DA value of the chitosan was 33 ± 2%.

2.2. Synthesis of C1

The synthesis of **C1** was performed as described previously by Goncalves et al. (2018). Chitosan (5 g) was added to a 500 mL round-bottom flask, together with 0.525 mols of pyridine-2-carbaldehyde (50 mL) dissolved in 125 mL of ethyl alcohol (99.8%). A reflux condenser with a drying tube filled with anhydrous CaCl_2 was attached to the flask. The suspension was heated at 80.0 °C for 18 h, under gentle agitation (300 rpm) in an oil bath (Model PC-420, Corning®). Subsequently, the cooled suspension was filtered under reduced pressure, using a sintered glass funnel (porosity 3), followed by washing with ethyl alcohol (95%), distilled water, ethyl alcohol (95%), and diethyl ether. The **C1** obtained was dried in an oven (Model 400/3ND, Nova Etica) at 70.0 °C for 20 min.

2.3. Characterization of C1

2.3.1. Elemental and spectroscopic analyses

Elemental carbon, hydrogen, and nitrogen analyses of the chitosan and **C1** were performed using an elemental CHNS/O analyzer (Model 2400 Series II, Perkin-Elmer). Before analysis, the materials were dried at 85.0 °C in an oven for 1 h. The analyses were performed in duplicate. Procedures used for characterization of the chitosan and **C1** by Fourier transform infrared (FTIR) and SS ^{13}C NMR spectroscopies were reported by Goncalves et al. (2018).

2.3.2. Surface analyses

The pH of zero charge (pH_{PZC}) of **C1** was determined by the method of Noh and Schwarz (1990). Aqueous 0.10 mol L^{-1} NaNO_3 solutions (150 mL) were prepared and the pH of each solution was adjusted to 3.00, 6.00, or 11.00 by adding drops of aqueous HNO_3 (0.1 mol L^{-1}) or NaOH (0.1 mol L^{-1}) solutions. Aliquots of 20.00 mL of each NaNO_3 solution at pH 3.00, 6.00, or 11.00 were then added to 125 mL Erlenmeyer flasks to

prepare aqueous suspensions of 0.05, 0.1, 0.5, 1.0, and 2.0% (w v⁻¹) of **C1**. The flasks were stirred at 130 rpm and 25.0 °C for 24 h in an orbital shaker incubator (Model TE-424, Tecnal). At the end of the experiment, the equilibrium pH of each suspension was measured using a pH meter (Model HI 223, Hanna Instruments). The convergence point of the three curves of equilibrium pH against **C1** concentration (w v⁻¹) gave the PZC value.

The surfaces of the chitosan and **C1** were analyzed by scanning electron microscopy (SEM) (Model 6510, JEOL). The materials were dried in an oven for 1 h at 80.0 °C, before metallization with a thin layer of carbon graphite (Model JEE-4C, JEOL).

The textural properties of **C1** were determined using N₂ adsorption and desorption isotherms obtained using a pore and surface area analyzer (Model Nova 1200e, Quantachrome). **C1** was degassed at 60.0 °C for 24 h before analysis. The specific surface area was determined by the method of Brunauer et al. (1938). The maximum pore diameter was determined by the method of Barrett et al. (1951).

2.4. Adsorption experiments

The **C1** adsorbent was used to adsorb oxyanions of Cr(VI) and Cu(II) from spiked aqueous solutions in batch mono- and bicomponent systems. The adsorption experiments were performed in duplicate, using the experimental conditions described in Table 1. The pH values and buffer solutions were chosen considering the solubility of Cu(II) and Cr(VI) in each buffer solution (Almeida et al., 2016) (see section 4.2.1). The equilibrium pH of each solution was measured using a pH meter (Model HI 223, Hanna Instruments). All flasks (250 mL Erlenmeyers) containing **C1** and solute solutions were stirred in an orbital shaker incubator (Model MA-830, Marconi), followed by a single filtration (C-41

(20 µm) filter paper) to separate the spent **C1** adsorbent and the liquid phase. The liquid phases were analyzed by flame atomic absorption spectrophotometry (FAAS) (Model SpectrAA 50B, Varian) ($\lambda_{\text{Cu}} = 324.7 \text{ nm}$, $\lambda_{\text{Cr}} = 425.4 \text{ nm}$) for determination of the Cr(VI) and Cu(II) concentrations (Elias et al., 2019). The FAAS analyses were performed in triplicate.

The adsorption capacity (q) of **C1** for oxyanions of Cr(VI) or Cu(II) was determined as follows:

$$q / (\text{mmol g}^{-1}) = \frac{(C_0 - C_x)V}{w_{\text{C1}}} \quad (1)$$

where, C_0 (mmol L⁻¹) is the initial concentration of oxyanions of Cr(VI) or Cu(II) in the aqueous solution, C_x (mmol L⁻¹) is the concentration of oxyanions of Cr(VI) or Cu(II) at time t or equilibrium, V (L) is the volume of Cr(VI) or Cu(II) aqueous solution, and w_{C1} (g) is the weight of **C1**.

Table 1

2.4.1. Isothermal titration calorimetry (ITC)

Isothermal titration calorimetry (ITC) experiments were conducted for single adsorption of Cr(VI) (at pH 3.6) and Cu(II) (at pH 5.5), using an Isothermal Titration Nanocalorimeter (Model TAM III, TA Instruments, USA) controlled by dedicated TAM Assistant™ software and equipped with two 4.00 mL reaction cells (sample and reference). Using a Hamilton syringe (500 µL) controlled by a piston pump, stepwise 20 µL injections of concentrated buffered aqueous solutions of the metal ions (500.0 mg Cr(VI) L⁻¹ or 270.0 mg Cu(II) L⁻¹) were titrated against a mixture of 8.00 mg

of **C1** and 2.70 mL of buffer solution in the reaction cell. The reference cell was filled with the same buffer solution, without the adsorbent. During titration, the time interval used between consecutive injections was 60 min and a propeller stirrer operating at 180 rpm was used to ensure homogenization of the suspension inside the reaction cell. Control experiments were performed by *i*) adding the metal ion solution to the buffer solution in the absence of **C1**, and *ii*) adding the buffer solution to the mixture of adsorbent and buffer solution, in order to discount the heat effect associated with the dilutions of the metal ion solutions and **C1** during the adsorption processes. The measurements were performed at a temperature of 25.0000 ± 0.0001 °C. The solutions were degassed for 10 min, prior to the titration experiments, in order to avoid bubble formation in the system. Each titration was performed in duplicate.

The change in enthalpy of adsorption for the metal ion adsorption on **C1** ($\Delta_{\text{ads}}H$), associated with the *i*-th injection in the titration experiment, was calculated as follows:

$$\Delta_{\text{ads}}H / (\text{kJ mol}^{-1}) = \frac{q_i - q_{i,\text{dil}}}{n_i} \quad (2)$$

where, q_i and $q_{i,\text{dil}}$ (kJ) are the energies absorbed or released in the sample reaction cell due to the titration processes in the presence of metal ions (Cr(VI) or Cu(II)) and adsorbent, and in the absence of metal ions or adsorbent, respectively, and n_i (mol) is the amount of metal ions adsorbed on **C1** during the same injection.

2.4.2. Thermodynamic parameters of adsorption

The approach used for determination of the changes in the standard free energy of adsorption ($\Delta_{\text{ads}}G^\circ$) for adsorption of Cu(II) and oxyanions of Cr(VI) on **C1** was that described by Liu (2009), as follows:

$$\Delta_{\text{ads}} G^{\circ} / (\text{kJ mol}^{-1}) = -RT \ln \left[\left(\frac{b}{\gamma_e} \right) (1 \text{ mol L}^{-1}) \right] \quad (3)$$

where, R is the gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), T (K) is the absolute temperature, and γ_e is the equilibrium activity coefficient.

The value of γ_e can be calculated from the extended Debye Hückel law (Debye and Hückel, 1923), as follows:

$$\log \gamma_e = \frac{-0,509 z^2 \sqrt{I_e}}{1 + \left(\frac{\alpha \sqrt{I_e}}{305} \right)} \quad (4)$$

where, z is the charge of the ion, I_e (mol L^{-1}) is the ionic strength at equilibrium, and α (pm) is the hydrated ion size ($\alpha_{\text{Cu}^{2+}} = 419 \text{ pm}$, $\alpha_{\text{HCrO}_4^-} = 375 \text{ pm}$) (Nightingale, 1959).

To obtain the changes in the standard enthalpy of adsorption ($\Delta_{\text{ads}} H^{\circ}$) for adsorption of Cu(II) and oxyanions of Cr(VI), the $\Delta_{\text{ads}} H$ versus equilibrium concentration of metal ion (C_e) curves (Figures not shown) were extrapolated to $C_e \rightarrow 0$. The changes in the standard entropy of adsorption ($\Delta_{\text{ads}} S^{\circ}$) for adsorption of oxyanions of Cr(VI) and Cu(II) were determined from the following classical thermodynamic relationship:

$$\Delta_{\text{ads}} G^{\circ} = \Delta_{\text{ads}} H^{\circ} - T \Delta_{\text{ads}} S^{\circ} \quad (5)$$

2.5. Characterization of C1 loaded with Cu(II) and/or Cr(VI)

C1 loaded with oxyanions of Cr(VI) and/or Cu(II) was analyzed by energy-dispersive X-ray (EDX) spectroscopy. The materials were dried in an oven at $80.0 \text{ }^{\circ}\text{C}$ for 1 h, followed by pressing 100 mg portions of the samples denoted **C1-Cu(II)**, **C1-Cr(VI)**, and **C1-Cu(II)-Cr(VI)** in a hydraulic press (Model 181-1110, Pike Technologies) for 1 min, at

6 tons, to obtain discs 13 mm in diameter. The discs were metalized with a thin layer of carbon graphite (Model JEE-4C, JEOL) before analysis. The surfaces of the materials were mapped using a scanning electron microscope (Model 6510, JEOL) equipped with an EDX spectrometer (Model X-Max, Oxford Instruments).

2.6. Desorption and reuse of spent adsorbent

The experiments of adsorption and desorption were carried out using the experimental conditions described in Table 2. After desorption, C1 loaded with Cr(VI) or Cu(II) was recovered by single filtration, washed with an excess of ultrapure water, and dried in an oven at 80.0 °C for 6 h (Elias et al., 2019). The other procedures were the same as described in Section 2.4. The desorption efficiency (E_{des}) was determined as follows (Elias et al., 2019):

$$E_{\text{des}} / \% = \left(\frac{C_e V}{Q_{\text{max}} w'_{\text{C1}}} \right) \times 100 \quad (6)$$

where, Q_{max} (mg g⁻¹) is the maximum adsorption capacity determined for Cr(VI) or Cu(II), and w'_{C1} (g) is the weight of C1 in C1 loaded with Cr(VI) or Cu(II) ($w_{\text{C1,M}}$).

The value of $w_{\text{C1,M}}$ was determined as follows (Elias et al., 2019):

$$w'_{\text{C1}} / \text{g} = \frac{w_{\text{C1,M}} w_{\text{C1}}}{\left(\frac{Q_{\text{max}} w_{\text{C1}}}{1000} \right) + w_{\text{C1}}} \quad (7)$$

The experiments of re-adsorption were carried out using the experimental conditions described in Table 2. The other procedures were the same as described in Section 2.4.

Table 2

The re-adsorption efficiency ($E_{\text{re-ads}}$) was determined as follows (Elias et al., 2019):

$$E_{\text{re-ads}} / \% = \left(\frac{Q_{\text{re-ads,max}}}{Q_{\text{max}}} \right) \times 100 \quad (8)$$

where, $Q_{\text{re-ads,max}}$ (mg g^{-1}) is the maximum adsorption capacity of **C1** determined after desorption.

The value of $Q_{\text{re-ads,max}}$ was obtained as follows (Elias et al., 2019):

$$Q_{\text{re-ads}} / (\text{mg g}^{-1}) = \frac{\left[(w_{\text{C1,M}} - w'_{\text{C1}})(1 - E_{\text{des}}/100) \right] - [(C - C_e)V]}{w'_{\text{C1}}} \quad (9)$$

3. Modeling of the adsorption data

3.1. Monocomponent adsorption

The data for adsorption of Cu(II) and oxyanions of Cr(VI) on **C1**, as a function of contact time, were modeled using pseudo-first order (Lagergren, 1898) and pseudo-second order models (Ho and McKay, 1999). The mechanism involved in the adsorption of Cu(II) and oxyanions of Cr(VI) on **C1** was investigated using the intraparticle diffusion (IPD) (Weber and Morris, 1963) and Boyd et al. (1947) models. The data for adsorption of oxyanions of Cr(VI) and Cu(II) on **C1**, as a function of initial solute concentration, were modeled using the Langmuir (1918), Sips (1948), and Redlich and Peterson (1959) models.

Microcal OriginPro® 2015 software was used to perform nonlinear regression (NLR) analysis of the monocomponent adsorption data and to estimate the parameters of the kinetic and equilibrium models. The reduced chi-square (χ^2_{red}) and residual sum of squares (RSS) error functions were used.

The equations of the kinetic and equilibrium models as well as the error functions can be found in the Supplementary Material.

3.2. Bicomponent adsorption

The data for the simultaneous adsorption of Cu(II) and oxyanions of Cr(VI) on **C1**, as a function of contact time, were modeled using the model of Corsel et al. (1986). The data for simultaneous adsorption of Cu(II) and oxyanions of Cr(VI) on **C1**, as a function of initial solute concentration, were modeled using the real adsorbed solution theory model (RAST) (Costa et al., 1981; Myers, 1983; Talu and Zwiebel, 1986). The equations of the Corsel and RAST models were those reported by Teodoro et al. (2017; 2018).

MATLAB[®] 2010a software (Mathworks Inc., Massachusetts) was used to model the bicomponent adsorption data and estimate the parameters of the kinetic and equilibrium models. The *RSS* error function was used. The computational methods used to solve the equations of the Corsel et al. (1986) and RAST (Costa et al., 1981; Myers, 1983; Talu and Zwiebel, 1986) models were those reported by Teodoro et al. (2017; 2018).

4. Results and discussion

4.1. Synthesis and characterization of C1

Figure 1 shows the synthesis scheme for preparation of **C1** from the reaction between chitosan and pyridine-2-carbaldehyde. It involved only one step and used ethanol as a green solvent. This synthesis was first reported by our research group (Goncalves et al., 2018). The characterization of the chitosan and **C1** by Fourier transform infrared (FTIR) and SS ¹³C NMR spectroscopies were reported by Goncalves et al. (2018).

The C, H, and N elemental analysis of the materials showed that the chitosan and **C1** presented carbon, hydrogen, and nitrogen contents of 41 ± 1 and $49 \pm 1\%$, 7.4 ± 0.2 and $6.2 \pm 0.2\%$, and 7.0 ± 0.2 and $9.0 \pm 0.2\%$, respectively. The contents of carbon and nitrogen increased, while the content of hydrogen decreased, after modification of the chitosan with pyridine-2-carbaldehyde ($C = 67.3\%$, $H = 4.71\%$, $N = 13.1\%$). This indicated that the introduction of pyridine moiety on the biopolymer chain was successfully accomplished.

The nitrogen atoms of the imine, pyridine, and remaining amine groups are involved in the adsorption interaction with both species, Cu(II) and Cr(VI), as will be discussed in section 4.2.

Figure 1

The pH of zero charge (pH_{PZC}) of **C1** was determined by the convergence point of three curves of pH (pH_i of 3.00, 6.00, and 11.00) plotted against the **C1** concentration ($w\ v^{-1}$) (Figure not shown), obtaining a value of 7.6 ± 0.8 . At $pH < pH_{PZC}$, the surface of **C1** is positively charged, due to protonation of the nitrogen atoms of imine, pyridine, and remaining amine groups not modified with pyridine-2-carbaldehyde. Therefore, it is expected that the adsorption of anionic species, such as $HCrO_4^-$, CrO_4^{2-} , and $Cr_2O_7^{2-}$, should be favored at $pH < pH_{PZC}$. Contrarily, the adsorption of cationic species, such as Cu^{2+} and $CuOH^+$, should be favored with increase of the pH, with the nitrogen atoms of the imine, pyridine, and remaining amine groups being deprotonated, hence decreasing the positive charge of the **C1** surface, as will be discussed in subsection 4.2.1.

Figure 2 presents SEM images of the chitosan and **C1** at $60\times$ and $3,000\times$ magnifications. As can be seen in Figures 2a and 2b ($60\times$ magnification), the physical aspect of the **C1**

particles appeared to be unchanged after chemical modification of the chitosan with pyridine-2-carbaldehyde. However, the SEM images at 3,000× magnification (Figures 2b and 2d) revealed that the surface texture of **C1** was significantly different from the chitosan surface texture. The **C1** surface was rougher than the chitosan surface, indicating that it had been chemically modified by the grafting of pyridine-2-carbaldehyde molecules. In addition, the **C1** surface presented some cracks, indicating that the **C1** particles swelled after chemical modification with pyridine-2-carbaldehyde.

Figure 2

The specific surface areas of the chitosan and **C1** were $19 \text{ m}^2 \text{ g}^{-1}$, the average diameter of micropores were $20 \text{ \AA}$ while the maximum pore diameters were 444 and $595 \text{ \AA}$, respectively. Therefore, chitosan and **C1** also present meso and macropores, respectively. These results showed that the chemical modification of chitosan with pyridine-2-carbaldehyde did not change the specific surface area of **C1**, compared to the non-modified chitosan. Contrarily, the maximum pore diameter increased after modification of the chitosan. To know the distribution of micro, meso, and macropores is important for the evaluation of ion diffusion and ion transportation process from the solution bulk to porous structure of the **C1** adsorbent (subsections 4.2.2 and 4.3.2).

The average particle size was 0.5 mm and no disintegration or swelling of the **C1** particles was observed during the adsorption experiments described in the following sections.

4.2. Monocomponent adsorption of Cu(II) and oxyanions of Cr(VI) on C1

4.2.1. Adsorption of Cu(II) and oxyanions of Cr(VI) on C1, as a function of solution pH

Figure 3a shows the changes in equilibrium adsorption capacity (q_e), as a function of solution pH, for the adsorption of Cu(II) and oxyanions of Cr(VI) on **C1**.

Figure 3

At low pH ($\text{pH} < 3.5$), the nitrogen atoms of imine, pyridine, and remaining amine groups on **C1** ($\text{pH}_{\text{PZC}} = 7.6 \pm 0.8$) are protonated ($\text{p}K_{\text{a,imine}} = 5-7$, $\text{p}K_{\text{a,pyridine}} = 5.2$), so Cu(II) adsorption was not observed (Figure 3a). From pH 4.0, the value of q_e for Cu(II) adsorption augmented with increasing solution pH up to pH 5.5, because the nitrogen atoms of the imine, pyridine, and remaining amine groups became deprotonated as the solution pH increased. This enabled interaction between the lone electron pairs of nitrogen atoms and the Cu(II) ions (Figure 1b, **C1**-Cu²⁺). The adsorption of Cu(II) was not evaluated at pH higher than 5.5, due to the formation of hydrolyzed Cu(II) species, such as Cu(OH)⁺ and Cu(OH)₂ (Eqs. (17)-(20)).

Cr(VI) can form various species in aqueous solution, such as H₂CrO₄, HCrO₄⁻, CrO₄²⁻, and Cr₂O₇²⁻, depending on the total Cr(VI) concentration, pH, and ionic strength (I) of the solution. Supplementary Figure 1 presents graphs of the fraction of Cr(VI) species, as a function of solution pH from 0 to 10, for total Cr(VI) concentrations of 0.77 and 3.85 mmol L⁻¹. At a total Cr(VI) concentration of 0.77 mmol L⁻¹ ($I = 0.05 \text{ mol L}^{-1}$), the HCrO₄⁻ species (fraction of ~0.9) predominates over the Cr₂O₇²⁻ species (fraction of ~0.1) in the pH range from 1 to 5. At pH 1.0, the HCrO₄⁻ species (fraction of ~0.85) still predominates over Cr₂O₇²⁻ (fraction of ~0.10) and H₂CrO₄ (fraction of ~0.05). Contrarily, as the solution pH increased from 5 to 8, the CrO₄²⁻ fraction increased from ~0.10 to 1.0, predominating over HCrO₄⁻ (which decreased from ~0.9 to 0) and Cr₂O₇²⁻ (which decreased from ~0.1 to 0).

At low pH ($\text{pH} < 4$), the nitrogen atoms of the imine, pyridine, and remaining amine groups on **C1** are protonated, resulting in strong electrostatic attraction between the positively charged **C1** surface and the negatively charged oxyanions of Cr(VI) (HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$) (Figure 1b). This explains the higher value of q_e for Cr(VI) adsorption at pH 3.5 (Figure 3a). At pH lower than 3.5, competition between HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ for **C1** surface sites, together with repulsive lateral interactions between adsorbed Cr(VI) species, could have contributed to decreasing the value of q_e for Cr(VI) adsorption. Anions with higher charge density and multivalent anions are more strongly adsorbed by electrostatic attraction (Lv et al., 2006). The charge/radius (Z/r) ratio of $\text{Cr}_2\text{O}_7^{2-}$ (2/2.92) (Haynes et al., 2014) is higher than that of HCrO_4^- (1/2.42) (Motzer, 2004), suggesting that $\text{Cr}_2\text{O}_7^{2-}$ is preferentially adsorbed on the **C1** surface in the pH range from 2 to 4, in the presence of HCrO_4^- . As the solution pH was increased from 3.5 to 8, the nitrogen atoms of the imine, pyridine, and remaining amine groups on **C1** were gradually deprotonated, hence decreasing the electrostatic attraction between the **C1** surface and the oxyanions of Cr(VI) (HCrO_4^- , CrO_4^{2-} , and $\text{Cr}_2\text{O}_7^{2-}$). At pH higher than 7 ($\text{pH}_{\text{PZC}} = 7.6 \pm 0.8$), the adsorption of Cr(VI) species (HCrO_4^- and CrO_4^{2-}) was close to zero, because the **C1** surface was almost deprotonated.

Therefore, the subsequent studies of adsorption of Cr(VI) and Cu(II) species on **C1** were carried out at the pH values of maximum adsorption. As pointed out by Wan Ngah et al. (2011), the solubility and swelling properties of raw chitosan are the main existing bottlenecks for its application as an adsorbent. On the other hand, **C1** stability (solubility and swelling) was not affected in the pH range studied. This is an advantage of **C1** in comparison to raw chitosan, which was soluble in the acidic pH values tested in the present study.

4.2.2. Adsorption of Cu(II) and oxyanions of Cr(VI) on C1, as a function of contact time

Figures 3b and 3c show the change in adsorption capacity (q_t), as a function of contact time, for the adsorption of Cu(II) and oxyanions of Cr(VI) on C1, respectively. In Table 3 are presented the kinetic parameters obtained by modeling the adsorption of Cu(II) and oxyanions of Cr(VI) on C1, using the PFO and PSO models, as well as the Boyd and intraparticle diffusion models. The PSO kinetic model provided the best description of the adsorption of oxyanions of Cr(VI) (HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$) and Cu(II) on C1. The values of the R^2 and χ^2_{red} error functions were higher and lower, respectively, comparing the PSO model with the PFO model. In addition, the values of $q_{e,\text{est}}$ (estimated equilibrium adsorption capacity) calculated using the PSO model were closer to the $q_{e,\text{exp}}$ values (experimental equilibrium adsorption capacity) for the adsorption of oxyanions of Cr(VI) and Cu(II) on C1. As can be seen in Figures 3b and 3c, q_e was reached at 240 and 360 min for the adsorption of Cu(II) and oxyanions of Cr(VI) on C1, respectively.

According to Plazinski et al. (2013), the PSO model can be interpreted in terms of surface reaction models or in terms of the intraparticle diffusion model. The first consider that the transfer of adsorbate throughout the solution/solid interface is the slowest step in the entire adsorption process. The second considers that the overall adsorption rate is controlled by the rate of adsorbate diffusion within the pores of the adsorbent (Plazinski et al., 2013). On the other hand, the PFO model can be interpreted considering that the adsorption kinetics is determined by the rate of diffusional transport of a solute (Plazinski et al., 2009) as suggested by Boyd et al. (1947). This model is a film diffusion model represented by an equation with the same analytical form as the PFO model

Table 3

The mechanisms of adsorption of Cu(II) and oxyanions of Cr(VI) on **C1** were evaluated from the Boyd and intraparticle diffusion plots. These graphs are available in the Supplementary Material (Supplementary Figures 2 and 3). The intraparticle diffusion plots for the adsorption of oxyanions of Cr(VI) and Cu(II) on **C1** showed two and three stages, respectively. The straight lines representing the first stages did not intersect the origin ($C \neq 0$), indicating that the adsorption was influenced by the diffusion of the ions through the thin solvent layer surrounding the **C1** particles. Two stages were observed for Cu(II) adsorption, reflecting a shift from film diffusion (first stage) to intraparticle diffusion (second stage), after 10 min.

The Boyd plots for adsorption of Cu(II) and oxyanions of Cr(VI) on **C1** were linear for $f < 0.85$ and presented intercept values close to zero, suggesting that external mass transfer of solute through the thin solvent layer affected the adsorption of both ions on **C1**. The effective diffusion coefficients (D_i) (Table 3) for adsorption of Cu(II) and oxyanions of Cr(VI) on **C1** were of the same order of magnitude ($10^{-11} \text{ m}^2 \text{ min}^{-1}$), with Cr(VI) ions diffusing 4-fold faster than Cu(II) ions from the bulk solution to the **C1** external surface. Although Cr(VI) ions are heavier than Cu(II) ions, the diffusion of Cr(VI) ions was faster than the diffusion of Cu(II) ions. This behavior may be explained by the larger hydrated ion size (α) of the Cu(II) ion ($\alpha_{\text{Cu}^{2+}} = 419 \text{ pm}$, $\alpha_{\text{HCrO}_4^-} = 375 \text{ pm}$, (Nightingale, 1959).

4.2.3. Adsorption of Cu(II) and oxyanions of Cr(VI) on C1, as a function of initial solute concentration

Adsorption isotherms are of fundamental importance for providing relevant information about adsorption systems. The isotherm represents the adsorption behavior of a solute on

an adsorbent, according to increasing solute concentration, at constant temperature and pH. The adsorption isotherm is also used to estimate the maximum adsorption capacity ($Q_{\max}$) of a solute on an adsorbent. Various isotherm models have been proposed for fitting the equilibrium data in the form of a plot of q_e against C_e . Some model equations have two or more adjustable parameters, such as those of the Langmuir (1918), Sips (1948), and Redlich and Peterson (1959) (R-P) models.

Figures 3d and 3e present plots of q_e against C_e for the adsorption of Cu(II) and oxyanions of Cr(VI) on **C1**, respectively. The isotherm models that best described the adsorption of Cu(II) on **C1** were the Langmuir and Sips models. The values of the adjustable parameters obtained by modeling the equilibrium data using the Langmuir, R-P, and Sips models are presented in Table 3. These models presented higher R^2 values and lower χ^2_{red} values (Table 3). The parameter n of the Sips isotherm reflects the heterogeneity of an adsorption system. The value of n for Cu(II) adsorption on **C1** was close to unity, suggesting that the Sips isotherm model could be reduced to the Langmuir isotherm model. The Langmuir model is based on premises that are not valid for the system investigated in the present study. Nevertheless, Langmuir model is as a suitable mathematical descriptor to estimate the maximum adsorption capacity. Aspects related to the heterogeneity of the adsorption sites will be discussed in more in-depth in thermodynamic studies (subsection 4.2.4).

The Sips model provided the best description of the adsorption of oxyanions of Cr(VI) on **C1**, with higher R^2 values and lower χ^2_{red} values (Table 3). Since the value of n was much smaller than unity, the Sips isotherm model could not be reduced to the Langmuir isotherm model for Cr(VI) adsorption.

Considering that Cu(II) and Cr(VI) were adsorbed on the same adsorbent (**C1**), the results suggested that: 1) Cu(II) adsorption occurred on homogeneous sites, and 2) Cr(VI)

adsorption did not occur on homogeneous sites. Hypothesis 1 is compatible with the formation of inner-sphere complexes, which requires a particular electronic configuration of the adsorbent (specific sites) and the adsorbate. Hypothesis 2 is compatible with the adsorption of different Cr(VI) species.

The value of $Q_{\max}$ for adsorption of oxyanions of Cr(VI) on **C1** was 2-fold higher than the value of $Q_{\max}$ for adsorption of Cu(II) on **C1**. A possible explanation for this result is that adsorption of Cu(II) on the **C1** surface may have been occurred by the formation of bidentate inner-sphere complexes with nitrogen atoms of imine and pyridine groups (Figure 1b) (Brown et al., 1995; Sposito, 2008). On the other hand, within the Cr(VI) concentration range studied (0.15-7 mmol L⁻¹), HCrO₄⁻ species prevailed over Cr₂O₇²⁻ species. This suggests the possible formation of outer-sphere complexes between two HCrO₄⁻ species and positively charged nitrogen atoms of imine and pyridine groups (Figure 1b) (Brown et al., 1995; Sposito, 2008).

C1 presented a higher $Q_{\max}$ than other bioadsorbents reported in the literature (Chen et al., 2016; Dong et al., 2010). For example, Chen et al. (2016) used carbonized crofton weed (*Eupatorium adenophorum*) and Dong et al. (2010) used a crosslinked amino starch for Cu(II) and Cr(VI) adsorption from aqueous solutions. Chen et al. (2016) reported $Q_{\max}$ values of 0.19 and 0.44 mmol g⁻¹ for adsorption of Cr(VI) and Cu(II), respectively (pH 5.0, 25 °C). The crosslinked amino starch reported by Dong et al. (2010) was produced by chemical modification of dialdehyde starch with ethylenediamine and presented $Q_{\max}$ values of 0.13 and 0.23 mmol g⁻¹ for adsorption of Cu(II) and Cr(VI), respectively (pH 3.0-5.0, 30 °C) (Dong et al., 2010). In a previous study, Almeida et al. (2016) reported the synthesis of an efficient adsorbent by quaternization of the amine group of chitosan and esterification of -OH groups with EDTA dianhydride. This chitosan derivative

showed $Q_{\max}$ values of 0.698 and 1.91 mmol g⁻¹ for adsorption of Cu(II) (pH 4.5, 25 °C) and Cr(VI) (pH 2.0, 25 °C), respectively. Table 4 shows different adsorbent materials that have been applied for the removal of both Cu(II) and Cr(VI) from aqueous solution.

The Langmuir constant, b , reflected the affinity of the C1 adsorption surface sites for oxyanions of Cr(VI) or Cu(II). The value of b was much higher for adsorption of Cu(II) than for adsorption of Cr(VI), which was in agreement with the hypotheses raised.

As discussed previously, Cr(VI) can form various species in aqueous solution (Supplementary Figure 1), depending on the chemical conditions of the solution. The speciation of Cr also depends on the redox conditions (solution Eh). The reduction of Cr(VI) to Cr(III) can occur under specific conditions that depend on the presence of light irradiation or substances that can promote reduction. For example, Fida et al. (2015) employed a bifunctional Ti-Fe kaolinite composite with adsorption and photocatalytic properties to remove Cr(VI) from water. According to Fida et al. (2015), the reduction of Cr(VI) to Cr(III) was promoted by visible light irradiation, associated with TiO₂ and the Fe(III)/Fe(II) redox cycle. Wang et al. (2020) reported the use of nanoscale Fe⁰ with a cellulose hydrogel coating for Cr(VI) reduction and adsorption. According to Wang et al. (2020), the cellulose hydrogel firstly promoted physical adsorption, transferring Cr(VI) from the solution to the Fe⁰ particles, where it was immobilized by electrostatic attraction. The Cr(VI) was then reduced to Cr(III) by Fe⁰ from the adsorbent.

Nevertheless, in the present study, the results did not indicate the occurrence of reduction of Cr(VI) to Cr(III). This reduction is also strongly dependent on the solution pH, according to the following chemical equation:

Therefore, the reduction of Cr(VI) to Cr(III) consumes H_3O^+ , consequently increasing the solution pH. However, there was no increase of the solution pH in any of the adsorption studies. Furthermore, the absence of change in the behavior of the curves of adsorption capacity for Cr(VI) as a function of contact time (Figure 3c) and equilibrium solute concentration (Figure 3e) provided additional evidence that there was no reduction of Cr(VI) to Cr(III). It should also be noted that the formation of Cr(III) would be observed by the appearance of a green coloration in the solution and on the adsorbent surface after adsorption. This was not observed. Therefore, there was no experimental evidence of the reduction of Cr(VI) to Cr(III), under the experimental conditions studied.

Thermodynamic analysis (subsection 4.2.4) provided further elucidation of the nature of the interactions involved in the Cr(VI) or Cu(II) adsorption on **C1**. For example, the values of $\Delta_{\text{ads}}H$ plotted against q_e , for the adsorption of Cr(VI) on **C1** (Figure 4), were much lower than the values expected for oxidation-reduction processes. Additionally, the energies were of the same order of magnitude as those obtained for Cu(II) adsorption. Therefore, these results support the hypothesis that there was no Cr(VI) reduction.

4.2.4. Adsorption thermodynamics analysis

ITC measurements were performed in order to obtain more information about the nature of the interactions governing the adsorption of Cu(II) and oxyanions of Cr(VI) on **C1**. ITC is a sensitive technique that provides the amount of energy released or absorbed in an isothermal thermodynamic process. Figure 4 shows the curves of $\Delta_{\text{ads}}H$ plotted against q_e , for the adsorption of oxyanions of Cr(VI) and Cu(II) on **C1** at 25 °C.

Figure 4

The adsorption processes of oxyanions of Cr(VI) and Cu(II) on **C1** were exothermic over the range of surface coverage of **C1** studied, changing from -30.3 ± 0.2 to -15.6 ± 0.1 kJ mol⁻¹ for Cr(VI) species and from -30.6 ± 0.6 to -10.8 ± 0.9 kJ mol⁻¹ for Cu(II). The $\Delta_{\text{ads}}H$ values were more negative for oxyanions of Cr(VI) than for Cu(II), indicating that the balance of the interactions involving the adsorption of Cr(VI) species was more favorable. As q_e increased, the adsorptions of oxyanions of Cr(VI) and Cu(II) became less enthalpically favorable, suggesting the existence of heterogeneous adsorption processes in both cases. Additionally, the slopes of the $\Delta_{\text{ads}}H$ versus q_e curves ($d\Delta_{\text{ads}}H/dq_e$) were very different, indicating different interactions for the adsorption of oxyanions of Cr(VI) and Cu(II) on **C1**.

In order to better understand these results, the $\Delta_{\text{ads}}H$ value observed for each q_e value could be considered as the sum of the following independent terms:

$$\Delta_{\text{ads}}H = \Delta_{\text{ads}}H^{\text{C1-M}} + \Delta_{\text{ads}}H^{\text{des}} + \Delta_{\text{ads}}H^{\text{M-M}} \quad (11)$$

where, $\Delta_{\text{ads}}H^{\text{C1-M}}$ is the change in the enthalpy of adsorption (negative) due to the formation of interactions between the metal ion species and the adsorption sites on **C1**; $\Delta_{\text{ads}}H^{\text{des}}$ is the change in the enthalpy of adsorption (positive or negative) associated with the desolvation processes of the metal ion species and the adsorbent surface sites for the formation of inner/outer-sphere complexes; and $\Delta_{\text{ads}}H^{\text{M-M}}$ is the change in the enthalpy of adsorption (positive or negative) associated with the absorption and release of energy when interactions between the metal ion species are formed on the **C1** surface and disrupted in the solution, respectively, during the adsorption process.

At the first adsorbed amount value in the $\Delta_{\text{ads}}H$ versus q_e curves, when the surface coverage and the concentration of the metal ion species in the bulk solvent were low, the

contribution of the $\Delta_{\text{ads}}H^{\text{M-M}}$ term was negligible and the $\Delta_{\text{ads}}H$ values were determined by the magnitudes of the $\Delta_{\text{ads}}H^{\text{C1-M}}$ and $\Delta_{\text{ads}}H^{\text{des}}$ terms. Since the process was exothermic under this condition, there should be an important contribution of the interactions between the **C1** adsorption sites and oxyanions of Cr(VI) or Cu(II), which released energy, because the desolvation of the functional groups containing nitrogen atoms and the metal ion species required a high amount of energy (Marcus, 1987b). Part of the desolvation energy was due to the dehydration of the metal ion species, with the displacement of water molecules from the solvation shells of the ions to bulk solution. Since Cu(II) could form inner-sphere complexes with the lone electron pairs of the nitrogen atoms on **C1**, the displacement of water molecules from the first solvation shell of these ions should result in a more endothermic $\Delta_{\text{ads}}H^{\text{des}}$ term for this metal ion, compared to the oxyanions of Cr(VI), which could form outer-sphere complexes. This could explain the less negative values of $\Delta_{\text{ads}}H$ for Cu(II) adsorption.

As q_e increased, repulsive lateral interactions between the adsorbed ions increased, due to the decreased distance between the adsorbed metal ion species on the **C1** surface, contributing to positive values for $\Delta_{\text{ads}}H^{\text{M-M}}$. At the same time, due to the heterogeneity of the adsorbent surface, the magnitudes of both $\Delta_{\text{ads}}H^{\text{des}}$ and $\Delta_{\text{ads}}H^{\text{C1-M}}$ were changed, contributing to the increase of $\Delta_{\text{ads}}H$ (less negative values).

The **C1** adsorbent possessed different functional groups containing nitrogen atoms (imine, pyridine, and remaining amine groups), which implied the existence of adsorption sites with different adsorption molar enthalpy changes. When the surface coverage increased, adsorption sites with lower adsorption molar enthalpy change were occupied by the ions, increasing the $\Delta_{\text{ads}}H^{\text{C1-M}}$ value. Additionally, for the pH range evaluated, especially pH 5.5, some of the functional groups on **C1** were partially protonated ($\text{p}K_{\text{a,imine}}$

= 5-7, $pK_{a,\text{pyridine}} = 5.2$), which provided a wider variety of functional groups for Cu(II) adsorption. Greater heterogeneity of the **C1** surface for Cu(II) adsorption could explain the higher slope of the $\Delta_{\text{ads}}H$ versus q_e curve for the adsorption of this species.

In order to evaluate the thermodynamically driven forces for the adsorption of the metal ion species and corroborate the hypothesis mentioned previously, adsorption thermodynamic parameters were obtained under the standard conditions. The values of $\Delta_{\text{ads}}G^\circ$, $\Delta_{\text{ads}}H^\circ$, and $T\Delta_{\text{ads}}S^\circ$ were -26 ± 2 , -33.0 ± 0.8 , and -7 ± 3 kJ mol⁻¹ for Cu(II) and -21 ± 3 , -35.2 ± 0.2 , and -14 ± 3 kJ mol⁻¹ for Cr(VI), respectively. For Cr(VI), it was considered that HCrO_4^- predominated over $\text{Cr}_2\text{O}_7^{2-}$ ($\alpha = 375$ pm, $\gamma_e = 0.415$, and $\Delta_{\text{ads}}G^\circ = -23 \pm 3$ kJ mol⁻¹, at pH 3.6), with an equilibrium concentration of 3.85 mmol L⁻¹ and I_e of 0.06 mol L⁻¹ (Supplementary Figure 1b). The values of $\Delta_{\text{ads}}G^\circ$ obtained in the present study were similar to those reported by Almeida et al. (2016) for Cr(VI) (-21 ± 1 kJ mol⁻¹) and Cu(II) (-20 ± 6 kJ mol⁻¹).

The change in the free energy of adsorption ($\Delta_{\text{ads}}G^\circ$) was negative for adsorption of Cu(II) and oxyanions of Cr(VI) on **C1**, indicating that under the standard conditions, the transfer processes of both species from the bulk solution to the adsorbent surface were favorable and that oxyanions of Cr(VI) and Cu(II) were concentrated on the **C1** adsorbent surface under the equilibrium condition. The $\Delta_{\text{ads}}H^\circ$ and $\Delta_{\text{ads}}S^\circ$ parameters were negative, indicating that the adsorption was enthalpically driven and entropically unfavorable. However, the entropy loss for the adsorption of oxyanions of Cr(VI) was much higher. The change in the standard entropy of adsorption is mainly due to the rotational, translational, and electrostatic contributions from the free metal ions in the bulk solution and the ion pairs formed on the **C1** adsorbent surface (Marcus, 1987a). The main change in the entropy of the system arises from *i*) decrease of the degrees of freedom of the metal

ion species, due to their transfer from the bulk solution to the **C1** surface, and *ii*) increase of the degrees of freedom of water molecules when they are released from the solvation shells of the ions and the **C1** surface sites to the bulk solution, because of the formation of inner/outer-sphere complexes. As the $\Delta_{\text{ads}}S^\circ$ value was negative, the entropy gain related to the process of release of water molecules did not exceed the entropy loss related to the process of formation of ion pairs, i.e. inner/outer-sphere complexes on the **C1** adsorbent surface. The lower loss of entropy for Cu(II) adsorption was probably due to the release of a greater number of water molecules more strongly bound to the metal ion solvation shell, for the formation of inner-sphere complexes with the **C1** adsorption sites, as well as the difference associated with the contribution of the rotational entropy of this type of complex (Marcus, 1987a).

4.3. Bicomponent adsorption of Cu(II) and oxyanions of Cr(VI) on C1

The presence of both oxyanions of Cr(VI) and Cu(II) cations in aqueous solution may lead to the formation of CuCrO₄ precipitate. Therefore, the solubility (S , mmol L⁻¹) of CuCrO₄ was calculated using Eq. (12).

$$S = (K_{\text{sp}} \alpha \beta)^{1/2} \quad (12)$$

with,

$$\alpha = \frac{[\text{H}_3\text{O}^+]^2}{K_{\text{a2}} K_{\text{a1}}} + \frac{[\text{H}_3\text{O}^+]}{K_{\text{a2}}} + 1 \quad (13)$$

$$\beta = 1 + \beta_1[\text{HO}^-] + \beta_2[\text{HO}^-]^2 + \beta_3[\text{HO}^-]^3 + \beta_4[\text{HO}^-]^4 \quad (14)$$

where, K_{sp} is the solubility product constant of CuCrO₄ ($K_{\text{sp}} = 3.6 \times 10^{-6}$ (Harris, 2010)), K_{a1} and K_{a2} are the ionization constants of acidic species of Cr(VI) (Eqs. (15)-(16)), and

$\beta_1, \beta_2, \beta_3$, and β_4 are the formation constants of Cu(II)-hydroxy complexes (Eqs. (17)-(20)). Here, the dimerization of chromate to dichromate (Eq. (21)) was not considered, because all the dichromate salts are soluble in water. Bicomponent adsorption studies (presented in the next sections) were performed using pH values and concentrations of Cu(II) and oxyanions of Cr(VI) at which CuCrO_4 precipitation does not occur.

4.3.1. Simultaneous adsorption of Cu(II) and oxyanions of Cr(VI) on C1, as a function of solution pH

Figure 5a presents a graph of q_e plotted against solution pH (from 3.6 to 5.5) for the simultaneous adsorption of Cu(II) and oxyanions of Cr(VI) on C1. If the value of $q_{\text{multi}}/q_{\text{mono}}$ is < 1 , the adsorption of a solute i is disfavored by the presence of a solute j . In contrast, when the value of $q_{\text{multi}}/q_{\text{mono}}$ is > 1 , the adsorption of a solute i is favored by the presence of a solute j . When the value of $q_{\text{multi}}/q_{\text{mono}}$ is 1, the presence of a solute i

does not affect the adsorption of a solute j . The values of $q_{\text{multi}}/q_{\text{mono}}$ (0.6-0.8) for Cr(VI) adsorption from pH 3.6 to 4.5 were lower than unity, showing that the presence of Cu(II) disfavored the adsorption of Cr(VI) on **C1**. However, from pH 5.0 to 5.5, where the CrO_4^{2-} concentration begins to increase, the presence of Cu(II) favored Cr(VI) adsorption ($q_{\text{multi}}/q_{\text{mono}} = 1.5$, at pH 5.0). This was indicative of cooperative adsorption between oxyanions of Cr(VI) and Cu(II). The values of $q_{\text{multi}}/q_{\text{mono}}$ (17.9-1.2) for Cu(II) adsorption from pH 3.6 to 4.5 were higher than unity, showing that the presence of oxyanions of Cr(VI) favored Cu(II) adsorption. This also indicated cooperative adsorption between Cu(II) and oxyanions of Cr(VI). However, from pH 5.0 to 5.5, the presence of oxyanions of Cr(VI) disfavored the Cu(II) adsorption ($q_{\text{multi}}/q_{\text{mono}} = 0.5$, at pH 5.0).

The Cu(II) ions were probably adsorbed on the **C1** surface by the formation of inner-sphere complexes, while oxyanions of Cr(VI) were adsorbed on the **C1** surface by the formation of outer-sphere complexes. These two types of adsorption, known as localized (specific, (Cu(II)) adsorption and delocalized (nonspecific, oxyanions of Cr(VI)) adsorption, allowed the formation of a Stern layer on the **C1** surface. As the solvated Cu(II) ions did not form complexes with oxyanions of Cr(VI) adsorbed on the **C1** surface, and vice-versa, they approached the **C1** surface and were attached by delocalized (nonspecific) adsorption (Sposito, 2008). Therefore, a hypothesis for the cooperative adsorption between oxyanions of Cr(VI) and Cu(II) ions was the formation of a diffuse ion swarm, involving ions fully dissociated from the **C1** surface functional groups and free to approach nearby adsorbed species on the **C1** surface (Sposito, 2008). This type of interaction only involves electrostatic bonding.

The highest simultaneous adsorption capacity (1.96 mmol g^{-1}) for oxyanions of Cr(VI) and Cu(II) was observed at pH 4.5. Therefore, a pH of 4.5 was considered as the optimum for simultaneous adsorption of both solutes on C1.

Figure 5

4.3.2. Simultaneous adsorption of Cu(II) and oxyanions of Cr(VI) on C1, as a function of contact time

The competitive model of Corsel et al. (1986) was adopted to describe the multicomponent adsorption kinetics. Although the PFO and PSO models can be used to model the individual adsorption kinetic curves in a competitive adsorption of metal ions in aqueous solution, these models cannot describe the interactions between ions. On the contrary, the competitive adsorption model developed by Corsel et al. (1986) can be used to model both adsorption kinetic curves simultaneously, allowing the understanding of the interactions between ions, i.e., how the adsorption of a species i affects the adsorption of a species j and vice versa. This model includes the intrinsic adsorption ($k(I)^{\text{app}_{\text{on}}}$) and desorption ($k(I)^{\text{app}_{\text{off}}}$) rate constants, which employ the adsorption capacity normalized by the specific area of the adsorbent (I). The model considers the deviations from ideal behavior assumed by the Langmuir model. The kinetic model of Corsel et al. (1986), which is based on first-order reaction kinetics, employs a generalized diffusion equation. It enables inclusion of the effect of the surrounding bulk medium (unstirred layer) (Teodoro et al., 2017).

In previous studies, the Corsel model (Corsel et al., 1986) was employed to model the kinetics of the competitive adsorption of metal cations (Teodoro et al., 2017) and cationic dyes (Fideles et al., 2019) on lignocellulosic materials. Teodoro et al. (2017) studied the

adsorption of the binary systems Cu(II)/Co(II), Cu(II)/Ni(II), and Co(II)/Ni(II) on a carboxylated cellulose derivative. Fidelis et al. (2019) studied the bicomponent adsorption of auramine-O and safranin-T on trimellitated sugarcane bagasse. In both studies, it was concluded that the Corsel model was more suitable for describing bicomponent adsorption systems, because it takes into consideration the competition between the adsorbate species for the adsorbent sites.

The kinetic parameters estimated by the Corsel et al. (1986) are presented in Table 5. Figure 5b presents a graph of $I(t)$ plotted against t . The equilibrium time ($t_{e,multi}$) for simultaneous adsorption of Cu(II) and oxyanions of Cr(VI) was 180 min, while the equilibrium times ($t_{e,mono}$) for monocomponent adsorption of Cu(II) and oxyanions of Cr(VI) were 240 and 360 min, respectively. This suggested that the presence of Cu(II) decreased the equilibrium time for adsorption of oxyanions of Cr(VI), and vice-versa. This result could be an indication of cooperative adsorption between Cr(VI) and Cu(II), due to electrostatic interaction between these ions. A possible cooperative effect in the adsorption of Cu(II) and Cr(VI) was also reported by Shen et al. (2012), who studied the use of amino-functionalized nano-Fe₃O₄ magnetic polymers for adsorption of Cu(II) (100 mg L⁻¹) and Cr(VI) (200 mg L⁻¹) co-existing in a water system. It was concluded that there might be cooperative adsorption processes, although competitive adsorption was observed at higher concentrations of Cr(VI) and Cu(II).

The association constant (K) is related to the affinity of a solute i for the surface adsorption sites of an adsorbent, in the presence of a solute j . The value of K is calculated by the ratio of the adsorption (k_{+1}) and desorption (k_{-1}) rate constants, k_{+1}/k_{-1} (Teodoro et al., 2017). The value of K was higher for Cr(VI) adsorption than for Cu(II) adsorption, indicating that the affinity of the C1 surface sites for oxyanions of Cr(VI), in the presence

of Cu(II), was higher than the affinity of the **C1** surface sites for Cu(II) ions, in the presence of oxyanions of Cr(VI). This behavior was not expected, because the value of b for monocomponent adsorption of Cu(II) ($17 \pm 1 \text{ L mmol}^{-1}$) was much higher than that for monocomponent adsorption of oxyanions of Cr(VI) ($3.8 \pm 0.5 \text{ L mmol}^{-1}$). This confirmed the non-ideal behavior of the adsorption of Cu(II) ions in the presence of oxyanions of Cr(VI), and vice-versa.

The interaction constants α and β for the adsorption and desorption of a solute at an adsorbent, respectively, provide useful information about lateral interactions between adsorbed species in multicomponent systems (Teodoro et al., 2017). Positive values of α indicated that oxyanions of Cr(VI) or Cu(II) ions did not tend to adsorb near other adsorbed species on the **C1** surface, which could be explained by repulsive potentials around species adsorbed on the surface. The value of α was higher for Cr(VI) adsorption than for Cu(II) adsorption, suggesting that oxyanions of Cr(VI) tended not to adsorb near Cu(II) ions already adsorbed on **C1** surface sites. In contrast, positive values of β indicated that oxyanions of Cr(VI) or Cu(II) ions tended to desorb from the **C1** surface when it became progressively saturated. The higher value of β for Cr(VI) adsorption, compared to Cu(II) adsorption, showed that oxyanions of Cr(VI) tended to desorb from the **C1** surface faster than Cu(II) ions. According to Cuypers et al. (1987), the greater the sum of the interaction constants ($\gamma = \alpha + \beta$), the greater the effect of a solute i on the adsorption of a solute j . At pH 4.5, the oxyanions of Cr(VI) had a greater influence on Cu(II) adsorption, compared to the influence of Cu(II) adsorption on the adsorption of oxyanions of Cr(VI). This was in agreement with the results obtained for the simultaneous adsorption (at pH 4.5) of oxyanions of Cr(VI) ($q_{\text{multi}}/q_{\text{mono}} = 0.8$) and Cu(II) ($q_{\text{multi}}/q_{\text{mono}} = 2.6$).

In the bicomponent adsorption, oxyanions of Cr(VI) presented a 3-fold higher effective diffusion coefficient (D_i), compared to Cu(II) ions. The thickness of the unstirred water layer (δ) surrounding the **C1** particles seemed to have a significant effect on the adsorption of Cu(II) ions and oxyanions of Cr(VI) on **C1**. The diameter of a water molecule is 0.278 nm (Zou et al., 2007), so the estimated thickness of the unstirred water layer was ~ 62 water molecules.

Table 5

4.3.3. Adsorption of Cu(II) and oxyanions of Cr(VI) on C1, as a function of initial metal ion concentration

Multicomponent isotherms are useful for describing the adsorption behavior of a mixture of solutes on an adsorbent. These isotherms can also assist in elucidating the influence of a solute i on the adsorption capacity of a solute j , as well as the selectivity of an adsorbent for a specific solute in a mixture of N solutes.

The ideal adsorbed solution theory model (IAST) was proposed by Myers and Prausnitz (1965) for describing the adsorption of a mixture of gases. Later, Radke and Prausnitz (1972) extended this model to the liquid phase. However, IAST is not suitable for describing the adsorption of solutes that present antagonistic or synergistic interactions (non-ideal behavior). The real adsorbed solution theory (RAST) was proposed by Costa et al. (1981). This model is an extension of the IAST model for describing the adsorption of solutes that present non-ideal behavior.

The RAST model was also successfully employed to model experimental equilibrium data for adsorption of the binary systems Cu(II)/Co(II), Cu(II)/Ni(II), and Co(II)/Ni(II) on a carboxylated cellulose derivative (Teodoro et al., 2017) as well as the bicomponent

adsorption of auramine-O and safranin-T on trimellitated sugarcane bagasse (Fideles et al., 2019).

Figure 5c shows the bicomponent isotherm for simultaneous adsorption of Cu(II) and oxyanions of Cr(VI) on **C1**. The values of $Q_{\max}$ for adsorption of Cu(II) and oxyanions of Cr(VI) on **C1** were 1.13 ± 0.01 and 0.98 ± 0.01 mmol g⁻¹, respectively. The sum of the $Q_{\max}$ values was 2.11 ± 0.03 mmol g⁻¹. The sums of the q_e values (at pH 4.5) for mono- and bicomponent adsorption of oxyanions of Cr(VI) and Cu(II), as a function of solution pH, were 1.9 ± 0.1 and 1.96 ± 0.03 mmol g⁻¹, respectively. This indicated that there was a slight increase in the total adsorption capacity for bicomponent adsorption, compared to monocomponent adsorption.

The bicomponent isotherm profiles showed that the q_e values for adsorption of Cu(II) and oxyanions of Cr(VI) on **C1** increased progressively with increasing equilibrium Cr(VI) and Cu(II) concentrations, until reaching a plateau.

Figure 6a shows plots of $q_{e,\text{exp}}$ against $q_{e,\text{est}}$ for simultaneous adsorption of Cu(II) and oxyanions of Cr(VI) on **C1**. The results indicated that the RAST-Sips model provided better prediction of the adsorption of oxyanions of Cr(VI) ($R^2 = 0.987$, $\chi^2 = 0.296$, $RSS = 0.057$), compared to the adsorption of Cu(II) ions ($R^2 = 0.924$, $\chi^2 = 1.139$, $RSS = 0.292$). The RAST model assumes deviations from ideal behavior for the adsorption of a solute present in a mixture of N solutes, compared to single component adsorption. Therefore, the activity coefficient (γ) was introduced in the RAST model. Figure 6b presents a graph of the experimental values of γ , as a function of reduced spreading pressure (Ψ), for the simultaneous adsorption of oxyanions of Cr(VI) and Cu(II) on **C1**. The values of γ for Cr(VI) and Cu(II) were higher than unity, indicating that the

adsorptions of oxyanions of Cr(VI) and Cu(II) on **C1** deviated from ideal behavior (Erto et al., 2012; Teodoro et al., 2017).

Figure 6c presents a graph of the experimental values of γ_{Cr} , as a function of the experimental values of γ_{Cu} , for the simultaneous adsorption of oxyanions of Cr(VI) and Cu(II) on **C1**. Linear regression of the data resulted in a high R^2 value (> 0.98) and low values of χ^2_{red} (5.76×10^{-5}) and RSS (8.06×10^{-4}), indicating that the Wilson model equations (Wilson, 1964) could be used for estimating the adjustable parameters (c , A_{12} , and A_{21}) (Teodoro et al., 2017).

The values of the adjustable parameters of the Wilson model for simultaneous adsorption of Cu(II) and oxyanions of Cr(VI) on **C1** ($i = 1 = \text{Cu(II)}$ and $j = 2 = (\text{Cr(VI)})$) were $c = 0.8516$, $A_{12} = 1.2432$, $A_{21} = 1.1404$, $R_i^2 = 0.9372$, $R_j^2 = 0.9193$, and $RSS = 0.0127$.

The interaction parameters A_{12} and A_{21} of the Wilson model were used to evaluate the effect of interaction between oxyanions of Cr(VI) and Cu(II) ions. The value of A_{12} was greater than the value of A_{21} , indicating that Cu(II) ions had a greater influence on the adsorption of oxyanions of Cr(VI) on **C1**, compared to the influence of oxyanions of Cr(VI) on the adsorption of Cu(II) ions. This was in agreement with the results obtained for the simultaneous adsorption of Cu(II) ions and oxyanions of Cr(VI), as a function of solution pH.

4.3.4. Energy dispersive X-ray spectroscopy (EDX)

Figure 7 presents SEM-EDX images of the **C1** surface loaded with Cu(II), oxyanions of Cr(VI), or both. Figures 7a and 7b show that the distributions of adsorbed Cr(VI) and Cu(II) ions along the **C1** surface were not homogeneous. This was confirmed by EDX microanalysis along lines with length of 1500 μm , drawn on the **C1** samples loaded with

Cr(VI) or Cu(II) ions (Supplementary Figure 4). The concentrations of Cu(II) ions or oxyanions of Cr(VI) on the **C1** surface were not constant along the line. Figure 7c shows an SEM-EDX image of the **C1** surface loaded with both Cr(VI) and Cu(II) ions present in an equimolar mixture, revealing non-uniform distributions of Cr(VI) and Cu(II) ions along the **C1** surface. In addition, there appeared to be a number of vacant adsorption sites on the **C1** surface loaded with both Cr(VI) and Cu(II) ions, when compared to SEM-EDX images of **C1** loaded with either Cr(VI) (Figure 7a) or Cu(II) (Figure 7b) ions. Since the total adsorption capacity of **C1** for Cr(VI) and Cu(II) ions did not decrease (as pointed out in Section 4.3.3), this was suggestive of cooperative adsorption between oxyanions of Cr(VI) and Cu(II) on **C1**. This was in agreement with the hypothesis discussed in Section 4.2.2, concerning the formation of a diffuse ion swarm.

Figure 7

4.4. Desorption and reuse of spent adsorbent

In Table 3 are presented the E_{des} values for the desorption of oxyanions of Cr(VI) and Cu(II) from **C1** using aqueous solutions of Na_2CO_3 (1.0 mol L^{-1}) and triethylenetetramine (0.01 mol L^{-1}), respectively. The value of E_{des} for Cu(II) (~96%) was higher than for Cr(VI) (~49%). The Cu(II) ions were almost completely desorbed from **C1**, because the complex formed between Cu(II) and triethylenetetramine (trien) is highly stable. Transition metals such as Cu(II) bind to the amine functions, forming polydentate complexes of high stability (Navarro et al., 2001). The formation constant (K_1) of the trien-Cu(II) complex has a high value, with $\log K_1$ of 20.4 at 25 °C (Dean and Lange, 1999).

The oxyanions of Cr(VI) were only partially desorbed from **C1**, presenting behavior different to that observed for Cu(II) desorption. The desorption of oxyanions of Cr(VI) was expected to occur by ion exchange, since the ions were adsorbed by electrostatic attraction (outer-sphere complexes). The size of HCrO_4^- is 2.42 Å (Sharma and Forster, 1994), while the size of CO_3^{2-} is 1.85 Å (Chen et al., 2012). Although the charge/radius (Z/r) ratio of HCrO_4^- (1/2.42) is higher than that of CO_3^{2-} (2/1.89), monovalent anions are easily exchanged by multivalent anions. Therefore, the use of a desorbent such as carbonate solution should enable the ion exchange of HCrO_4^- by CO_3^{2-} . On the other hand, the partial desorption of oxyanions of Cr(VI) from different adsorbents has been reported to be due to the phenomenon of aging (Kuo and Bembenek, 2008; Moreira et al., 2018). According to Kuo and Bembenek (2008), oxyanions of Cr(VI) freshly loaded onto adsorbents can be easily desorbed.

In Table 3 are presented the values of $E_{\text{re-ads}}$ for re-adsorption of oxyanions of Cr(VI) and Cu(II) on the spent **C1** adsorbent. The value of $E_{\text{re-ads}}$ for Cr(VI) re-adsorption was ~36%. This was expected, due to the low E_{des} value for Cr(VI) desorption from **C1**. After desorption, a significant amount of oxyanions of Cr(VI) remained on the **C1** surface, decreasing the number of free adsorption sites available for re-adsorption of Cr(VI) species. Although the $E_{\text{re-ads}}$ value for Cr(VI) was considered low, this did not prevent the reuse of **C1**, since the material was still able to adsorb oxyanions of Cr(VI). On the other hand, the $E_{\text{re-ads}}$ value for Cu(II) was ~100%, showing that the spent **C1** adsorbent was able to adsorb the same amount of Cu(II) ions as in the first adsorption cycle. This demonstrated the excellent reuse potential of **C1** for the adsorption of cations.

5. Conclusions

The imine and pyridine groups introduced on **C1** were able to adsorb oxyanions of Cr(VI) by the formation of outer-sphere complexes ($\Delta_{\text{ads}}H^{\circ} = -35.2 \pm 0.2$, $T\Delta_{\text{ads}}S^{\circ} = -14 \pm 3$), while Cu(II) ions were adsorbed by the formation of inner-sphere complexes ($\Delta_{\text{ads}}H^{\circ} = -33.0 \pm 0.8$, $T\Delta_{\text{ads}}S^{\circ} = -7 \pm 3$), as shown by the thermodynamic parameters of adsorption. **C1** was able to simultaneously adsorb oxyanions of Cr(VI) and Cu(II) ions in the pH range 3.6-5.5, showing the versatility of this material for water treatment. The maximum adsorption capacities (at pH 4.5) of **C1** for oxyanions of Cr(VI) and Cu(II) ions were 0.98 ± 0.01 and 1.13 ± 0.01 mmol g⁻¹, respectively. Although **C1** was able to adsorb Cu(II) and Cr(VI) simultaneously (at pH 3.6-4.5), better adsorption performance was observed for single solute adsorption, with Q_{max} values of 3.8 ± 0.1 mmol g⁻¹ (at pH 3.6) and 1.84 ± 0.03 mmol g⁻¹ (at pH 5.5) for Cr(VI) and Cu(II), respectively. The reuse of **C1** was investigated, with Cu(II) ions being almost completely desorbed (~96%) and fully re-adsorbed (~100%). For Cr(VI) ions, the desorption was incomplete (~49%), resulting in low re-adsorption (~36%). **C1** was demonstrated to be an excellent adsorbent for cations of Cu(II), while its use for adsorption of oxyanions of Cr(VI) was limited by its partial reuse capacity.

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References

- Abou El-Reash, Y.G., 2016. Magnetic chitosan modified with cysteine-glutaraldehyde as adsorbent for removal of heavy metals from water. *J. Environ. Chem. Eng.* 4, 3835-3847. <https://doi.org/10.1016/j.jece.2016.08.014>.
- Adamczuk, A., Kołodyńska, D., 2015. Equilibrium, thermodynamic and kinetic studies on removal of chromium, copper, zinc and arsenic from aqueous solutions onto fly ash coated by chitosan. *Chem. Eng. J.* 274, 200-212. <https://doi.org/10.1016/j.cej.2015.03.088>.
- Ahmad, M., Manzoor, K., Ikram, S., 2017. Versatile nature of hetero-chitosan based derivatives as biodegradable adsorbent for heavy metal ions; a review. *Int. J. Biol. Macromol.* 105, 190-203. <https://doi.org/10.1016/j.ijbiomac.2017.07.008>.
- Almeida, F.T.R.d., Ferreira, B.C.S., Moreira, A.L.d.S.L., Freitas, R.P.d., Gil, L.F., Gurgel, L.V.A., 2016. Application of a new bifunctionalized chitosan derivative with zwitterionic characteristics for the adsorption of Cu^{2+} , Co^{2+} , Ni^{2+} , and oxyanions of Cr^{6+} from aqueous solutions: Kinetic and equilibrium aspects. *J. Colloid Interf. Sci.* 466, 297-309. <http://dx.doi.org/10.1016/j.jcis.2015.12.037>.
- Anush, S.M., Vishalakshi, B., 2019. Modified chitosan gel incorporated with magnetic nanoparticle for removal of Cu(II) and Cr(VI) from aqueous solution. *Int. J. Biol. Macromol.* 133, 1051-1062. <https://doi.org/10.1016/j.ijbiomac.2019.04.179>.
- ATSDR, 2011. Toxic Substances Portal - Arsenic. CCA -Treated Wood, Division of Toxicology and Human Health Sciences, Atlanta, GA, USA.
- Ayres, R.U., Ayres, L.W., Råde, I., 2003. The Life Cycle of Copper, Its Co-Products and Byproducts, 1st ed. Springer Netherlands.

899 Barrett, E.P., Joyner, L.G., Halenda, P.P., 1951. The Determination of Pore Volume and
 900 Area Distributions in Porous Substances. I. Computations from Nitrogen
 901 Isotherms. J. Am. Chem. Soc. 73, 373-380. <https://doi.org/10.1021/ja01145a126>.

902 Boyd, G.E., Adamson, A.W., Myers, L.S., 1947. The exchange adsorption of ions from
 903 aqueous solutions by organic zeolites. II. Kinetics. J. Am. Chem. Soc. 69, 2836-
 904 2848. <https://doi.org/10.1021/ja01203a066>.

905 Brown, G.E., Parks, G.A., O'Day, P.A., 1995. Sorption at mineral-water interfaces:
 906 Macroscopic and microscopic perspectives, in: Vaughan, D.J., Patrick, R.A.D.,
 907 editors(Eds.), Mineral surfaces. Chapman & Hall, London, pp. 129-183.

908 Brunauer, S., Emmett, P.H., Teller, E., 1938. Adsorption of gases in multimolecular
 909 layers. J. Am. Chem. Soc. 60, 309-319. <https://doi.org/10.1021/ja01269a023>.

910 Chen, J., Song, D., Yang, P., 2016. Study on adsorption of Cu(II)–Cr(VI) binary system
 911 by carbonized *Eupatorium adenophorum*. Sep. Sci. Technol. 51, 749-758.
 912 <https://doi.org/10.1080/01496395.2015.1131720>.

913 Chen, J., Song, Y., Shan, D., Han, E.-H., 2012. Study of the corrosion mechanism of the
 914 in situ grown Mg–Al–CO₃²⁻ hydrotalcite film on AZ31 alloy. Corros. Sci. 65,
 915 268-277. <https://doi.org/10.1016/j.corsci.2012.08.026>.

916 Choudhary, S., Goyal, V., Singh, S., 2015. Removal of copper(II) and chromium(VI)
 917 from aqueous solution using sorghum roots (*S. bicolor*): a kinetic and
 918 thermodynamic study. Clean Technol. Envir. 17, 1039-1051.
 919 <https://doi.org/10.1007/s10098-014-0860-2>.

920 Corsel, J.W., Willems, G.M., Kop, J.M.M., Cuypers, P.A., Hermens, W.T., 1986. The
 921 role of intrinsic binding rate and transport rate in the adsorption of prothrombin,
 922 albumin, and fibrinogen to phospholipid bilayers. J. Colloid Interf. Sci. 111, 544-
 923 554. [http://dx.doi.org/10.1016/0021-9797\(86\)90058-5](http://dx.doi.org/10.1016/0021-9797(86)90058-5).

924 Costa, E., Sotelo, J.L., Calleja, G., Marrón, C., 1981. Adsorption of binary and ternary
 925 hydrocarbon gas mixtures on activated carbon: Experimental determination and
 926 theoretical prediction of the ternary equilibrium data. *AIChE Journal*. 27, 5-12.
 927 <https://doi.org/10.1002/aic.690270103>.

928 Cuypers, P.A., Willems, G.M., Hemker, H.C., Hermens, W.T., 1987. Adsorption kinetics
 929 of protein mixtures. A tentative explanation of the Vroman effect. *Ann. N.Y.*
 930 *Acad. Sci.* 516, 244-252. <https://doi.org/10.1111/j.1749-6632.1987.tb33045.x>.

931 De Gisi, S., Lofrano, G., Grassi, M., Notarnicola, M., 2016. Characteristics and
 932 adsorption capacities of low-cost sorbents for wastewater treatment: A review.
 933 *Sustainable Materials and Technologies*. 9, 10-40.
 934 <https://doi.org/10.1016/j.susmat.2016.06.002>.

935 Dean, J.A., Lange, N.A., 1999. *Lange's Handbook of chemistry*, 15th ed. McGraw-Hill,
 936 New York, USA.

937 Debye, P., Hückel, E., 1923. Zur Theorie der Elektrolyte. I. Gefrierpunktniedrigung
 938 und verwandte Erscheinungen. *Physikalische Zeitschrift*. 24, 185–206.

939 Divya, K., Jisha, M.S., 2018. Chitosan nanoparticles preparation and applications.
 940 *Environ Chem Lett*. 16, 101-112. <https://doi.org/10.1007/s10311-017-0670-y>.

941 Dong, A., Xie, J., Wang, W., Yu, L., Liu, Q., Yin, Y., 2010. A novel method for amino
 942 starch preparation and its adsorption for Cu(II) and Cr(VI). *J. Hazard. Mater.* 181,
 943 448-454. <https://doi.org/10.1016/j.jhazmat.2010.05.031>.

944 Elias, M.M.C., Ferreira, G.M.D., de Almeida, F.T.R., Rosa, N.C.M., Silva, I.A.,
 945 Filgueiras, J.G., de Azevedo, E.R., da Silva, L.H.M., Melo, T.M.S., Gil, L.F.,
 946 Gurgel, L.V.A., 2019. Synthesis and application of sugarcane bagasse cellulose
 947 mixed esters. Part I: Removal of Co²⁺ and Ni²⁺ from single spiked aqueous

948 solutions in batch mode using sugarcane bagasse cellulose succinate phthalate. J.
 949 Colloid Interf. Sci. 533, 678-691. <https://doi.org/10.1016/j.jcis.2018.08.109>.

950 Erto, A., Lancia, A., Musmarra, D., 2012. A Real Adsorbed Solution Theory model for
 951 competitive multicomponent liquid adsorption onto granular activated carbon.
 952 Micropor. Mesopor. Mat. 154, 45-50.
 953 <http://dx.doi.org/10.1016/j.micromeso.2011.10.041>.

954 Fida, H., Guo, S., Zhang, G., 2015. Preparation and characterization of bifunctional Ti–
 955 Fe kaolinite composite for Cr(VI) removal. J. Colloid Interf. Sci. 442, 30-38.
 956 <https://doi.org/10.1016/j.jcis.2014.11.023>.

957 Fideles, R.A., Teodoro, F.S., Xavier, A.L.P., Adarme, O.F.H., Gil, L.F., Gurgel, L.V.A.,
 958 2019. Trimellitated sugarcane bagasse: A versatile adsorbent for removal of
 959 cationic dyes from aqueous solution. Part II: Batch and continuous adsorption in
 960 a bicomponent system. J. Colloid Interf. Sci. 552, 752-763.
 961 <https://doi.org/10.1016/j.jcis.2019.05.089>.

962 Goncalves, F.J., Kamal, F., Gaucher, A., Gil, R., Bourdreux, F., Martineau-Corcos, C.,
 963 Gurgel, L.V.A., Gil, L.F., Prim, D., 2018. Synthesis, characterisation and
 964 application of pyridine-modified chitosan derivatives for the first non-racemic
 965 Cu-catalysed Henry reaction. Carbohydr. Polym. 181, 1206-1212.
 966 <https://doi.org/10.1016/j.carbpol.2017.12.012>.

967 Harris, D.C., 2010. Quantitative Chemical Analysis, 8th ed. W. H. Freeman, New York,
 968 USA.

969 Haynes, W.M., Lide, D.R., Bruno, T.J., 2014. CRC Handbook of Chemistry and Physics,
 970 95th ed. Taylor & Francis, Boca Raton, FL, USA.

971 Ho, Y.S., McKay, G., 1999. Pseudo-second order model for sorption processes. Process
 972 Biochem. 34, 451-465. [http://dx.doi.org/10.1016/S0032-9592\(98\)00112-5](http://dx.doi.org/10.1016/S0032-9592(98)00112-5).

973 Kumar, R., Barakat, M.A., Taleb, M.A., Seliem, M.K., 2020. A recyclable
 974 multifunctional graphene oxide/SiO₂@polyaniline microspheres composite for
 975 Cu(II) and Cr(VI) decontamination from wastewater. *J. Clean Prod.* 268, 122290.
 976 <https://doi.org/10.1016/j.jclepro.2020.122290>.

977 Kuo, S., Bembenek, R., 2008. Sorption and desorption of chromate by wood shavings
 978 impregnated with iron or aluminum oxide. *Bioresour. Technol.* 99, 5617-5625.
 979 <https://doi.org/10.1016/j.biortech.2007.10.062>.

980 Kurita, K., 2001. Controlled functionalization of the polysaccharide chitin. *Prog Polym*
 981 *Sci.* 26, 1921-1971. [http://dx.doi.org/10.1016/S0079-6700\(01\)00007-7](http://dx.doi.org/10.1016/S0079-6700(01)00007-7).

982 Kyzas, G.Z., Bikiaris, D.N., Mitropoulos, A.C., 2017. Chitosan adsorbents for dye
 983 removal: a review. *Polym. Int.* 66, 1800-1811. <https://doi.org/10.1002/pi.5467>.

984 Lagergren, S.Y., 1898. Zur theorie der sogenannten adsorption gelöster stoffe, kungliga
 985 svenska vetenskapsakademiens. *Handlingar.* 24, 1-39.

986 Langmuir, I., 1918. The adsorption of gases on plane surfaces of glass, mica and platinum.
 987 *J. Am. Chem. Soc.* 40, 1361-1403. <https://doi.org/10.1021/ja02242a004>.

988 Li, R., Liang, W., Huang, H., Jiang, S., Guo, D., Li, M., Zhang, Z., Ali, A., Wang, J.J.,
 989 2018. Removal of cadmium(II) cations from an aqueous solution with
 990 aminothiourea chitosan strengthened magnetic biochar. *J. Appl. Polym. Sci.* 135,
 991 46239. <https://doi.org/10.1002/app.46239>.

992 Li, Y., Xu, C., Qiu, T., Xu, X., 2015. Crosslinked electro-spun chitosan nanofiber mats
 993 with Cd(II) as template ions for adsorption applications. *J. Nanosci. Nanotechno.*
 994 15, 4245-54. <https://doi.org/10.1166/jnn.2015.10197>.

995 Liu, Y., 2009. Is the free energy change of adsorption correctly calculated? *J. Chem. Eng.*
 996 *Data.* 54, 1981-1985. <https://doi.org/10.1021/Je800661q>.

997 Lv, L., He, J., Wei, M., Evans, D.G., Duan, X., 2006. Factors influencing the removal of
 998 fluoride from aqueous solution by calcined Mg–Al–CO₃ layered double
 999 hydroxides. J. Hazard. Mater. 133, 119-128.
 1000 <https://doi.org/10.1016/j.jhazmat.2005.10.012>.

1001 Marcus, Y., 1987a. Solvent release upon ion association from entropy data. J Solution
 1002 Chem. 16, 735-744. <https://doi.org/10.1007/BF00652576>.

1003 Marcus, Y., 1987b. The thermodynamics of solvation of ions. Part 2. The enthalpy of
 1004 hydration at 298.15 K. J. Chem. Soc., Faraday Trans. 1 F. 83, 339-349.
 1005 <https://doi.org/10.1039/F19878300339>.

1006 Moreira, A.L.d.S.L., Pereira, A.d.S., Speziali, M.G., Novack, K.M., Gurgel, L.V.A., Gil,
 1007 L.F., 2018. Bifunctionalized chitosan: A versatile adsorbent for removal of Cu(II)
 1008 and Cr(VI) from aqueous solution. Carbohydr. Polym. 201, 218-227.
 1009 <https://doi.org/10.1016/j.carbpol.2018.08.055>.

1010 Morrison, R.D., Murphy, B.L., 2010. Environmental Forensics: Contaminant Specific
 1011 Guide, 1st ed. Academic Press, USA.

1012 Mosa, K.A., Saadoun, I., Kumar, K., Helmy, M., Dhankher, O.P., 2016. Potential
 1013 biotechnological strategies for the cleanup of heavy metals and metalloids. Front
 1014 Plant Sci. 7, 303-303. <https://doi.org/10.3389/fpls.2016.00303>.

1015 Motzer, W.E., 2004. Chemistry, Geochemistry, and Geology of Chromium and
 1016 Chromium Compounds, in: Guertin, J., Jacobs, J.A., Avakian, C.P., editors(Eds.),
 1017 Chromium(VI) Handbook. 1st edition. CRC Press, Boca Raton, FL, USA, pp. 23-
 1018 92.

1019 Mulligan, C., Bronstein, J.M., 2020. Wilson Disease: An Overview and Approach to
 1020 Management. Neurol. Clin. 38, 417-432.
 1021 <https://doi.org/10.1016/j.ncl.2020.01.005>.

1022 Myers, A.L., 1983. Activity coefficients of mixtures adsorbed on heterogeneous surfaces.
 1023 AICHE Journal. 29, 691-693. <https://doi.org/10.1002/aic.690290428>.

1024 Myers, A.L., Prausnitz, J.M., 1965. Thermodynamics of mixed-gas adsorption. AICHE
 1025 Journal. 11, 121-127. <https://doi.org/10.1002/aic.690110125>.

1026 Navarro, R.R., Tatsumi, K., Sumi, K., Matsumura, M., 2001. Role of anions on heavy
 1027 metal sorption of a cellulose modified with poly(glycidyl methacrylate) and
 1028 polyethyleneimine. Water Res. 35, 2724-2730. [https://doi.org/10.1016/S0043-](https://doi.org/10.1016/S0043-1354(00)00546-7)
 1029 [1354\(00\)00546-7](https://doi.org/10.1016/S0043-1354(00)00546-7).

1030 Neeli, S.T., Ramsurn, H., Ng, C.Y., Wang, Y., Lu, J., 2020. Removal of Cr (VI), As (V),
 1031 Cu (II), and Pb (II) using cellulose biochar supported iron nanoparticles: A kinetic
 1032 and mechanistic study. J. Environ. Chem. Eng. 8, 103886.
 1033 <https://doi.org/10.1016/j.jece.2020.103886>.

1034 Nightingale, E.R., 1959. Phenomenological theory of ion solvation. Effective radii of
 1035 hydrated ions. J. Phys. Chem. 63, 1381-1387.
 1036 <https://doi.org/10.1021/j150579a011>.

1037 Noh, J.S., Schwarz, J.A., 1990. Effect of HNO₃ treatment on the surface-acidity of
 1038 activated carbons. Carbon. 28, 675-682. [https://doi.org/10.1016/0008-](https://doi.org/10.1016/0008-6223(90)90069-B)
 1039 [6223\(90\)90069-B](https://doi.org/10.1016/0008-6223(90)90069-B).

1040 NPIC, 2014. Chromated Copper Arsenate (CCA) Wood Preservatives, Oregon State
 1041 University, Corvallis, OR, USA.

1042 O'Connell, D.W., Birkinshaw, C., O'Dwyer, T.F., 2008. Heavy metal adsorbents
 1043 prepared from the modification of cellulose: A review. Bioresour. Technol. 99,
 1044 6709-6724. <http://dx.doi.org/10.1016/j.biortech.2008.01.036>.

1045 Plazinski, W., Dziuba, J., Rudzinski, W., 2013. Modeling of sorption kinetics: the pseudo-
 1046 second order equation and the sorbate intraparticle diffusivity. *Adsorption*. 19,
 1047 1055-1064. <https://doi.org/10.1007/s10450-013-9529-0>.

1048 Plazinski, W., Rudzinski, W., Plazinska, A., 2009. Theoretical models of sorption kinetics
 1049 including a surface reaction mechanism: A review. *Adv. Colloid Interface Sci.*
 1050 152, 2-13. <http://dx.doi.org/10.1016/j.cis.2009.07.009>.

1051 Purkayastha, D., Mishra, U., Biswas, S., 2014. A comprehensive review on Cd(II)
 1052 removal from aqueous solution. *J Water Process Eng.* 2, 105-128.
 1053 <https://doi.org/10.1016/j.jwpe.2014.05.009>.

1054 Radke, C.J., Prausnitz, J.M., 1972. Thermodynamics of multi-solute adsorption from
 1055 dilute liquid solutions. *AIChE Journal*. 18, 761-768.
 1056 <https://doi.org/10.1002/aic.690180417>.

1057 Rahimi, K., Mirzaei, R., Akbari, A., Mirghaffari, N., 2018. Preparation of nanoparticle-
 1058 modified polymeric adsorbent using wastage fuzzes of mechanized carpet and its
 1059 application in dye removal from aqueous solution. *J. Clean Prod.* 178, 373-383.
 1060 <https://doi.org/10.1016/j.jclepro.2017.12.213>.

1061 Rahman, N., Hossen, M.S., Miah, A.R., Marjub, M.M., Dafader, N.C., Shahnaz, S.,
 1062 Alam, M.F., 2019. Removal of Cu(II), Pb(II) and Cr(VI) ions from aqueous
 1063 solution using amidoximated non-woven polyethylene-g-acrylonitrile fabric. *J.*
 1064 *Environ. Health Sci.* 17, 183-194. <https://doi.org/10.1007/s40201-019-00339-0>.

1065 Ramos, S.N.d.C., Xavier, A.L.P., Teodoro, F.S., Elias, M.M.C., Gonçalves, F.J., Gil,
 1066 L.F., de Freitas, R.P., Gurgel, L.V.A., 2015. Modeling mono- and multi-
 1067 component adsorption of cobalt(II), copper(II), and nickel(II) metal ions from
 1068 aqueous solution onto a new carboxylated sugarcane bagasse. Part I: Batch

1069 adsorption study. Ind. Crop. Prod. 74, 357-371.
 1070 <http://dx.doi.org/10.1016/j.indcrop.2015.05.022>.
 1071 Redlich, O., Peterson, D.L., 1959. A useful adsorption isotherm. J. Phys. Chem. 63, 1024-
 1072 1024. <https://doi.org/10.1021/j150576a611>.
 1073 Sarkar, M., Rahman, A., Islam, J., Ahmed, K., Uddin, M., Bhounik, N., 2015. Study of
 1074 hydrochemistry and pollution status of the Buriganga river, Bangladesh.
 1075 Bangladesh Journal of Scientific and Industrial Research. 50, 123-134.
 1076 <https://doi.org/10.3329/bjsir.v50i2.24353>.
 1077 Sarkar, M., Rahman, A.K.M.L., Bhounik, N.C., 2017. Remediation of chromium and
 1078 copper on water hyacinth (*E. crassipes*) shoot powder. Water Resour. Ind. 17, 1-
 1079 6. <https://doi.org/10.1016/j.wri.2016.12.003>.
 1080 Shanthi, T., Selvarajan, V.M., 2013. Removal of Cr(VI) and Cu(II) Ions from Aqueous
 1081 Solution by Carbon Prepared from Henna Leaves. J. Chem. 2013, 304970.
 1082 <https://doi.org/10.1155/2013/304970>.
 1083 Sharma, D.C., Forster, C.F., 1994. The treatment of chromium wastewaters using the
 1084 sorptive potential of leaf mould. Bioresour. Technol. 49, 31-40.
 1085 [https://doi.org/10.1016/0960-8524\(94\)90170-8](https://doi.org/10.1016/0960-8524(94)90170-8).
 1086 Shen, H., Pan, S., Zhang, Y., Huang, X., Gong, H., 2012. A new insight on the adsorption
 1087 mechanism of amino-functionalized nano-Fe₃O₄ magnetic polymers in Cu(II),
 1088 Cr(VI) co-existing water system. Chem. Eng. J. 183, 180-191.
 1089 <https://doi.org/10.1016/j.cej.2011.12.055>.
 1090 Silva-Yumi, J., Escudey, M., Gacitua, M., Pizarro, C., 2018. Kinetics, adsorption and
 1091 desorption of Cd(II) and Cu(II) on natural allophane: Effect of iron oxide coating.
 1092 Geoderma. 319, 70-79. <https://doi.org/10.1016/j.geoderma.2017.12.038>.

1093 Sips, R., 1948. On the structure of a catalyst surface. J. Chem. Phys. 16, 490-495.
 1094 <http://dx.doi.org/10.1063/1.1746922>.

1095 Sposito, G., 2008. The Chemistry of Soils, ed. Oxford University Press, New York, USA.

1096 Sudha Bai, R., Abraham, T.E., 2003. Studies on chromium(VI) adsorption–desorption
 1097 using immobilized fungal biomass. Bioresour. Technol. 87, 17-26.
 1098 [https://doi.org/10.1016/S0960-8524\(02\)00222-5](https://doi.org/10.1016/S0960-8524(02)00222-5).

1099 Talu, O., Zwiebel, I., 1986. Multicomponent adsorption equilibria of nonideal mixtures.
 1100 AIChE Journal. 32, 1263-1276. <https://doi.org/10.1002/aic.690320805>.

1101 Teodoro, F.S., Adarme, O.F.H., Gil, L.F., Gurgel, L.V.A., 2017. Synthesis and
 1102 application of a new carboxylated cellulose derivative. Part II: Removal of Co^{2+} ,
 1103 Cu^{2+} and Ni^{2+} from bicomponent spiked aqueous solution. J. Colloid Interf. Sci.
 1104 487, 266-280. <http://dx.doi.org/10.1016/j.jcis.2016.10.043>.

1105 Teodoro, F.S., Elias, M.M.C., Ferreira, G.M.D., Adarme, O.F.H., Savedra, R.M.L.,
 1106 Siqueira, M.F., da Silva, L.H.M., Gil, L.F., Gurgel, L.V.A., 2018. Synthesis and
 1107 application of a new carboxylated cellulose derivative. Part III: Removal of
 1108 auramine-O and safranin-T from mono- and bi-component spiked aqueous
 1109 solutions. J. Colloid Interf. Sci. 512, 575-590.
 1110 <https://doi.org/10.1016/j.jcis.2017.10.083>.

1111 Teodoro, F.S., Ramos, S.N.d.C., Elias, M.M.C., Mageste, A.B., Ferreira, G.M.D., da
 1112 Silva, L.H.M., Gil, L.F., Gurgel, L.V.A., 2016. Synthesis and application of a new
 1113 carboxylated cellulose derivative. Part I: Removal of Co^{2+} , Cu^{2+} and Ni^{2+} from
 1114 monocomponent spiked aqueous solution. J. Colloid Interf. Sci. 483, 185-200.
 1115 <http://dx.doi.org/10.1016/j.jcis.2016.08.004>.

1116 Uddin, M.K., 2017. A review on the adsorption of heavy metals by clay minerals, with
 1117 special focus on the past decade. Chem. Eng. J. 308, 438-462.
 1118 <https://doi.org/10.1016/j.cej.2016.09.029>.
 1119 Wan Ngah, W.S., Teong, L.C., Hanafiah, M.A.K.M., 2011. Adsorption of dyes and heavy
 1120 metal ions by chitosan composites: A review. Carbohydr. Polym. 83, 1446-1456.
 1121 <http://dx.doi.org/10.1016/j.carbpol.2010.11.004>.
 1122 Wang, Y., Yu, L., Wang, R., Wang, Y., Zhang, X., 2020. A novel cellulose hydrogel
 1123 coating with nanoscale Fe⁰ for Cr(VI) adsorption and reduction. Sci. Total
 1124 Environ. 726, 138625. <https://doi.org/10.1016/j.scitotenv.2020.138625>.
 1125 Weber, W.J., Morris, J.C., 1963. Kinetics of adsorption on carbon from solution. J. San.
 1126 Eng. Div. 89, 31-60.
 1127 WHO, 1996a. Chromium in Drinking-water. Background document for development of
 1128 WHO Guidelines for Drinking-water Quality: Guidelines for drinking-water
 1129 quality, 2nd ed. World Health Organization, Geneva, Switzerland.
 1130 WHO, 1996b. Copper in Drinking-water. Background document for development of
 1131 WHO Guidelines for Drinking-water Quality: Guidelines for drinking-water
 1132 quality, 2nd ed. World Health Organization, Geneva, Switzerland.
 1133 Wilbur, S., Abadin, H., Fay, M., Yu, D., Tencza, B., 2012. Toxicological profile for
 1134 chromium, ed. US Department of Health and Human Services, Public Health
 1135 Service, Agency for Toxic Substances and Disease Registry, Atlanta, USA.
 1136 Wilson, G.M., 1964. Vapor-Liquid equilibrium. XI. A new expression for the excess free
 1137 energy of mixing. J. Am. Chem. Soc. 86, 127-130.
 1138 <https://doi.org/10.1021/ja01056a002>.

1139 Wu, F.-C., Tseng, R.-L., Juang, R.-S., 2010. A review and experimental verification of
 1140 using chitosan and its derivatives as adsorbents for selected heavy metals. J.
 1141 Environ. Manage. 91, 798-806. <http://dx.doi.org/10.1016/j.jenvman.2009.10.018>.

1142 Wu, R.X., Zheng, G.F., Li, W.W., Zhong, L.B., Zheng, Y.M., 2018. Electrospun chitosan
 1143 nanofiber membrane for adsorption of Cu(II) from aqueous solution: Fabrication,
 1144 characterization and performance. J. Nanosci. Nanotechno. 18, 5624-5635.
 1145 <https://doi.org/10.1166/jnn.2018.15433>.

1146 Xin, S., Zeng, Z., Zhou, X., Luo, W., Shi, X., Wang, Q., Deng, H., Du, Y., 2017.
 1147 Recyclable *Saccharomyces cerevisiae* loaded nanofibrous mats with sandwich
 1148 structure constructing via bio-electrospraying for heavy metal removal. J. Hazard.
 1149 Mater. 324, 365-372. <https://doi.org/10.1016/j.jhazmat.2016.10.070>.

1150 Xu, Q., Wang, Y., Jin, L., Wang, Y., Qin, M., 2017. Adsorption of Cu (II), Pb (II) and Cr
 1151 (VI) from aqueous solutions using black wattle tannin-immobilized
 1152 nanocellulose. J. Hazard. Mater. 339, 91-99.
 1153 <https://doi.org/10.1016/j.jhazmat.2017.06.005>.

1154 Yan, R., Luo, D., Fu, C., Tian, W., Wu, P., Wang, Y., Zhang, H., Jiang, W., 2020.
 1155 Simultaneous Removal of Cu(II) and Cr(VI) Ions from Wastewater by
 1156 Photoreduction with TiO₂–ZrO₂. J Water Process Eng. 33, 101052.
 1157 <https://doi.org/10.1016/j.jwpe.2019.101052>.

1158 Yu, Z., Song, W., Li, J., Li, Q., 2020. Improved simultaneous adsorption of Cu(II) and
 1159 Cr(VI) of organic modified metakaolin-based geopolymer. Arabian J. Chem. 13,
 1160 4811-4823. <https://doi.org/10.1016/j.arabjc.2020.01.001>.

1161 Zou, C., Fothergill, J.C., Rowe, S.W. A "water shell" model for the dielectric properties
 1162 of hydrated silica-filled epoxy nano-composites. 2007 IEEE International
 1163 Conference on Solid Dielectrics, 2007, pp. 389-392.

Figure 1. Scheme illustrating (a) the synthesis of **C1** from chitosan and pyridine-2-carbaldehyde, and (b) the suggested mechanism for removal of Cu(II) and an oxyanion of Cr(VI) (HCrO_4^-) by the **C1** adsorbent.

Figure 2. SEM images of chitosan (a and c) and **C1** (b and d) at 60 $\times$ and 3,000 $\times$ magnifications.

Figure 3. Profiles of the adsorption capacity, as a function of (a) solution pH for adsorption of Cu(II) and Cr(VI), (b) contact time for the adsorption of Cu(II), (c) contact time for the adsorption of Cr(VI), (d) equilibrium solute concentration for adsorption of Cu(II), and (e) equilibrium solute concentration for adsorption of Cr(VI). Experimental conditions: (a) $[\text{Cu(II)}] = [\text{Cr(VI)}] = 0.77 \text{ mmol L}^{-1}$, 130 rpm, 25 $^\circ\text{C}$, 0.2 g L^{-1} **C1**, and 360 min contact time; (b) and (c) ($[\text{Cu(II)}] = [\text{Cr(VI)}] = 0.77 \text{ mmol L}^{-1}$, 130 rpm, 25 $^\circ\text{C}$, 0.2 g L^{-1} **C1**, pH 5.5 for Cu(II), and pH 3.6 for Cr(VI)); and (d) and (e): 130 rpm, 25 $^\circ\text{C}$, 0.2 g L^{-1} **C1**, pH 5.5 and 360 min for Cu(II), and pH 3.6 and 240 min for Cr(VI).

Figure 4. Changes in enthalpy of adsorption, as a function of q_e , for adsorption on **C1** of Cu(II) at pH 5.5 and oxyanions of Cr(VI) at pH 3.6, at 25 $^\circ\text{C}$.

Figure 5. Profiles of the simultaneous adsorption of Cu(II) and Cr(VI) on **C1**: (a) adsorption capacity as a function of solution pH, (b) adsorption capacity normalized by the specific surface area ($I(t)$), as a function of contact time, and (c) equilibrium adsorption capacity (q_e), as a function of equilibrium solute concentration. Experimental conditions: (a) 25 $^\circ\text{C}$, 130 rpm, $[\text{Cu(II)}] = [\text{Cr(VI)}] = 0.77 \text{ mmol L}^{-1}$, 0.2 g L^{-1} **C1**, and 180 min contact time; (b) $[\text{Cu(II)}] = [\text{Cr(VI)}] = 0.77 \text{ mmol L}^{-1}$, 130 rpm, 25 $^\circ\text{C}$, 0.2 g L^{-1} **C1**, pH 5.5 for Cu(II), and pH 3.6 for Cr(VI); and (c) 130 rpm, 25 $^\circ\text{C}$, 0.2 g L^{-1} **C1**, pH 4.5, and 180 min contact time.

Figure 6. Plots for simultaneous adsorption of oxyanions of Cr(VI) and Cu(II) on **C1** of (a) experimental equilibrium adsorption capacity ($q_{e,\text{exp}}$) against estimated equilibrium adsorption capacity ($q_{e,\text{est}}$); (b) experimental activity coefficients of Cu(II) and Cr(VI), as a function of reduced spreading pressure, and (c) experimental activity coefficient of Cr(VI) plotted against experimental activity coefficient of Cu(II). Experimental conditions: (a) $[\text{Cu(II)}]_0 = [\text{Cr(VI)}]_0 = 0.05\text{-}4.0 \text{ mmol L}^{-1}$, 180 min, 25 $^\circ\text{C}$, pH 4.5, 130 rpm, and 0.2 g L^{-1} **C1**.

Figure 7. SEM-EDX images with surface mapping for (a) oxyanions of Cr(VI), (b) Cu(II), and (c) oxyanions of Cr(VI) and Cu(II) adsorbed on **C1** ($[\text{Cu(II)}] = [\text{Cr(VI)}] = 0.77 \text{ mmol L}^{-1}$, 130 rpm, 25 $^\circ\text{C}$, 0.2 g L^{-1} **C1**, 360 and 240 min contact times for individual adsorptions of Cu(II) and Cr(VI), respectively, and 180 min contact time for simultaneous adsorption of Cu(II) and Cr(VI)).

Figure 1.

Figure 2a

Figure 2b

Figure 2c

Figure 2d

Figure 3a

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1223 Figure 3e

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1225 Figure 4

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1227 Figure 5a

Figure 5b

Figure 5c

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1239 Figure 7a

Figure 7b

Figure 7c