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Performance of Oxalic Acid-Chitosan/Alumina Ceramic Biocomposite for the Adsorption of a Reactive Anionic Azo Dye

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Abstract

A biocomposite system was developed and tested for the removal of the azo dye Reative Red (RR195) from wastewater. The biocomposite was synthesized using ceramic particles containing 75% alumina which were coated using chitosan crosslinked with oxalic acid. The biocomposite showed high performance at low pH (maximum adsorption capacity= 345.3mg.g⁻¹ at pH=2). The physico-chemical and structure characteristics of the matrix were evaluated by Z-potential, FTIR-ATR, SEM-EDS, DRX and porosity. Langmuir sorption isotherm and Pseudo Second order model gave the best fit. The electrostatic interaction between RR195 (due to the sulfonate groups) and the free amino groups of chitosan, enabled successive desorption/regeneration cycles. The maximum removal percentage (>80%) occurred at pH=2 due to the crosslinking effect. Experiments at different temperatures allowed the calculation of thermodynamic parameters (ΔG , ΔS , ΔH); adsorption was spontaneous, exothermic and enthalpy controlled. The presence of inorganic ions ($\text{NO}_3^- > \text{Cl}^-$) was analyzed during the adsorption process. This novel biocomposite can be applied as a cost-effective and environmentally friendly adsorbent for anionic azo dye removal from wastewater. The application of chitosan crosslinked with oxalic acid as a coating of the ceramic support enhanced the adsorption capacity and enabled its use under acidic conditions without solubilization.

Key words

Biocomposite; Cross-linked Chitosan; Dye adsorption; Alumina Ceramic

1. Introduction

The global production of dyes reaches nearly 800,000 tons per year (Manzoor and Sharma 2020). According to estimates, in the textile industry around 100 tons of dyes are discharged due to the coloring of fibers, which generates a great environmental problem (Yagub et al. 2014). The wastewater containing these pollutants directly affects the photosynthetic capacity of aquatic plant

39 species. Additionally the chemical structure of the dyes contributes to a high level of organic matter
40 content negatively affecting the water quality (Crini 2006).

41 More than 10,000 dyes are used in the textile industry, from these 70% are azo dyes (Hassaan
42 and Nemr 2017). The presence of azo-reactive dyes cause human health problems being
43 responsible for mutagenesis and leading to several pathologies such as carcinogenesis, respiratory
44 deficiency and jaundice (Alver and Metin, 2012; Vakili et al., 2014) . Structurally, azo dyes are ionic
45 molecules consisting of a chromophore (azo group, $-N=N-$) and sulfonate groups ($-SO_3^-$)
46 (Hunger, 2003, Hassaan and Nemr, 2017).

47 Adsorption is applied for dye removal of wastewater (Crini and Badot 2008); it is highly used due
48 to the facility of full-scale operation, in addition, different inexpensive materials with low toxicity levels
49 can be used as adsorbents (Crini et al. 2019). The introduction of efficient sorbents as biocomposite
50 materials is an alternative to conventional adsorbents. Biocomposite sorbents are heterogeneous
51 systems containing two or more constituents that produce a synergistic effect by improving their
52 adsorption capacity, therefore these materials are used in the water purification technologies
53 (Srinivasan and Viraraghavan, 2010). In order to formulate biocomposite sorbents, two types of
54 materials are necessary: an inorganic support and a biodegradable active component. A widely used
55 biopolymer is chitosan (Ch) because it has proven to be an effective adsorbent (Crini 2015) .

56 Ch is a nitrogenous (amino-based) polysaccharide (poly- β -(1 $\rightarrow$ 4)-2-amino-2-deoxy-D-glucose);
57 this biopolymer is non-toxic obtained from chitin, formed by de-acetylated units (β -(1-4)-D-
58 glucosamine) and acetylated units (N-acetyl-D-glucosamine). Ch is characterized for its a natural
59 poly-cationic, this is due to the existence of structurally de-acetylated units that generate free amino
60 groups (NH_3^+) (in acidic conditions); this property allows chitosan to be used for the treatment of
61 wastewater (Crini and Badot 2008). The protonated amino groups of Ch allow the adsorption of dyes
62 by an electrostatic attraction mechanism (Crini and Badot 2008). Pérez-Calderón et al.,(2018)
63 reported the use of chitosan coacervated hydrogels (CP) for the adsorption of the azo dye Reactive
64 Red 195 (RR195) demonstrating that this material has an excellent removal performance.

65 Wastewater contaminated with dyes is often acidic enabling the solubilization of chitosan due to
66 the protonation of the amine groups, therefore biopolymer modification using cross-linking agents
67 can usually circumvent the problem of instability at low pH (Crini et al. 2019). Covalent cross-linking
68 agents have been used, in particular glutaraldehyde and epichlorhydrin (Crini et al. 2019), although
69 these compounds generate high performance adsorbent materials but they are highly toxic (Leung
70 2001) therefore their application in the treatment of wastewater is impractical. Another type of
71 mechanism is the ionic cross-linking, consisting in the formation of ionic bonds between the amino
72 groups of Ch and the anions of the cross-linking agent (Jóźwiak et al. 2017). The main advantage of
73 chitosan ionic cross-linking is that it generates materials with good chemical stability in acidic media
74 (Crini et al. 2019) and the possibility of functionalizing the biopolymer material in the synthesis of

biocomposite sorbents.

Dicarboxylic acids are used as ionic crosslinkers, in this case the oxalic acid (OA) has been used as a Ch cross-linking agent with low toxicity compared to other types of cross-linkers (Fadzallah et al., 2014; Jóźwiak et al., 2017) due to that OA is a natural compound in some plants (e.i black tea) (Ghosh and Ali 2012). OA has a $pK_a=1.2$, otherwise it dissociates in an aqueous medium into oxalate ions ($-C_2O_4^{2-}$), these conditions cause the Ch to dissolve and reticulate due to electrostatic interactions between the amino and oxalates groups (Fadzallah et al. 2014).

Cross-linked chitosan/oxalic acid hydrogels (ChOxb) have been used for the removal copper (II) (Mi et al. 2015) and Reactive Black 5 (Jóźwiak et al. 2017). Pérez-Calderón et al., (2020) reported the use of ChOxb for RR195 removal, increasing the adsorption capacity with respect to chitosan coacervated hydrogels (CP) (Pérez-Calderón et al. 2018).

Biocomposites matrices constituted by inorganic supports and Ch have been evaluated for the adsorption of synthetic dyes (Zhang et al., 2012; Barik et al., 2019). Biocomposites formulated with pure alumina and Ch crosslinked with oxalic acid have been developed and used for the adsorption of chromium (Boddu et al. 2003; Darjito et al. 2014) and fluorine (Li et al. 2013). There is scarce information concerning the combined use of inorganic materials such as alumina ceramic as a support for chitosan, where the adsorption of azo dyes occurs at the films surface.

The objectives of the present study were: a) to synthesize crosslinked oxalic acid-chitosan/alumina ceramic biocomposite (BChA) for the adsorption of a reactive azo dye (RR195); b) to characterize the morphology and structure of BChA by using instrumental techniques such as Fourier transform infrared spectroscopy with attenuated total reflection (FTIR-ATR), Scanning electron microscopy with energy dispersive X-ray analysis (SEM-EDS), X-ray diffraction, thermogravimetric analysis, mercury inclusion porosimetry and Z-potential; c) to analyze the interactions present between the alumina ceramic support and the ionic cross-linked chitosan film; d) to determine the removal percentage and adsorption capacity in batch adsorption experiments under different experimental conditions; e) to test different equations for describing adsorption kinetics (Pseudo first order, Pseudo second order, Elovich, Intraparticle diffusion, and the mixed surface reaction and diffusion-controlled kinetic model; f) to obtain the adsorption isotherms and to select the appropriate model (Langmuir, Freundlich, Temkin, Redlich-Peterson or Dubinin-Radushkevich) that best fits experimental results using regression analysis and statistical tests; g) to calculate thermodynamic parameters of the sorption process: enthalpy (ΔH), Gibbs free energy (ΔG) and entropy (ΔS); h) to evaluate the effect of different competitive ions present in the solution on the adsorption of the dye; i) to study the desorption process and regeneration of the biocomposite by applying adsorption/desorption cycles; j) to characterize the interactions between the biocomposite material and the RR195 dye, using different techniques: Z-potential; FTIR-ATR, SEM-EDS.

112 2. Materials and methods

113 2.1. Reagents

114 Chitosan was obtained from Sigma-Aldrich (St. Louis, MO, USA) in flake form. Using the
115 potentiometric titration (Broussignac 1968) method the deacetylation degree was 79.5%(SD=2.7)
116 and 75.3%(SD=1.1) determined by FTIR method (Brugnerotto et al. 2001); the viscometric method
117 using an Ostwald capillary viscometer allowed to determine the molecular weight which was
118 $2.83 \times 10^5 \text{ g.mol}^{-1}$.

119 Oxalic acid dehydrated was obtained from BioPack (Buenos Aires, Argentina). Reactive Red 195
120 (RR195) azo dye was provided by Chromeco S.A (Gral. Pacheco, Argentina), its molecular structure
121 is shown Fig.A1 (Supplementary Information).

122 2.2. Synthesis of the absorbent biocomposite material

123 The crosslinked oxalic acid-chitosan/alumina ceramic biocomposite (BChA) was synthesized
124 using ceramic particles alumina (CerPa) and cross-linked chitosan with oxalic acid (OA). Chitosan
125 (Ch) solutions were prepared by mixing Ch flakes with 10% w.v⁻¹ OA solution; two concentrations of
126 Ch solution were prepared (2 and 1% w.v⁻¹). The solutions were stirred for 10 h at 55°C, under these
127 conditions the Ch was ionically cross-linked with the OA (Fadzallah et al. 2014; Mi et al. 2015; Pérez-
128 Calderón et al. 2020).

129 CerPa were formulated with 75 wt% alumina, 20 wt% bauxite, 2 wt% kaolin and 2 wt% talc as
130 support material. CerPa were synthesized using an Eirich High Intensity Mixer Machine (Model
131 R20E, Erich Industrial Ltd., Brazil) where the two process steps, mixing and granulating, are
132 performed in the same equipment.

133 The particles were obtained through batch experiments where the material and water were
134 combined to form a homogeneous mixture and the spherical geometry was achieved by adjusting
135 the speed of the mixing tool. The particles were sieved to obtain diameters between 14 and 16 ASTM
136 meshes (diameters between 1.18-1.40 mm). The CerPa were dried in a conventional oven and
137 calcined at 1500°C for 2 h in a high temperature oven MHI (USA). The lack of RR195 adsorption
138 capacity of CerPa was tested by mixing CerPa and RR195; this experiment corroborated that this
139 individual material did not show adsorption properties.

140 BChA was prepared by coating the CerPa with the cross-linked chitosan solution. The coating
141 capacity of CerPa was directly related to the presence of alumina in the inorganic material; this
142 assumption was corroborated by formulating CerPa without alumina and observing in this case that
143 film-forming capacity was weak and the biopolymer detached from the CerPa after being in contact
144 in a solution. The method described by Boddu et al.,(2003) was implemented with the following
145 modifications: (i) Dried CerPa was activated by stirring the particles in a OA 10% w.v⁻¹ solution for 4
146 h at 25°C, after this step the material was filtered and washed with distilled water; finally the activated
147 CerPa was dried in a vacuum oven LiTekvo model DZF-6030A (LiTekvo Instruments, Minhang

148 District, Shanghai, China) at 70°C and reduced pressure of 100 mmHg to a constant dry weight. (ii)
149 The activated CerPa was mixed with 1% w.v⁻¹ cross-linked chitosan solution under constant shaker
150 stirring at 25°C for 17h. To finish the first coating, the material was dried at 55°C in a Heratherm
151 OMS 60 forced convection oven (Thermo Scientific, Germany) for 24 h. (iii) The second coating was
152 performed by mixing the product of the previous step with 2% w.v⁻¹ cross-linked chitosan solution
153 under constant stirring at 25°C for 17h. The excess of filmogenic solution was removed; in addition
154 it was neutralized with 1 N sodium hydroxide, standing for 3 h for subsequent washing with distilled
155 water until neutral, obtaining the BChA. (iv) BChA was dried at 55°C for 24h in a forced convection
156 oven.

157 The amount of biopolymer in the BChA was determined by weight loss after calcination of the
158 biocomposite at 750°C for 10h using a muffle. The test was performed in triplicate and the results
159 were expressed as a percentage of cross-linked chitosan coating (% CCh) calculated according to
160 Eq.1:

$$161 \quad \%CCh = \frac{W_m - W_c}{W_m} \times 100 \quad (1)$$

162 where W_m is the mass of the dry sample and W_c of the ashes. This information is important to
163 express the amount of adsorbent in terms of the active material during the adsorption process.

164 **2.3. Characterization of bio-composite**

165 Characterization of BChA and the materials used in this work were performed using: Fourier
166 transform infrared spectroscopy with a attenuated total reflection accessory (FTIR-ATR), scanning
167 electron microscopy equipped with energy dispersive X-ray spectrometry (SEM-EDS), X-ray
168 diffraction (XDR), Thermogravimetric analysis (TGA) and Z-Potencial (ZP).

169 FTIR-ART was carried out using a Thermo Nicolet iS10 spectrometer (Thermo Scientific, MA,
170 U.S.A). FTIR Spectra were obtained in %Transmittance mode with 4 cm⁻¹ spectral resolutions and
171 34 scans. ATR accessory consisted of diamond crystal (nominal angle of incidence=42°). XRD was
172 performed on sample powders; diffractograms were obtained using an X-ray diffractometer Philips
173 PW-3710 using Cu-K α radiation and Ni at constant voltage (40 kV, 35 mA). TGA was performed with
174 a thermogravimetric analyzer Rigaku (Thermo Plus EVO2, Osaka, Japan) using N₂ with inert gas.
175 Surface morphology was studied using SEM-EDS, therefore a NeoScope Benchtop JEOL JCM-6000
176 microscope (JEOL, U.S.A) equipped with energy dispersion spectrometry X-ray (EDS) unit JEOL
177 WX-36210DPP was employed.

178 ZP was measured to characterize the surface charges of the material; a nanoparticle analyzer
179 SZ-100-Z (Horiba Instruments Inc., Kyoto, Japan) provided with a laser diode model JUNO 10G-HO
180 (Showa Optronics Co., Ltd., Yokohama, Japan) operating at 532 nm was used. ZP of the material
181 was determined by using a solution containing grinded BChA with an electrode cell (carbon, 6 mm);
182 ZP was reported as the average of five determinations per sample. The isoelectric point (pH_{IEP}) of

the material was established by means of the ZP determined at different pH (Pérez-Calderón et al. 2020).

Microstructural properties such as pore size distribution and specific surface were determined by mercury intrusion porosimetry using a porosimeter Pascal 440 (Thermo Fischer Scientific, Belgica). The mean diameter of the biocomposite and the layer of the cross-linked chitosan was determined by analyzing at least fifty micrographs of BChA using a MZ-10F stereomicroscope with DFC490 camera (Leica Microscopy Ltd, Germany) that were processed using the Image-J software.

2.4. Batch adsorption studies

Batch assays were carried out for the adsorption of RR195 onto the crosslinked oxalic acid-chitosan/alumina ceramic biocomposite (BChA) varying: dosage of the biocomposite (0.43-4.25 g.L⁻¹), pH (2-12) and contact time (0-24 h). Initial concentration (C₀) and dye solution volume were 150 mg.L⁻¹ and 0.02 L, respectively. The initial pH of the dye solution was adjusted with hydrochloric acid and sodium hydroxide 0.1M; an orbital shaker with temperature control, was used to maintain constant conditions during the experiment (125 rev.min⁻¹, 298K). The final dye concentration (C_f) was determined by UV-visible spectrophotometry using Hach DR-2800 spectrophotometer (Loveland, Colorado, USA) at a wavelength of 538 nm.

The results were evaluated by determining the percentage of dye removal (%RE) and the adsorption capacity (Q) at a given time t (Q_t) using Eq. 2 and Eq.3.

$$\%RE = \frac{C_0 - C_f}{C_0} \times 100 \quad (2)$$

$$Q_t = \frac{(C_0 - C_t)}{W} \times V \quad (3)$$

where C_t is the concentration at a given time t, V is the volume of the solution (L) and W is the dose of BChA (g) in terms of the mass of coating using the cross-linked chitosan.

Under equilibrium conditions, the percentage removal (%RE_e) was calculated using Eq.2 by replacing C_f with C_e (equilibrium concentration) and the adsorption (Q_e) was calculated using Eq.3 by replacing C_t with C_e.

2.5. Kinetics, adsorption Isotherms and thermodynamic studies

The assays were carried out using the doses that achieved the best adsorption performances. Moreover, different pH values were tested to evaluate the cross-linking effect of chitosan on the chemical stability of the biocomposite. The equations used for kinetics, isotherm and thermodynamic studies are shown in Table 1 (Eqs. 4 to 12).

Kinetic studies were carried out using different C₀ of RR195 (100, 200 mg.L⁻¹); the dye concentration was determined at different tested times (C_t) in order to calculate Q_t using Eq.3. The kinetic models tested were Pseudo first order (Ps1 Eq.4), Pseudo second order (Ps2 Eq.5), Elovich (Eq.7), Intraparticle diffusion (Eq.8) and the Mixed surface reaction (Eq.9) and diffusion-controlled

217 kinetic model (MSR-DCK Eq.10).

218 The adsorption isotherms studies were tested at different initial concentrations of RR195 ($C_0=70$ -
219 500 mg.L^{-1}), Q_e was determined using Eq.3 by replacing C_t with C_e (equilibrium concentration).
220 Different models (Table 1) were used to evaluate the adsorption equilibrium conditions of the
221 biocomposite (Langmuir (Eq.13), Freundlich (Eq.15), Temkin (Eq.16), Redlich-Peterson (R-P
222 Eq.17), and Dubinin-Radushkevich (D-R Eq.18)).

223 To determine the thermodynamic parameters the sorption isotherms were determined at different
224 temperatures (298, 308 and 318 K). Using Van't Hoff equation (Eq.21) the enthalpy (ΔH) and entropy
225 (ΔS) were calculated. In this case, equilibrium partition constant (K_P) was obtained in order to
226 determine the thermodynamic parameters (Zhang et al. 2014; Tran et al. 2017; Pérez-Calderón et
227 al. 2018, 2020). K_P was estimated as described in Pérez-Calderón et al., (2020, 2018); K_P (Eq.22 in
228 Table 1)) considers the ratio between the activity of the dye adsorbed by the solid (a_s) and the activity
229 of the dye in the solution at equilibrium (a_e). Another possibility is to express K_P in terms of the ratio
230 between activity coefficients (γ); in this case K_P is the ratio between the activity coefficient of the
231 adsorbed dye (γ_s) and the activity coefficient of the dye in the solution at equilibrium (γ_e). If γ is used,
232 the adsorbed dye concentration (C_s Eq.24) and the dye concentration in equilibrium (C_e) must be
233 considered.

234 The activity coefficient (γ) approaches unity when the $(C_s) \rightarrow 0$ and $(C_e) \rightarrow 0$, therefore Eq.22 can
235 be written as Eq.23, plotting $\ln(C_s/C_e)$ vs C_s and extrapolating to $C_e \rightarrow 0$; K_P was calculated at each
236 experimental temperature (Tran et al.,2017). The Gibbs free energy (ΔG) was calculated using
237 Eq.25.

238 **2.6. Regeneration of the Biocomposite and Effect of Competitive Ions**

239 Consecutive cycles of desorption/adsorption were conducted; for the regeneration stage, RR19
240 was desorbed from the BChA used in a previous adsorption experiment with an initial dye
241 concentration of $C_0=200\text{mg.L}^{-1}$. BChA was kept in contact with Milli-Q water (0.020 L) at highly
242 alkaline conditions ($\text{pH}=12$), and the test was performed at a constant agitation and temperature.

243 The regenerated biocomposite material was dried in a forced convection oven at 55°C until
244 constant weight and submitted to adsorption cycles with a RR195 initial concentration of $C_0=200$
245 mg.L^{-1} ($V=0.020 \text{ L}$); in this way three adsorption cycles were completed with two intermediate
246 desorption cycles.

247 The presence of inorganic ions was analyzed in the adsorption process by evaluation of %RE,
248 the tested ions were: Cl^- and NO_3^- , at a concentration of 5 mmol.L^{-1} ; in all cases the solutions were
249 prepared with Milli-Q water. For the assays the C_0 of dye was 200 mg L^{-1} and the salts used were
250 KCl and KNO_3 .

251 **2.7. Statistical analysis**

252 For the batch adsorption assays the equilibrium isotherms, kinetic equations and thermodynamic

parameters were evaluated from linear and non-linear regressions using Origin-Pro 8 software (Origin Lab Corporation, Northampton, Ma., U.S.A.) The goodness of fit was evaluated taking into account the determination coefficient (R^2), mean average perceptual error (MAPE) and chi-square distribution error (χ^2); MAPE and χ^2 were determined with the Eqs.26 and 27 respectively, where y_e is the experimental value and y_p is the value predicted by the model.

$$\text{MAPE} = \frac{\sum |(y_e - y_p)/y_e|}{n} \times 100 \quad (26)$$

$$\chi^2 = \sum \frac{(y_e - y_p)^2}{y_p} \quad (27)$$

The analysis of variance (ANOVA) was conducted to assess significant differences between the samples; means were compared by a Fisher LSD test using a 95% confidence level (significant difference, $P \leq 0.05$).

3. Results and Discussion

3.1. Characterization of the Biocomposite

3.1.1. Surface properties and morphology

The mean diameter of crosslinked oxalic acid-chitosan/alumina ceramic biocomposite (BChA) and alumina ceramic particles (CerPa) was 1.35 mm (SD=0.98) and 1.18 mm (SD=0.35), respectively; these values were obtained from micrographs (Fig.1a-b) of the materials, which were analyzed using Image-J software. Micrographs of the surface morphology of CerPa and BChA obtained by SEM before the adsorption process are shown in Fig.1a-b. SEM micrograph of BChA (Fig.1b) showed the presence of chitosan (Ch) evidenced by a smoother and softer surface of the biocomposite compared with the surface of CerPa (Fig.1a). The surface morphology of the BChA was attributed to the cross-linked Ch film that coated the surface of the ceramic particle. EDS microanalysis spectrum (Fig. 1b) shows that the surface of BChA contained oxygen (O), carbon (C), nitrogen (N) and aluminum (Al). The weight percentage of C in BChA was 28.57%, being this value higher than in CerPa (8.26 %, Fig.1a). In addition the EDS spectrum of BChA showed the presence of N, due to the cross-linked chitosan coating (ChC) on the ceramic material.

Surface microstructural properties were determined by mercury intrusion porosimetry; the pore size diameter determined was 1165.2 nm for CerPa and 394.5 nm for BChA and the specific surface area of these materials were $0.496 \text{ m}^2.\text{g}^{-1}$ and $1.42 \text{ m}^2.\text{g}^{-1}$ for CerPa and BChA, respectively. The increase in the specific surface of the biocomposite is attributed to the cross-linked chitosan coating over the surface (micropores and crevices) of CerPa; similar results were reported Zhang et al., (2012).

The amount of biopolymer that is coating the CerPa was determined by calcination of BChA, and the results were expressed as percentage cross-linked chitosan coating (%CCh). According to Eq.1, %CCh was 1.7% (SD=0.4), this result is important since it is the amount of active sorbent material

287 that generates interactions with dye molecules.

288 **3.1.2. Structural characterization**

289 **3.1.2.1. FTIR-ATR analysis**

290 FTIR-ATR spectra of Ch, OA, CerPa and BChA are observed in Fig.1 c-d. Previous studies
291 describe the results of Ch (Pérez-Calderón et al. 2018, 2020) and OA (Pérez-Calderón et al., 2020
292) spectra; an overview of the bands characteristics is shown in Table A1 (Supplementary
293 information).

294 The characteristic bands of CerPa (Fig.1d) were located: a) at 653 cm^{-1} for the $\text{O} - \text{Al} - \text{O}$ bending
295 (Li et al.,2013); b) at 824 cm^{-1} for the $\text{Al} - \text{O}$ stretching (Jagtap et al.,2011); (c) at 625,1318 and 1096 cm^{-1}
296 characteristics for alumina (Jagtap et al.,2011); in addition, bands between $500\text{-}1000\text{ cm}^{-1}$
297 characteristic for aluminum oxides (Jagtap et al.,2011) were observed.

298 OA was used to bind the alumina of the CerPa and Ch; BChA was synthesized by (i) activation
299 of CerPa with OA and (ii) coating with an ionic modified Ch solution. Different chemical reactions
300 are generated in these stages. In the first stage, the use of OA generates the esterification reaction
301 between the alumina of the CerPa and the oxalate ion, producing the alumina oxalate (III) complex
302 (Boddu et al.,2003; Dobson and McQuillan, 1999); this reaction is represented in Fig.2a. Fig.1d
303 shows in the spectrum of BChA, the presence of the band at 1723 cm^{-1} characteristic of the stretching
304 of $-\text{C} = \text{O}$ group of the ester group confirming the presence of this type of bond.

305 In the second stage, an electrostatic interaction between the alumina oxalate (III) complex and
306 the protonated free amino groups of Ch (Boddu et al.,2003; Darjito et al., 2014) occurs, being this
307 reaction represented in Fig.2b. Results show the chemical interaction between the different
308 constituents (inorganic support and biopolymer) of the new synthesized biocomposite generates an
309 active and stable matrix.

310 The coating of the CerPa was carried out using ionic crosslinked chitosan where the ionic
311 interaction occurs between the carboxylate anions of OA and the protonated amino group of the Ch
312 (Pérez-Calderón et al. 2020).

313 Fig.1d shows the existence of oxalic/chitosan ion cross-linking was evidenced: a) at 1685 cm^{-1}
314 band shift of the symmetric stretching of the carboxylic group originally present at 1698 cm^{-1} of the
315 OA spectrum (Mi et al.,2015); b) at 1517 cm^{-1} the shift and deformation of the band of the amino
316 group originally overlapped at 1550 cm^{-1} , due to the ionic interaction of the protonated amino group
317 of the chitosan molecule with the carboxyl anions of the OA (Fadzallah et al.,2014; Mi et al.,2015;
318 Pérez-Calderón et al.,2020); the reaction is represented in Fig. 2c. Fig.1d, confirms the presence of
319 Ch in BChA; the observed bands were: a) at 2951 cm^{-1} and 2885 cm^{-1} the symmetrical stretching of
320 the $-\text{CH}$ aliphatic and vibration of the $\text{C} - \text{H}$ tensions, respectively; b) at 1065 cm^{-1} and 1027 cm^{-1}
321 the bands correspond to the vibrations of the stretching of the $-\text{C} - \text{OH}$ group characteristic of
322 polysaccharides. In addition, in the spectrum of the BChA, the band at 1397 cm^{-1} , which is

characteristic of the asymmetric stretching of $-C=O$ provided by the OA, and at 659 cm^{-1} , the $-Al-O-Al$ bending, were observed.

3.1.2.2. XDR and TGA analysis

Fig.1e shows the diffractograms for CerPa and BChA. For CerPa it was confirmed that the predominant phase was α -alumina due to the presence of several diffraction peaks at $2\theta=25.59^\circ$, 35.16° , 27.58° , 43.36° , 52.44° , 57.48° , 66.48° and 68.16° (Feret et al.,2000). In addition, small peaks were observed at $2\theta=36.84^\circ$, 59.56° and 64.94° that are of spinel ($MgAl_2O_4$) and at 22.24° due to cristobalite (SiO_2); this was corroborated with results obtained by EDS microanalysis presented in Fig.1a showing the existence of magnesium (Mg) and silicon (Si).

For BChA, the characteristic diffraction peaks of the CerPa were observed. In addition, three new peaks were presented in the positions $2\theta=14.42^\circ$, 24.69° and 30.30° , attributed to the OA/Ch cross-linking (Mi et al. 2015).

The TGA curves of Ch, OA and BChA are shown in Fig.1f. For Ch, a weight loss was observed at 100°C , typical of water release. Weight losses occurred also at 277°C and 642°C , that are characteristic of the total melting and decomposition of the biopolymer (Rekik et al., 017). OA TGA curve showed at 143°C a distinct weight loss attributed to the complete dehydration of the sample (Mi et al. 2015); at 173°C , unstable intermediates such as H_2O , CO and CO_2 are released, and finally at 214°C the total decomposition of the OA is produced.

For BChA an initial weight loss attributed to the release of water is shown; subsequently at 244°C the thermal event is due to the rupture of the electrostatic interaction in the ionic cross-linking of Ch with OA (Mi et al. 2015). The weight loss at 458°C can be attributed to the breakdown of the ester bond of the alumina (III) oxalate complex, and finally at 638°C the total weight loss characteristic of biopolymer fusion occurred. The percentage of total weight loss for the BChA corresponded to 2.04%; this is comparable to the %CCh determined by weight loss the biocomposite from calcination (%CCh=1.7).

3.2. Experimental adsorption conditions: Effect of time, doses and pH

The removal of RR195 using BChA was analyzed and the effect of contact time on Q, testing different sorbent doses is shown in Fig. 3a. Q increased with time achieving asymptotic values at equilibrium (Q_e); at this condition, the amount of dye that is adsorbed is in a dynamic equilibrium state with the amount of dye that is desorbed from the sorbent (Li et al. 2013). Fig. 2a shows that for concentrations ranging between 0.85 and 4.25 g.L^{-1} the equilibrium was achieved after 15h, however using the lowest dose (0.43 g.L^{-1}) this equilibrium condition was not reached even after 25 h. Fig.3b shows %RE_e and Q_e as functions of sorbent doses; non-significant differences in %RE_e, were found for sorbent doses ranging between 0.85 and 4.25 g.L^{-1} , therefore the lowest dose (0.85 g.L^{-1}) was chosen to be used in the subsequent studies, because it led to the highest Q_e .

Fig.3c shows the variation of the %RE_e dye with pH. The pH of the solution influences the degree

of protonation of the sorbent, thus determining the specific charge of the binding sites and the absorption performance of the sorbent (Crini et al. 2019). Pérez-Calderón et al.,(2020, 2018) reported that RR195 adsorption was favored by using chitosan-based sorbent materials, under acidic conditions ($\text{pH} < 4$); this is due to the electrostatic attraction between the positive charged surface of the material by protonation of the free amino groups (NH_3^+) of the chitosan and the sulfonated ($-\text{SO}_3^-$) groups of RR195 (Crini and Badot, 2008).

Fig.3c shows that the highest %RE_e was at $\text{pH}=2$ (%RE_e=91.33 SD=0.15). The ability to adsorb at this very low pH condition can be attributed to the stable structure of the biopolymer gained by the ionic cross-linking of Ch with OA which avoids the solubilization of the biopolymer (Gonçalves et al. 2019). Pérez-Calderón et al., (2020, 2018) reported that the maximum adsorption of RR195 onto ChOxb and CP materials was at $\text{pH}=4$. In comparison, crosslinked chitosan bond to the ceramic material (BChA) showed maximum adsorption at $\text{pH}=2$ resulting in a material with better adsorption performance and mechanical stability. The reasons for this improvement are the larger exposed active surface of the material and the increase of the number of free amino groups allowing them to interact more effectively with the sulfonic groups of the dye (Li et al., 2013).

Since the pK_a of chitosan is 6.5, at $\text{pH} > 6.5$ the amino groups are not likely to be protonated and the adsorption process of the anionic azo dye will not be favored which in turn will decrease the %RE_e. At $\text{pH} > 7$ the existence of electrostatic repulsion forces between the dye anions and the unprotonated surface of the adsorbent causes the further decrease of the %RE_e.

In order to know the isoelectric point (pH_{IEP}) of BChA, the change of Z-potential (ZP) at different pH values before and after removal was studied (Fig 3c). According to the results obtained, the pH_{IEP} was between pH 6-7 before and after adsorption; in this range, the biocomposite has a surface charge near to neutrality. In BChA, the decrease of ZP, after the adsorption shows that the amino groups of the material interact electrostatically with the dye molecules (Pérez-Calderón et al. 2020).

3.3. Interaction between the biocomposite and the RR195 dye

The interaction between the sorbent material (BChA) and the dye was analyzed. Fig.4a shows the micrograph obtained by stereomicroscopy, and the characteristic color of the dye can be observed at the surface of the BChA. The EDS microanalysis spectrum at the surface of the BChA after adsorption (Fig.4b) shows the presence of sulfur (S), corroborating the existence of RR195 interacting with BChA.

Fig.4c shows a cross-section of BChA after adsorption, in which it was possible to observe the dye adsorbed on the coated CerPa from the image analysis using Image-J; the thickness of the attached film was $7.23 \mu\text{m}$ (SD=0.6).

FTIR-ART transmission spectra of the material after adsorption process (BChA+RR195) is shown in Fig.4d; the FTIR-ATR spectra of the RR195 dye is shown in Fig.A2 (Supplementary Information) and the analysis of the main bands is described in Table A2 (Supplementary Information).

The main changes in the BChA+RR195 (after adsorption) spectra with respect to BChA were the presence and changes of the following bands : a) at 3455 cm^{-1} due to high interactions of hydrophilic nature (stretching groups $-\text{NH}$, $-\text{OH}$ and the resonant aromatic structure $=\text{CH}$ of the dye); b) the reduced intensity of the band at 1517 cm^{-1} , can be attributed to electrostatic interactions and/or hydrogen bonds between the amino groups of chitosan and ionic sulfonated groups of the dye (Wang et al. 2016); c) at 1319 cm^{-1} due to the $\text{S}=\text{O}$ vibrations of SO_2 group of the dye molecule; d) at 1612 cm^{-1} corresponding to the vibrational stretching of the aromatic cycle of the dye (this band was originally located at 1617 cm^{-1} in the spectrum of the dye (Fig.A2)).

As was mentioned in section 3.2.1, changes in pH_{IEP} were not observed before and after adsorption, therefore it can be concluded that the interactions were of an electrostatic nature ($\text{NH}_3^+ \cdots \text{SO}_3^-$) between biocomposite and dye (Liu and Zhang 2015; Pérez-Calderón et al. 2018, 2020).

3.4. Adsorption Kinetics

Adsorption kinetics assays were carried out using a dose of 0.85 g.L^{-1} of biocomposite and different initial dye concentrations ($C_0=100, 200\text{ mg.L}^{-1}$). In order to study the effect of pH on the adsorption kinetics, experiments at pH=2 and 4 were conducted. Results of the adsorption kinetics are depicted in Fig.5 a-b, showing that after 17h equilibrium conditions were established for both pH values and C_0 tested; the maximum adsorption performance was reached at pH=2.5 ($Q_e(17\text{h})=203.98\text{ mg.g}^{-1}(\text{SD}=2.4)$ $C_0=200\text{mg.L}^{-1}$), with an increase in the removal capacity compared to pH=4 ($Q_t(17\text{h})=176.01(\text{SD}=0.45)\text{ g.L}^{-1}$ $C_0=200\text{ mg.L}^{-1}$) but not in the rate of the process. Results confirm that under conditions of high acidity (pH=2) protonation of the free amino groups in the matrix generates a significant increase of the adsorption capacity.

Different kinetic equations (Table 1) were tested and corresponding parameters were calculated from non-linear regressions. Experimental results were analyzed by Pseudo First Order (Ps1; Eq.(4)), Pseudo Second Order (Ps2; Eq.(5)), Elovich (Eq.(7)), Intraparticle Diffusion (Eq.(8)) and Mixed Diffusion and Adsorption Model (MSR-DCK; Eq.(9)).

Pseudo first order (Ps1, Eq.4 Table 1) and Pseudo second order equation (Ps2, Eq5 Table 1) are often used to model adsorption kinetics. Elovich's empirical model (Eq.7 Table 1) is used to describe mechanisms of chemisorption. In Eq.7 the constants α_E is the initial adsorption rate related to chemisorption; and β_E is desorption rate constants at the surface coverage. The intraparticle diffusion model (Eq.8 Table 1) describes two regions corresponding to: surface adsorption (rapid external diffusion) and intra-particle diffusion stage (Weber and Morris 1963).

The MSR-DCK model (Haerifar and Azizian 2013) considers that the diffusion of the dye molecules in the sorbent and its adsorption in the active sites of the biocomposite occur simultaneously, the analytical solution (Eq.9 Table 1) was reported by Haerifar and Azizian (2013); where the relative equilibrium uptake (w_{eq}) is $0 \leq w_{\text{eq}} \leq 1$. The effect of diffusion was introduced by the coefficient b (Eq.12 Table 1).

The obtained model parameters are shown in Table 2. Goodness of fit was evaluated using the determination coefficient (R^2), mean average perceptual error (MAPE; Eq.26) and chi-square distribution error (χ^2 ; Eq.27).

Analyzing the fitting of the non-linear regressions R^2 , MAPE and χ^2 ; it can be concluded that Ps2 model provided the best fit with the experimental data.

According to the results of Fig.5 a-b, the experimental Q_e values were 109.92 mg.g⁻¹(SD=1.8) and 203.98 mg.g⁻¹(SD=2.4), at pH=2 for C_0 values of 100 and 200 mg.L⁻¹ respectively; at pH=4 the obtained values of Q_e were 103.53 mg.g⁻¹ (SD=0.13) and 176.01 mg.g⁻¹(SD=0.45), respectively.

According to Eq.6, t/Q_t vs time was plotted for each C_0 . Fig.A3 (Supplementary Information) shows that a completely linear relationship was obtained, so it can be concluded that the removal process is controlled only by adsorption (Haerifar and Azizian 2013). Zhang et al.,(2012) reported that for methyl orange adsorption using unmodified Ch/alumina biocomposite the model that best fit was Ps2.

3.5. Adsorption isotherms

The isothermal equations that have been tested in the present work are shown in Table 1: Langmuir (Eq.13), Freundlich (Eq.15), Temkin (Eq.16), Redlich-Peterson (RP, Eq.17), Dubinin-Radushkevich (DR, Eq.18), in order to know the maximum adsorption capacity. The isotherms were analyzed at pH 2 and 4 and the results are shown in Fig.5 c-d.

Langmuir model (Eq.13 Table 1) assumed that adsorption occurs in a single layer and can occur explicitly at a finite (fixed) number of specific localized sites, without any lateral interaction and without steric hindrance between the adsorbed molecules (Vijayaraghavan et al. 2006). The maximum adsorption capacity (Q_m , mg.g⁻¹) and the affinity of the adsorbate for the adsorbent (K_L , L.mg⁻¹) were calculated (Eq.13). Q_m was evaluated at different temperatures showing that higher temperatures favored the adsorption process

Table 3 shows the results obtained for this model, Q_m at 298K and pH=2 was 333.9 mg.g⁻¹ and for pH=4 the value of Q_m was 254.3 mg.g⁻¹. These results show the advantages of using a crosslinked Ch with OA since it increased the adsorption capacity at a very low pH, because the coating also stabilized the structure of the BChA avoiding biopolymer solubilization. Moreover, according to these results, Q_m is the highest reported for RR195 removal in comparison with other sorbents materials. Table 4 shows different adsorbents used for the removal of RR195 in decreasing order of Q_m . As can be seen, BChA is the material with the best adsorption capacity for the RR195 removal.

Several authors have used the separation factor (R_L) to analyze the results of Langmuir's model. R_L was calculated using the Eq.14 (Table 1) which takes into account the constant (K_L) determined from the non-linear regression of Eq.13 and the initial concentration (C_0). R_L value indicates the adsorption nature to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$) (Zhang et al., 2014); according to the results shown in Table 3 for the different tests the

467 process is favorable.

468 On the other hand, plotting R_L vs C_0 (Fig.A4 a-b; Supplementary Information) the R_L values
469 decreased with respect to the increase of the initial dye concentration, this indicates that the process
470 was favored at high initial dye concentrations (Zhang et al. 2014).

471 Freundlich model considers a heterogeneous adsorption surface of the adsorbent (Freundlich
472 1906). The equation that represent Freundlich's model (Eq.15) is presented in Table 1. The
473 parameters of this model are the adsorption capacity coefficient K_F ($(\text{mg.g}^{-1}) (\text{mg.L}^{-1})^{-1/n}$) and the value
474 of adsorption intensity parameter n (dimensionless) which indicates the favorability of the adsorption
475 (Mckay et al. 1982).

476 Temkin (Temkin and Pyzhev 1940) model is given by Eq.16 (Table 1); $A_t(\text{L.mg}^{-1})$ is the equilibrium
477 constant representing the maximum binding energy and B_t is a coefficient related to the adsorption
478 heat. The R-P model (Redlich and Peterson 1959) combines both Freundlich and Langmuir models
479 and it is an empirical equation that includes three parameters (Eq.17 Table 1), it can be used in a
480 range of concentrations to explain the equilibrium of adsorption in homogeneous or heterogeneous
481 systems. Eq.17 describes this isotherm where, $K_{RP}(\text{L.g}^{-1})$ and $\alpha_{RP}(\text{L.mg}^{-1})$ are the constants of the
482 R-P isotherm and β_{RP} is an exponent with values ranging between 0 and 1; the results of this model
483 are shown in Table 3.

484 D-R model assumes two possible mechanisms (physical or chemical); Eq.18 in Table 1
485 represents this model, where $\epsilon(\text{kJ.mol}^{-1})$ is Polanyi's potential, that is calculated using Eq.19 where
486 R represent the gas constant ($8.314 \times 10^{-3} \text{ kJ.K}^{-1}.\text{mol}^{-1}$) and T the temperature (K). From the value of
487 B_{DR} (determined by regression Eq.18) it is possible to calculate the average free adsorption energy
488 ($E, \text{kJ.mol}^{-1}$) using Eq.20, where E defines the mechanism of adsorption: chemisorption (E is >8
489 kJ.mol^{-1}) or physisorption ($E < 8 \text{ kJ.mol}^{-1}$) (Dubinin and Radushkevich 1947); values of E (Table 3)
490 indicate that the process is governed by physisorption.

491 According to the statistical parameters (R^2 , MAPE and χ^2) shown in Table 3, Langmuir was the
492 model that best fitted the experimental data; Fig.5 c-d shows predicted values in a dashed line.

493 3.6. Thermodynamic parameters

494 To determine the thermodynamic parameters, K_P values were calculated from intercepts obtained
495 from $\ln(C_s/C_e)$ vs C_s plots for each of the temperatures tested (as explained in the section 2.5); the
496 results of the linear regressions are presented in the Fig.6 a-b.

497 According to Eq.21 (Table 1), ΔH and ΔS were determined by plotting $\ln(K_P)$ as a function of T^{-1}
498 (Fig.5-c-d), and the results are shown in Table 4 for pH 2 and 4; these were considered satisfactory
499 because the R^2 of the linear regressions were near 1 (at pH= 2, $R^2=0.99$ and at pH=4, $R^2=0.96$). ΔG
500 was calculated using Eq.25; ΔG values (<0) indicate that RR195 adsorptions is a spontaneous and
501 favorable process and the degree of spontaneity of the reaction decreased with increasing
502 temperature (Zheng et al. 2015).

ΔH Values (<0) implies that the adsorption phenomenon is exothermic. In this case, the absorbed energy generated from the rupture of the bond between the water molecules and the sorbent in the process of desorption of the solvent (water) is less than the total energy released in the formation of the bond between the sorbent and the dye molecules resulting in the release of extra energy in the form of heat (Saha and Chowdhury 2011).

Adsorption ΔH values in the range from 80 to 200 kJ.mol⁻¹ characterize chemical adsorption process (Saha and Chowdhury 2011); according to the results obtained (Table 5) and the nature of colorant-sorbent interactions mentioned in section 3.3, it is possible to conclude that the adsorption process is of physical/chemical nature.

The results for ΔS (<0) indicate that the process is governed by enthalpy, this implies a decrease in the disorder at the solid/liquid interface during the adsorption process which causes the adsorbed dye molecules to escape from the solid to the liquid phase (Saha and Chowdhury 2011).

Similar results of spontaneous and favorable process ($\Delta G < 0$), exothermic ($\Delta H < 0$) and $\Delta S < 0$ were reported for the adsorption of Reactive Red 189 onto epichlorohydrin-crosslinked chitosan beads (Chiou and Li 2003) and adsorption of methyl orange azo dye using unmodified Ch/alumina (Zhang et al. 2012).

3.7. Regeneration and desorption of the biocomposite and effect of competitive ions

Fig.7 shows the results of three adsorption cycles ($C_0=200$ mg.L⁻¹; pH=2) and two desorption cycles (pH=12) of RR195 using BChA. In the desorption stage it was evident that the BChA was capable of being regenerated and used in consecutive cycles of adsorption. The desorption of BChA was achieved by exposure to alkaline medium which deprotonated the amino groups of the biocomposite affecting the electrostatic interactions between the dye and the sorbent material (Crini and Badot 2008)

Using BChA, the time required to complete the first and second desorption cycles was 3h and 1.9 h respectively; these values were shorter than in the case of ChOxb, with desorption times of 15 h and 15.2 h for the first and second cycle respectively (Pérez-Calderón et al. 2020).

In the second and third adsorption cycles Q_e values of 182.9 mg.g⁻¹ (SD=0.04) and 122.5 mg.g⁻¹ (SD=0.18) were reached respectively, indicating a reduction of 5.5% and 36.6% in the adsorption capacity of BChA with respect to the first cycle of adsorption; on the other hand the %RE achieved after the third cycle of adsorption was 52.4%(SD=0.08). These results indicate that BChA is a material that can be regenerated and reused for the adsorption of RR195 while maintaining its structure and activity.

The effect of competitive ions at the tested concentration (5 mmol.L⁻¹) showed that for Cl⁻ and NO₃⁻ the %RE was 83.3 (SD=1.3) and 70.1% (SD=1.0) respectively, indicating that the presence of these ions does not have a pronounced negative effect on the process. In the case of NO₃⁻, the %RM was lower due to the electronegativity of the ions which generates electrostatic interactions between

ions and the protonated amino groups in the BChA affecting the dye removal process (Pérez-Calderón et al. 2020).

4. CONCLUSIONS

Crosslinked oxalic acid-chitosan/alumina ceramic biocomposite (BChA) was synthesized as a novel sorbent material for the removal of an anionic reactive azo dye (RR195) from wastewater. The biocomposite was prepared using ceramic particles containing 75% alumina which were coated with chitosan previously crosslinked with oxalic acid. The physico-chemical and structural characteristics of BChA allowed to identify the presence of cross-linked chitosan in the biocomposite, interacting by electrostatic bonds with alumina (III) oxalate compound, product of the functionalization of the ceramic support.

Batch experiments showed that the maximum removal percentage (>80%) occurs at pH=2 due to the crosslinking effect of the oxalic acid. This result shows that the coating of cross-linked oxalic acid-chitosan improved adsorption performance for RR195 compared to other chitosan-synthesized materials; this improvement is attributed to the increase of exposed free amino groups on the active surface of BChA. Another reason is the stable structure of the chitosan gained by the ionic cross-linking with oxalic acid which avoids the solubilization of the biopolymer in acid medium.

Langmuir equation gave the best fit to the experimental sorption isotherm. The BChA showed a high adsorption capacity (367 mg.g^{-1} at pH=2, 318 K) which is the highest reported for RR195 removal in comparison with other sorbents materials.

The governing adsorption mechanism was the electrostatic interaction between the anionic dye (due to the sulfonate groups) and the free amino groups of the cross-linked chitosan, enabling the successive desorption/regeneration cycles of the biocomposite. The kinetic behavior corresponded to a pseudo second order model. Experiments performed at different temperatures allowed the calculation of the thermodynamic parameters showing that the adsorption process was spontaneous, exothermic and enthalpy controlled.

The presence of different tested anions affected the removal according to $\text{NO}_3^- > \text{Cl}^-$ due to the competing effect for the free amino sites.

The novel biocomposite showed a better stability at low pH and can be applied as a cost-effective and environmentally friendly sorbent for azo anionic dye removal from wastewater. The use of the oxalic acid cross-linked chitosan coating on a ceramic support improved the adsorption capacity compared to other materials and allowed the use of the sorbent in acidic.

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579 **CONSENT FOR PUBLICATION**

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581 **AUTHOR CONTRIBUTIONS**

582 **Peréz-Calderón, John:** Conceptualization, Methodology, Investigation, Formal analysis, Writing-
583 Original Draft & Visualization; **Scian, Alberto; Ducos, Martin:** Methodology, Resources; Data
584 Curation; **Santos, M. Victoria:** Conceptualization, Formal analysis, Methodology, Writing-Review &
585 Editing. **Zaritzky Noemí:** Conceptualization, Methodology, Supervision, Writing-Review & Editing,
586 Project administration, Funding acquisition.

587 **AVAILABILITY OF DATA**

588 The datasets used and/or analysed during the current study are available from the corresponding
589 author on reasonable request.

590 **COMPETING INTERESTS**

591 The authors of the manuscript title ***“Performance of Oxalic Acid-Chitosan/Alumina***
592 ***Ceramic Biocomposite for the Adsorption of a Reactive Anionic Azo Dye”***, certify that
593 they have NO affiliations with or involvement in any organization or entity with any financial
594 interest or non-financial interest in the subject matter or materials discussed in this
595 manuscript.

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717 FIGURES CAPTIONS

718 **Figure 1.** Structural characterization for alumina ceramic particles (CerPa), cross-linked oxalic acid-
 719 chitosan/alumina ceramic biocomposite (BChA), Chitosan (Ch) and Oxalic Acid (OA): SEM surface
 720 morphology and EDS microanalysis spectrum of: **a)** CerPa. **b)** BChA. FTIR-ART transmission
 721 spectra: **c)** Ch, OA. **d)** CerPa, BChA. **e)** X-ray diffraction spectra of CerPa, BChA. **f)** TGA analysis
 722 of Ch, OA and BChA.

723 **Figure 2.** Schematic diagram of the: **a)** Complexation of alumina from the ceramic particle by oxalic
 724 acid reaction. **b)** Electrostatic interaction between the free amino group of chitosan and the alumina
 725 (III) oxalate complex. **c)** oxalic acid cross-linking the chitosan molecule by means of ionic interactions

726 **Figure 3. a)** Effects of time and BChA doses on adsorption capacity (Q) **b)** Equilibrium removal
 727 ($RE_e\%$) and equilibrium capacity (Q_e) as functions of BChA doses **c)** Effect of pH on RE_e and Z
 728 potential before and after adsorption. Different letters in the RE_e and Q_e indicate significant
 729 differences between the samples ($P \leq 0.05$).

730 **Figure 4. a)** Stereomicroscope and SEM micrographs of crosslinked oxalic acid-chitosan/alumina
 731 ceramic biocomposite (BChA) after adsorption of Reactive Red 195 (RR195). **b)** Microanalysis
 732 spectrum EDS of the surface BChA after adsorption of RR195. **c)** Micrograph of the cross-section
 733 after the adsorption process. **d)** FTIR-ART transmission spectra of BChA after adsorption of dye
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735 **Figure 5.** Adsorption kinetics of Reactive Red 195 onto crosslinked oxalic acid-chitosan/alumina
 736 ceramic biocomposite (BChA) at different initial concentrations. **a)** 100 mg.L^{-1} **b)** 200 mg.L^{-1} .
 737 Adsorption isotherms of Reactive Red 195 using BChA at different pH: **c)** pH=2, **d)** pH= 4. Symbols
 738 represent experimental values and dash lines correspond to the fitting of the non-linear regression
 739 using: **a-b)** Pseudo second order (Ps.2 Order) model and **c-d)** Langmuir model.

741 **Figure 6.** Plot of $\ln(C_s/C_e)$ vs. C_s to obtain the partition constant in equilibrium (K_P) for
 742 thermodynamic parameters determination at different pHs: **a)** pH=2, **b)** pH= 4, The lines represent
 743 linear regressions at each temperature. The table inserted in the graph shows the K_P values obtained;
 744 the standard deviation of the values are given between brackets. Plot of $\ln(K_P)$ vs T^{-1} at different
 745 pH: **c)** pH=2, **d)** pH= 4.

747 **Figure 7.** Adsorption/desorption cycles of Reactive Red 195 (RR195) using crosslinked oxalic acid-
 748 chitosan/alumina ceramic biocomposite (BChA).

Figures

Figure 1

Structural characterization for alumina ceramic particles (CerPa), cross-linked oxalic acid-chitosan/alumina ceramic biocomposite (BChA), Chitosan (Ch) and Oxalic Acid (OA): SEM surface

morphology and EDS microanalysis spectrum of: a) CerPa. b) BChA. FTIR-ART transmission spectra: c) Ch, OA. d) CerPa, BChA. e) X-ray diffraction spectra of CerPa, BChA. f) TGA analysis of Ch, OA and BChA.

Figure 2

Schematic diagram of the: a) Complexation of alumina from the ceramic particle by oxalic acid reaction. b) Electrostatic interaction between the free amino group of chitosan and the alumina (III) oxalate complex. c) oxalic acid cross-linking the chitosan molecule by means of ionic interactions

Figure 3

a) Effects of time and BChA doses on adsorption capacity (Q) b) Equilibrium removal (REe%) and equilibrium capacity (Q_e) as functions of BChA doses c) Effect of pH on %REe and Z potential before and after adsorption. Different letters in the %REe and Q_e indicate significant differences between the samples ($P \leq 0.05$).

Figure 4

a) Stereomicroscope and SEM micrographs of crosslinked oxalic acid-chitosan/alumina ceramic biocomposite (BChA) after adsorption of Reactive Red 195 (RR195). b) Microanalysis spectrum EDS of the surface BChA after adsorption of RR195. c) Micrograph of the cross-section after the adsorption process. d) FTIR-ART transmission spectra of BChA after adsorption of dye (BChA+RR195).

Figure 5

Adsorption kinetics of Reactive Red 195 onto crosslinked oxalic acid-chitosan/alumina ceramic biocomposite (BChA) at different initial concentrations. a) 100 mg.L^{-1} b) 200 mg.L^{-1} . Adsorption isotherms of Reactive Red 195 using BChA at different pH: c) pH=2, d) pH= 4. Symbols represent experimental values and dash lines correspond to the fitting of the non-linear regression using: a-b) Pseudo second order (Ps.2 Order) model and c-d) Langmuir model.

Figure 6

Plot of $\ln(C_s/C_e)$ vs. C_s to obtain the partition constant in equilibrium (K_p) for thermodynamic parameters determination at different pHs: a) pH=2, b) pH= 4, The lines represent linear regressions at each temperature. The table inserted in the graph shows the K_p values obtained; the standard deviation of the values are given between brackets. Plot of $\ln(K_p)$ vs T^{-1} at different pH: c) pH=2, d) pH= 4.

Figure 7

Adsorption/desorption cycles of Reactive Red 195 (RR195) using crosslinked oxalic acid-chitosan/alumina ceramic biocomposite (BChA).

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