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Adsorventes alternativos a partir de gelatina recuperada de resíduos de couro e nanotubos de carbono para remoção de contaminantes emergentes

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“Nunca deixe mentes pequenas te convencerem que seus sonhos são grandes demais” (Autor desconhecido)”.

RESUMO

As indústrias de transformação de peles animais em couro são responsáveis pela geração de resíduos sólidos ricos em colágeno. A gelatina é um biopolímero que pode ser obtido a partir da hidrólise do colágeno, e tem se mostrado promissora em estudos envolvendo a produção de adsorventes. Os nanotubos de carbono (CNT's), são utilizados como reforços para matrizes poliméricas, visto que o uso de CNT's puros como adsorvente ocasiona o bloqueio dos filtros industriais, sendo que o processo de separação é difícil. Assim, esse trabalho teve por objetivo o desenvolvimento de esferas compósitas a partir de gelatina recuperada de resíduos de couro curtido ao cromo (RCCC) e CNT's. Para fins de comparação, foram produzidas esferas padrão, contendo apenas a gelatina comercial ou a gelatina RCCC. O método de emulsificação por gotejamento foi empregado no preparo das esferas, com concentração 8% (m/m) das gelatinas comercial e RCCC (m/v), respectivamente, e adições de 0 e 5% (m/m) de CNT's em relação a massa de gelatina. Os adsorventes obtidos foram caracterizados por Microscopia Eletrônica de Varredura (MEV), Espectroscopia no Infravermelho por Transformada de Fourier (FTIR), Termovogravimetria (TGA), Ponto de carga zero (pH_{PZC}), Difração por Raios-X (DRX), e Capacidade de inchaço e de retenção de água também foram determinadas. Os ensaios de adsorção em batelada (equilíbrio, cinético e de dessorção e reúso) foram conduzidos utilizando o corante amarelo tartrazina e o diclofenaco de sódio como modelos experimentais. Na caracterização das esferas adsorventes, verificou-se superfície lisa, diâmetro em torno de 1,0 mm, pH_{PZC} de 5,0 e 5,5 para as esferas compósitas, e sem adição de CNT's, respectivamente. A análise de FTIR indicou estruturas químicas bem semelhantes entre os dois tipos de gelatina (comercial e RCCC). A adição dos nanotubos ao compósitos foi comprovada a partir da análise de DRX. Na termogravimetria, dois eventos de perda de massa em 225 ºC e 325 ºC foram observados, relacionados a evaporação da água e despolimerização das proteínas da gelatina, respectivamente. As capacidades de adsorção do corante amarelo tartrazina variaram de 131,32 a 263,13 $mg.g^{-1}$, enquanto que para o diclofenaco as variações foram de 17,51 a 36,35 $mg.g^{-1}$. Na modelagem matemática, os modelos de Langmuir, Freundlich e Redlich-Peterson apresentaram coeficientes de determinação (R^2>0,90), sendo eficientes para descrever a adsorção de tartrazina e diclofenaco de sódio pelas esferas adsorventes. As classificações dos perfis das curvas isotérmicas foram alteradas em função do material utilizado, sugerindo mudanças de mecanismo, onde, as interações eletrostáticas e as ligações de hidrogênio, possivelmente, foram os mecanismos envolvidos na adsorção do corante e diclofenaco, respectivamente. Na cinética, para ambos os materiais, a densidade de adsorção do corante continou a aumentar após 300 min, enquanto que para o diclofenaco, após 80 min a taxa de adsorção tornou-se constante. Na regeneração, ambas as esferas foram utilizadas por até 10 ciclos, com capacidades de adsorção em torno de 100 $mg.g^{-1}$. De forma geral, a adição de CNT's não proporcionou aumento nas capacidades de adsorção das gelatinas comercial e RCCC, e a gelatina como material único, mostrou-se um adsorvente promissor. Além disso, a gelatina RCCC apresentou capacidades de adsorção similares à gelatina comercial.

Palavras-chave: Adsorção. Curtume. Biopolímero. Compósito

ABSTRACT

Industries of the transformation of animal hides into leather are responsible for the generation of solid waste in collagen. Gelatin is a biopolymer that can be obtained from collagen hydrolysis and has been promising in studies involving the production of adsorbents. Carbon nanotubes (CNT's) are used as reinforcements for polymeric matrices, since the use of pure CNT's powder as an adsorbent causes the blocking of industrial filters, and the separation process is difficult. Thus, this work aimed to develop composite beads from gelatin recovered from chromium-tanned leather wastes (RCTLW) and CNT's. For comparison purposes, standard beads were produced, containing only commercial gelatin or RCCC gelatin. The drip emulsification method was used in the preparation of the beads, with a concentration of 8% (w/w) of commercial and RCTLW (w/v) gelatins, respectively, and additions of 0 and 5% (w/w) of CNT's in relation to the gelatin weight. The adsorbents were characterized by Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR), Thermovogravimetry (TGA), Point of zero charge (pH_{PZC}). Composite beads (CNT's and gelatin) were further characterized by X-Ray Diffraction (XRD), and the Swelling and Water retention capacities were also determined. The batch adsorption tests (equilibrium, kinetic, and desorption, and reuse) were conducted using the tartrazine yellow dye and diclofenac sodium as experimental models. In the characterization of the adsorbent beads, it was found smooth surface, diameter around 1.0 mm, pH_{PZC} of 5.0 and 5.5 for the composite beads, and without the addition of CNT's, respectively. The FTIR analysis indicates similar structures between the two types of gelatin (commercial and RCTLW). The addition of CNT's to composites was proven from the XRD analysis. In thermogravimetry, two weight loss events at 225 ºC and 325 ºC were observed, related to water evaporation and depolymerization of gelatin protein, respectively. The adsorption capacities of the tartrazine varied from 131.32 to 263.13 $mg.g^{-1}$, while for diclofenac the variations were from 17.51 to 36.35 $mg.g^{-1}$. In mathematical modeling, the Langmuir, Freundlich, and Redlich-Peterson models coefficients of determination (R^2>0.90), being efficient to describe the adsorption of tartrazine and diclofenac by the adsorbent beads. The classifications of the profiles of the isothermal curves were changed according to the material used, suggesting changes in the mechanism. Electrostatic interactions and hydrogen bonds possibly were the mechanisms involved in the adsorption of the tartrazine and diclofenac, respectively. In kinetics, for both materials, the adsorption density of the dye continued to increase after 300 min, while for diclofenac, after 80 min the adsorption rate became constant. In regeneration, both beads were used for up to 10 cycles, with an adsorption resource of around 100 $mg.g^{-1}$. In general, the addition of CNT's did not increase the adsorption capacities of commercial gelatins and RCTLW, and gelatin as a single material showed a promising adsorbent. Also, the RCTLW showed adsorption capacities similar to commercial gelatin, therefore, the present work can contribute as a basis for further studies in the field of materials science and adsorption.

Keywords: Adsorption. Tannery. Biopolymer. Composite

SUMÁRIO

1. INTRODUÇÃO

O Brasil dispõe do maior rebanho bovino do mundo, com aproximadamente 215 milhões de cabeças de gado, sendo maior exportador de carne bovina do mundo (ABIEC, 2019). A cadeia de produção do couro é ampla, abrangendo as indústrias coureiras, que são responsáveis pelo processamento da pele animal para produção de bolsas, sapatos, cintos, roupas, calçados, entre uma variedade de outros produtos, no entanto, resíduos sólidos são gerados. Estima-se que para cada 1000 kg de peles são obtidos apenas 200 kg de couro curtido, sendo o remanescente do processamento (aparas, pós, etc), classificado como resíduo sólido (SUNDAR et al., 2011; DWIVEDI et al., 2019).

Os resíduos sólidos amplamente gerados nas etapas de processamento do couro (com ou sem curtimento), são ricos em colágeno, sendo esse composto proteico promissor para obtenção de diversos produtos, como cola, ração animal, fertilizantes, peptídeos de colágeno e gelatina (MASILAMANI et al., 2016; RAHMAWATI et al., 2018).

A gelatina é um biopolímero resultante da desnaturação parcial do colágeno, e pode ser extraída dos resíduos sólidos da indústria coureira empregando hidrólise alcalina e térmica (SCOPEL et al., 2019). Essa macromolécula tem sido amplamente empregada em pesquisas voltadas para produção de adsorventes, pois apresenta excelente capacidade de formação de gel, baixo custo de aquisição, biodegradabilidade e hidrofobicidade (WAN et al., 2000; YILMAZ; SANLIER, 2013). Em virtude de sua estrutura química suscetível, também é possível a preparação de materiais compósitos utilizando-a como base, melhorando sua capacidade como material adsorvente (YANG et al., 2015).

A produção de compósitos tem sido amplamente difundida na área de adsorção, devido à necessidade de materiais com maior potencial de remoção de íons metálicos, corantes e outros poluentes tóxicos (BERBER, 2020). Nesse contexto, os nanotubos de carbono (CNT's) podem ser aplicados como reforço de matrizes poliméricas (ZHU et al., 2013; SABER-SAMANDARI et al., 2017), devido ao seu tamanho na faixa de nanômetros, distribuição uniforme dos poros, área superficial específica elevada e resistência mecânica (WANG et al., 2004; PILLAY; CUKROWSKA; COVILLE, 2009), proporcionando o aprimoramento das propriedades mecânicas de polímeros como a gelatina, bem como a redução da taxa de degradação.

A facilidade de separação e recuperação do material após utilização também é outro fator favorável na utilização dos compósitos de gelatina e CNT's, pois o uso apenas dos CNT's não é economicamente, nem tecnicamente viável, já que a separação é difícil, ocasionando o

bloqueio dos filtros industriais, sendo requerido o processo de centrifugação para remoção completa dos mesmos (TOFIGHY; MOHAMMADI, 2010; ZHOU et al., 2014).

Diante desse contexto, o presente estudo teve como objetivo o desenvolvimento de adsorventes alternativos a partir de gelatina recuperada de resíduos de couro curtido ao cromo trivalente e nanotubos de carbono.

Para alcançar o objetivo principal, os seguintes objetivos específicos foram delineados:

a) extrair e concentrar a gelatina presente nos resíduos de couro curtido ao cromo trivalente;
b) produzir as esferas adsorventes a partir de gelatina recuperada de resíduos de couro curtido ao cromo (III) e nanotubos de carbono;
c) caracterizar química, física e morfologicamente os materiais adsorventes;
d) obter os dados cinéticos, de equilíbrio e de reciclo dos materiais adsorventes;
e) comparar as capacidades de adsorção das esferas de gelatina recuperada dos resíduos de couro curtido ao cromo (III) e gelatina comercial, com e sem adição de nanotubos e carbono;
f) compreender os mecanismos envolvidos no processo de adsorção a partir da modelagem matemática dos dados experimentais obtidos.

Este trabalho está estruturado em 6 capítulos, conforme especificado a seguir:

No capítulo 2, é apresentado o artigo de revisão bibliográfica do presente trabalho. O artigo intulado*: "Production and environmental applications of gelatin-based composite adsorbents for contaminants removal: a review*", aborda o uso da gelatina como base para preparo de materiais adsorventes, bem como, as principais caracteristicas químicas da gelatina, técnicas de produção de adsorventes a partir da mesma, e os principais materiais obtidos para remoção de contaminantes emergentes.

Os materiais e métodos, bem como os resultados e a discussão serão apresentados nos artigos escritos como resultados deste trabalho de mestrado.

No capítulo 3, é apresentado o primeiro artigo oriundo deste trabalho, intulado "*Emerging contaminants adsorption by beads from Chromium (III) tanned leather waste recovered gelatin"*. Este artigo aborda a produção, caracterização das esferas adsorventes a partir de gelatina comercial e recuperada de resíduos de couro, e posterior aplicação das mesmas na adsorção do corante amarelo tartrazina e diclofenaco de sódio de soluções aquosas, por meio de ensaios de equilibrio, cinético e de reúso.

No capítulo 4, é apresentado o segundo artigo oriundo deste trabalho, intulado "*Adsorption diclofenac sodium by composite beads prepared from tannery-wastes derived gelatin and carbon nanotubes"*. Este artigo aborda a produção, caracterização das esferas compósitas adsorventes a partir de gelatina comercial e nanotubos de carbono e gelatina recuperada de resíduos de couro e nanotubos de carbono, e posterior aplicação desses compóstos na adsorção de diclofenaco de sódio de soluções aquosas, por meio de ensaios de equilíbrio e cinético.

No capítulo 5, é apresentado o terceiro artigo oriundo deste trabalho, intulado "*Tannery wastes-derived gelatin and carbon nanotubes composite beads: Adsorption and reuse studies using tartrazine yellow dye"*. Este artigo é uma continuidade do artigo apresentado no capítulo 4, e apresenta os dados de adsorção (isotermas, cinéticas e reúso) das esferas compósitas de gelatina comercial e nanotubos de carbono e gelatina recuperada de resíduos de couro e nanotubos de carbono, na adsorção do corante amarelo tartrazina.

No capítulo 6, são apresentadas as conclusões gerais e as sugestões para trabalhos futuros.

2. ARTIGO DE REVISÃO

PRODUCTION AND ENVIRONMENTAL APPLICATIONS OF GELATIN-BASED COMPOSITE ADSORBENTS FOR CONTAMINANTS REMOVAL: A REVIEW

Artigo publicado no periódico: Environmental Chemistry Letters, v.18, n.6, 2021. DOI: https://doi.org/10.1007/s10311-021-01184-0

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Abstract

Industrial activities generate considerable volumes of wastewater, containing organic and inorganic contaminants. Adsorption is recognized as an efficient method for wastewater treatment, due to its ease of operation, convenience, and efficiency. However, finding suitable adsorbent materials that are abundant, cheap, and efficient, remains a challenge. Gelatin is considered a promising adsorbent, due to its abundant surface of active groups, with characteristics of water-solubility, nontoxicity and, biodegradability. Also, gelatin allows the addition of other compounds in the gel network, overcoming some disadvantages such as low mechanical resistance to temperature and humidity.here we review the production of gelatin-based composites including beads/spheres, hydrogels, aerogels, and films, and their use to remove toxic metals, dyes, nitrate, phosphate, and oily contaminants from aqueous matrices. Considerations economic, environmental, and real applications aspects are also discussed.

Keywords: Adsorption; Biopolymer; Preparation methods; Emerging contaminants.

3. ARTIGO EXPERIMENTAL 1

EMERGING CONTAMINANTS ADSORPTION BY BEADS FROM CHROMIUM (III) TANNED LEATHER WASTE RECOVERED GELATIN

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Abstract

Tannery industries generate wastes that are rich in collagen and can be used to extract the gelatin. Gelatin is a macromolecule with excellent gel formation capacity, low acquisition cost, in addition to biodegradable and hydrophobic characteristics, with an abundance of chemical groups favorable to the adsorption technique. Thus, this work aimed to produce an alternative adsorbent from gelatin extracted from chromium (III) tanned leather wastes for application to remove emerging contaminants from aqueous solutions. Tartrazine yellow dye (TYD) and diclofenac sodium (DCF) were used as experimental models. The adsorbents were produced in beads shape, by drip emulsification. Commercial gelatin beads were also prepared for comparison purposes. The beads were characterized by SEM, TGA, FTIR, and pHpzc. The beads were subjected to equilibrium, kinetics, and desorption and reuse tests. The RCTLW gelatin beads showed a maximum adsorption capacity of 263.13 and 36.65 $mg.g^{-1}$, for TYD and DCF, respectively. In kinetics, the adsorption density continued to increase after 300 min for TYD and was reached in the first 80 min for DCF. Mathematical modeling suggests that TYD adsorption follows the Freundlich model, while DCF is better represented by the

Langmuir model. The PFO model best predicted TYD adsorption, while for DCF, both models of PFO and PSO can describe the kinetic data. The RCTLW gelatin beads showed promise for use for up to 10 cycles without loss of adsorption capacity, ending the 10^{th} cycle with a capacity of around 100 $mg.g^{-1}$ and 45% regeneration.

Keywords: Biopolymer; Chromium; Tartrazine; Diclofenac sodium; Reutilization.

4. ARTIGO EXPERIMENTAL 2

ADSORPTION OF DICLOFENAC SODIUM BY COMPOSITE BEADS PREPARED FROM TANNERY WASTES-DERIVED GELATIN AND CARBON NANOTUBES

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Abstract

Diclofenac is an emerging contaminant belonging to the class of pharmaceutical and personal care products, and its presence in drinking water has been reported in several studies nowadays. The adsorption technique has been highlighted due to its operational simplicity, removal efficiency, and low cost, allowing the use of materials of residual origin. Gelatin has favorable characteristics for the production of adsorbent composites, and it can also be obtained from solid wastes from the tannery industry. Thus, this work aimed to produce composite beads based on gelatin recovered from leather wastes tanned with chromium (III) and the addition of carbon nanotubes, to remove diclofenac sodium. For comparison purposes, a composite based on commercial gelatin and carbon nanotubes was also produced. The composite beads were produced using the drip emulsification method. Equilibrium and kinetic tests were performed, and the materials were characterized by Scanning Electron Microscopy (SEM),

Thermogravimetric Analysis (TGA), Fourier Transform Infrared (FTIR) Spectroscopy, X-ray diffraction (XRD), Point of zero charge (pHpzc), and Swelling and Water retention capacities. The composite based on gelatin recovered from chromium tanned leather waste and carbon nanotubes showed an adsorption capacity of around 20.57 $mg.g^{-1}$, close to the estimated value for commercial gelatin and carbon nanotubes, that was 26.97 $mg.g^{-1}$. The Freundlich model showed a better fit to the experimental equilibrium data. In adsorption kinetics, the Pseudo-second order model better described the kinetic behavior of removing diclofenac sodium by composite beads.

Keywords: Adsorbent Composite; Carbon nanotubes; Leather waste; Pharmaceuticals; Emerging contaminant.

5. ARTIGO EXPERIMENTAL 3

TANNERY WASTES-DERIVED GELATIN AND CARBON NANOTUBES COMPOSITE BEADS: ADSORPTION AND REUSE STUDIES USING TARTRAZINE YELLOW DYE

Artigo em revisão no periódico: Revista Matéria (UFRJ), submetido em: 19/03/2021.

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Abstract

Tartrazine yellow is a dye commonly used in the food, textile, cosmetic and pharmaceutical industries. The effluents generated containing this contaminant must be treated since it presents potential carcinogenicity to the cells. The adsorption stands out among the other techniques used to remove dye from wastewater due to its ease of operation and implementation, and high removal rate. However, the production of effective and low-cost adsorbents is a constant challenge. Gelatin is a promising compound for the production of adsorbent composites, enabling the improvement of its low mechanical properties and accelerated degradation, by the addition of carbonaceous, such as carbon nanotubes (CNT's). Taking into account economic and environmental aspects, gelatin can still be recovered from chromium-tanned leather wastes (RCTLW). Thus, this work aimed to study the adsorption of the tartrazine yellow dye by adsorbent composites based on (1) commercial gelatin/CNT's beads and (2) RCTLW gelatin/CNT's beads. The commercial and RCTLW gelatin composite beads showed an adsorption capacity of 202.39 and 131.32 $mg.g^{-1}$, respectively, estimated by the Langmuir

model. In adsorption kinetics, the density continued to increase after 300 min for both the composite materials, with better prediction of the pseudo-first order model. In the reuse study, the commercial and RCTLW gelatin composite beads proved to be usable for up to 10 cycles, with regenerations of 45 to 68% and 45 to 61%, respectively. In general, the composite beads of gelatin showed promise for the adsorption of dyes, mainly RCTLW gelatin, since it makes possible the use and minimization of wastes.
Keywords: Gelatin Composites; Leather waste; Carbon nanotubes; Tartrazine.

5.1 INTRODUCTION

Synthetic dyes are widely used by industries to improve the consumption characteristics and appearance of their products. However, during processing, the dyes don't completely fix in the manufactured products, generating colored effluents (HESSEL et al., 2007; LONG et al., 2011; ANDRADE et al., 2014; RIGUETO et al., 2020a).

In the food, textile, cosmetic and pharmaceutical industries, the Tartrazine yellow dye (TYD) is commonly used. Regarding its molecular structure, it has aromatic rings and its metabolic and degradation products (aromatic amines, benzidines and benzene sulfonic acids) are carcinogenic, mutagenic and DNA adducts, and can induce harmful effects to cells (RATNA; PADHI, 2012; MARTINI et al., 2018).

The techniques commonly used for the treatment of wastewater to remove dyes are flocculation/coagulation, precipitation, photocatalytic degradation, biological oxidation, ion exchange, advanced oxidative processes, bioremediation, membrane separation, and adsorption (PIASKOWSKI et al., 2018; RIGUETO et al., 2020b). Adsorption stands out due to its ease of operation and implementation, high removal rate, and low cost, depending on the adsorbent material used (ZHUO et al., 2017). In this context, obtaining and producing effective and low-cost adsorbents are constant challenges because, in addition to the economic bias and adsorption capacity, the material must show chemical, mechanical stability, and potential for reuse (DOTTO; McKAY, 2020).

Gelatin is a promising adsorbent material, as it presents favorable characteristics such as biodegradability, low cost, wide availability, capacity to form a gel, and to has a chemical structure and surface that is favorable to adsorption (NINAN et al., 2013; DERKATCH et al., 2016; HAYEEYE et al., 2017). However, as a disadvantage, gelatin when in its natural form has low mechanical resistance and accelerated degradability in wet conditions, factors that limit its application as an adsorbent (HUI et al., 2015).

Therefore, the production of composite materials has been widespread in the adsorption area, aiming to improve the mechanical, thermal, and chemical properties of the base adsorbent material, uniting it with other compounds (BERBER, 2020). One of the materials that can be used to obtain composite materials are carbon nanotubes (CNT's), which have high hydrothermal stability, high surface/volume ratio, and excellent mechanical properties, thus can overcoming the disadvantages of gelatin as an adsorbent (DEMCZYK et al., 2002; ZHOU et al., 2014; KARKEH-ABADI et al., 2016; SABER-SAMANDARI et al., 2017).

Also, gelatin can be recovered from chromium-tanned leather waste (RCTLW), adding value to an industrial waste generated in several countries, with high polluting potential, minimizing environmental impacts (SCOPEL et al., 2019; 2020; RIGUETO et al., 2020c; 2021). It is also noteworthy that, several studies have addressed the use of commercial gelatin as a basis for the production of adsorbent composites for the removal of dyes (MA et al., 2019), metals (HERMAN et al., 2020), and drugs (ULFA et al., 2020), however, research using gelatin recovered from residual sources for use as an adsorbent is scarce.

Thus, this work aimed to study the adsorption of the tartrazine yellow dye by an adsorbent composite from gelatin recovered from chromium-tanned leather wastes (RCTLW) and carbon nanotubes (CNT's). For comparison purposes, commercial gelatin/CNT's beads were also used in the adsorption tests.

5.2 MATERIAL AND METHODS

5.2.1 Materials

The materials used in this work were: commercial gelatin powder type B (La Casella, Brazil), multi-walled carbon nanotubes functionalized by oxidation (Nanotec, UFMG, Brazil) with a surface area of 132.99 $m^2.g^{-1}$ and pore radium of 18.29 Å, glutaraldehyde (Neon, Brazil), acetone (Neon, Brazil), and tartrazine yellow dye (Duas Rodas, Brazil). All reagents used were of analytical grade.

The chromium-tanned leather wastes were kindly donated by a leather company in the north of the state of Rio Grande do Sul, Brazil.

5.2.2 Extraction and concentration of gelatin from tannery wastes

The extraction of gelatin RCTLW was performed by alkaline hydrolysis according to the method of Scopel et al. (2019). The concentration was carried out in membranes, followed

by precipitation in ice-cold acetone at -4ºC, according to the method described by Rigueto et al. (2021a).

5.2.3 Synthesis and characterization of composite beads

The composite beads were prepared by the drip emulsification method described by Rigueto et al. (2021a) adapted from Saber-Samandari et al. (2017).

The composite beads used in this study has been previously characterized by Rigueto et al. (2021a), and shows diameters less than 1.5 mm, good thermal stability up to 300 ºC, point of zero charge around 5.0, capacity to swell twice as much as its own size, and water retention capacities close to 80%.

5.2.4 Batch adsorption tests

The equilibrium and adsorption kinetics tests were performed by the batch system, and the pH of the solutions of TYD was adjusted to 2.5, as suggested by Dotto et al. (2011). Adjustments were made using 0.05 $mol.L^{-1}$ HCl or NaOH solutions.

Initially, equilibrium tests were performed to construct the adsorption isotherms, using an adsorbent dosage of 0.4 $g.L^{-1}$ of the composite beads and 50 mL of the TYD solution in concentrations of 37.5, 50, 100, 150, 200, 300, and 400 $mg.L^{-1}$, in 250 mL conical flasks, maintained at 25 ºC, and 120 rpm in a shaker incubator (Marconi, MA-420, Brazil). The absorbance readings were performed at 1h intervals until the adsorption equilibrium was established.

The adsorption kinetics was performed using 50 mL of the TYD solution, in the initial concentration of 100 $mg.L^{-1}$ and adsorbent dosage of 0.4 $g.L^{-1}$, in 250 mL conical flasks, maintained at 25 ºC and 120 rpm in a shaker incubator (Marconi, MA-420, Brazil). Readings were taken at 10, 15, 30, 45, 60, 90, 120, 150, 180, and 210 min.

All tests were performed in duplicate, with subsequent reading on a spectrophotometer (Tecnal, UV-5100, Brazil), at a wavelength of 529 nm. An external calibration curve ($y= 0.0352x + 0.0003$) with $R^2=1$, was used to quantify the tartrazine yellow dye. From the concentration data obtained, the amount of adsorbed was calculated according to Equation 1.

$$q = \frac{V(C_0 - C)}{w} \quad (1)$$

Where q is the amount of contaminant adsorbed per gram of adsorbent ($mg.g^{-1}$), C_0, and C are the concentrations of the initial and final aqueous solutions, respectively ($mg.L^{-1}$), v is the volume of the solution (L), and w is the weight of adsorbent (g).

5.2.5 Mathematical modeling

In mathematical modeling, the Langmuir, Freundlich, and Redlich-Peterson models were fitted to the experimental equilibrium data, while the pseudo-first order, pseudo-second order, and Elovich models to the kinetic experimental data, as shown in Table 1.

Table 1: Kinetic and equilibrium models used in mathematical modeling of experimental adsorption data of diclofenac sodium by gelatin composite beads

Kinetic models	Equations		Parameters
Pseudo-first order	$q(t) = q_1(1 - e^{-k_1 t})$	(2)	k_1 (min^{-1}) constant rate of pseudo-first order; q_1 ($mg.g^{-1}$) theoretical value of the adsorption capacity.
Pseudo-second order	$q(t) = \frac{t}{(1/k_2 q_2{}^2) + (t/q_2)}$	(3)	k_2 ($g.mg^{-1}.min^{-1}$) constant rate of pseudo-second order; q_2 ($mg.g^{-1}$) theoretical value of the adsorption capacity.
Elovich	$q(t) = \frac{1}{\beta} ln(1 + \alpha\beta t)$	(4)	α ($mg.g^{-1}.min^{-1}$) initial rate of adsorption and β ($g.mg^{-1}$) is the desorption constant of Elovich model.
Isotherm models	**Equations**		**Parameters**
Langmuir	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$	(5)	q_m ($mg.g^{-1}$) maximum adsorption capacity; K_L ($L.mg^{-1}$) Langmuir constant.
Freundlich	$q_e = K_F C_e^{1/n}$	(6)	K_F ($mg.g^{-1}$).($mg.L^{-1}$)$^{-1/n}$ Fre undlich constant; $1/n$ (-) heterogeneity factor.
Redlich-Peterson	$q_e = \frac{K_{RP} C_e}{1 + \alpha C_e^{\beta}}$	(7)	K_R ($L.g^{-1}$) Redlich-Peterson constant; α ($mg.L^{-1}$)$^{-\beta}$ Redlich-Peterson constant; β (-) heterogeneity factor.

The models presented in Table 1 were fitted to the experimental data by the nonlinear regression technique, through the Gaus-Newton method, by minimizing the objective function sum of squares of the residues. The modeling mathematical was performed using the software Statistica 7.0 (Statsoft, USA).

5.2.6 Desorption and reuse studies

The desorption and reuse of composite beads were evaluated using the tartrazine yellow dye adsorption. In 50 mL Falcon conical centrifuge tubes, approximately 0.05 g of adsorbent and 30 mL of the 200 mg.L^{-1} TYD solution were added, with a pH previously adjusted to 2.5. The tubes remained in the shaker at 120 rpm and 25 ºC for 2h. Subsequently, an aliquot of the solutions was collected for spectrophotometric reading, and the removal capacity was calculated according to Equation 8.

$$Removal\ (\%) = \left(\frac{C_0 - C_{ads}}{C_0}\right) x\ 100 \quad (8)$$

where C_0 is the initial concentration (mg.L^{-1}) and C_{ads} is the final concentration after the adsorption cycle (mg.L^{-1})

For the desorption tests, after the mentioned adsorption step, the composite beads were washed with distilled water to remove the dye solution present on the surface, and then, in 50 mL Falcon conical centrifuge tubes, 0.05 mol.L^{-1} NaOH solution was added remaining in a shaker (120 rpm, 25 ºC) for 15 min. Afterward, aliquots of the samples were taken to read the concentration in a spectrophotometer, and then, the degree of regeneration was calculated, according to Equation 9.

$$Regeneration\ (\%) = \frac{(m_{des}\ x\ 100)}{m_{ads}} \quad (9)$$

where m_{des} is the amount of dye adsorbed in the desorption cycle (mg), and m_{ads} is the amount of dye adsorbed in the adsorption cycle (mg).

Ten adsorption/desorption cycles were evaluated and the percentage of removal and regeneration was determined in each cycle.

5.3 RESULTS AND DISCUSSION

5.3.1 Adsorption isotherms

To evaluate the adsorption, it is necessary to produce equilibrium curves by means of adsorption isotherms at equilibrium. These curves are projected through a relationship between equilibrium adsorption capacity (q_e) versus equilibrium adsorbate concentration in the fluid phase (C_e), at a constant temperature (WONG et al., 2004). These curves demonstrate an adsorption capacity of an adsorbent by a solute under the adopted experimental conditions (CHAKRABORTY et al., 2005).

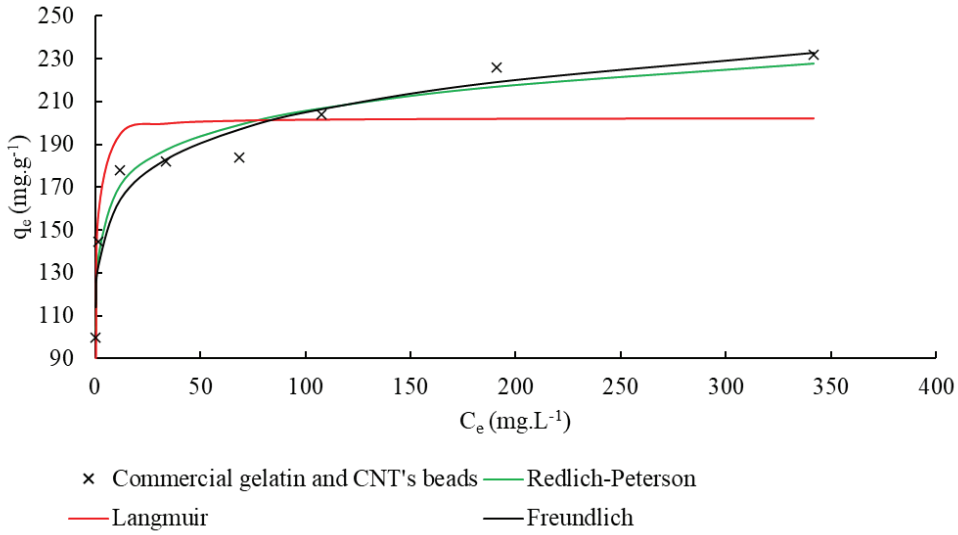
The adsorption isotherms of the TYD by the commercial/CTN's beads and RCTLW gelatin/ CNT's beads are shown in Figure 1 (a) and (b), respectively.

The profiles of equilibrium curves (Figure 1), can be classified according to Giles et al. (1960), for TYD adsorption, the isothermal curves have an "H1" and "L2" profile for Commercial and RCTLW gelatin composite beads, respectively. Class L curves (Normal or Langmuir type) describes that as adsorption occurs, fewer active sites will be available and there will be less probability that a solute molecule will bind to the adsorbent, so to increase the solute adsorption, higher concentrations of the solution are needed. Class H curves (high affinity) shows that there is a high affinity between adsorbate and the adsorbent, indicating chemical adsorption and by electrostatic forces. Also, subclass 1 for class H shows that the adsorption sites were not fully occupied and suggests a Freundlich isotherm. Subclass 2 for class L and H describes that there was complete saturation of the adsorbent monolayer, where the solute has a high affinity for the solvent, in this case, the data can be represented by Langmuir isotherm (GILES et al., 1960; PICCIN et al., 2017).

The adsorption isotherms models are used to understand the equilibrium relationship between the solid and liquid phases. These models have parameters that allow obtaining the maximum adsorption capacity, which indicates the quality of the adsorbent and also identifies the type of interaction between the adsorbent and adsorbate (PICCIN et al., 2017).

Figure 1: Adsorption isotherms of TYD (25 ºC, 120 rpm, pH 2.5, and adsorbent dosage of 0.4 $g.L^{-1}$) by (a) Commercial gelatin/CTN's beads, and (b) RCTLW gelatin/CNT's beads

a)



b)

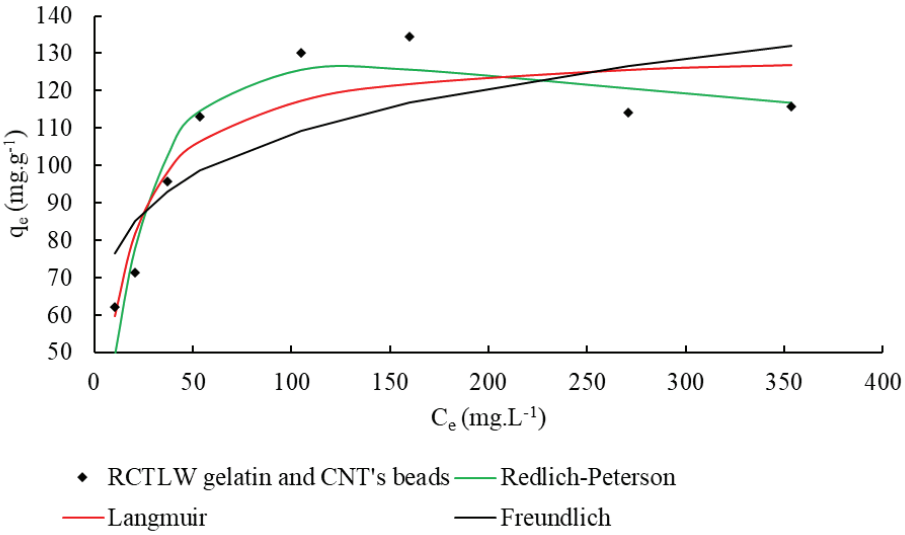


Table 2 presents the values of the parameters of the Langmuir, Freundlich, and Redlich-Peterson isothermal models fitted to the experimental data of adsorption of the TYD by the commercial gelatin/CNT's beads and RCTLW gelatin/CNT's beads.

Table 2 shows that the Redlich-Peterson model presented better fit to the experimental data, with coefficients of determination (R^2 and $R^2_{adj.}$) greater than or close to 0.9. Redlich-Peterson (R-P) model combines elements of the Langmuir and Freundlich models, so that in low concentrations it follows the Langmuir model and in high concentrations it follows

Freundlich model. However, when the value of β is close to 1, the parameters qm and KR are reduced to the parameters qm and K_L of Langmuir (TOLAZZI et al., 2018). Another interpretation that can be adopted is that the R-P model indicates a Freundlich isotherm when the constants K_R and aR are >> 1 and β = 1 (KUMAR et al., 2007).

Table 2: Equilibrium model parameters for TYD adsorption by commercial gelatin/CNT's beads and RCTLW gelatin/CNT's beads.

Isotherm/Parameter	Tartrazine yellow dye	
	Commercial gelatin/CNT's beads	RCTLW gelatin/CNT's beads
Langmuir		
q_m ($mg.g^{-1}$)	202.39	131.32
K_L ($L.mg^{-1}$)	2.17	0.08
R^2	0.78	0.83
$R^2_{adj.}$	0.77	0.82
Freundlich		
K_F ($mg.g^{-1}$) ($mg.L^{-1}$)$^{-1/n}$	126.93	53.29
n_F (-)	9.61	6.47
R^2	0.94	0.62
$R^2_{adj.}$	0.93	0.60
Redlich-Peterson		
K_R ($L.mg^{-1}$)	1437.56	5.81
a_R (($mg.L^{-1}$)$^{-\beta}$)	10.21	0.014
β (-)	0.917	1.20
R^2	0.96	0.90
$R^2_{adj.}$	0.95	0.89

According to the R-P parameters, commercial gelatin and CNT's beads present a β value close to 1, and values of K_R and a_R >> 1, showing that the model that represents these data is the Freundlich model. For RCTLW gelatin/CNT's beads the R-P model shows values of β close to 1, and values of K_R and a_R lower or tending to 1, then the model that represents these data is Langmuir model.

Langmuir model presented better fits to RCTLW gelatin/CNT's beads data, indicating that adsorption doesn't occur beyond the monolayer coverage, the active sites are energetically homogeneous and each site can hold only one adsorbate molecule (PICCIN et al., 2017). The maximum adsorption capacity (Table 2) for this material was 131.32 $mg.g^{-1}$.

Comparing the adsorption capacities of the tartrazine yellow dye, with the study by Rigueto et al. (2021b) who used beads from commercial (257.46 $mg.g^{-1}$) and RCTLW (263.13 $mg.g^{-1}$) gelatins without the addition of carbon nanotubes, it appears that the addition of this component to the matrix of the gelatin caused a reduction in the capacity and affinity

adsorptions of the dye. This behavior may be associated with the point of zero charge of the CNT's, which is 3.10 (Annex E), this value being close to the pH of the dye solutions (2.5) used in the adsorption tests.

Other studies that used gelatin-based composites for dye adsorption, reported the monolayer adsorption capacities estimated by the Langmuir model. Alinejad-Mir et al. (2018) in the adsorption of direct yellow 12 from aqueous solutions using an iron oxide-gelatin nano adsorbent, found q_m=1250 $mg.g^{-1}$ and Saber-Samandari et al. (2017) using gelatin-based magnetic nanocomposite beads comprising carboxylic acid functionalized carbon nanotube in the adsorption of methylene blue and direct red 80, obtained value of q_m=1428.5 and 714.2 $mg.g^{-1}$, respectively.

The Freundlich model suggests that adsorption occurs on a heterogeneous surface, with energy and affinity non-uniform on the surface (SABER-SAMANDARI et al., 2015). Freundlich model described better fits to commercial gelatin and CTN's beads. The parameter nF also suggests that adsorption is favorable when their values are between 1 to 10, in this work was obtained values of 9.61 and 6.47 (Table 2) for commercial gelatin/CNT's beads and RCTLW gelatin/CNT's beads, respectively.

Regarding to the dye adsorption mechanism by the gelatin composite beads, research reports that the main interaction is by electrostatic forces, and when in acid pH the amino and hydroxyl groups of gelatin are protonation, attracting the sulfonated groups of the dye structure favoring adsorption (AHMAD et al., 2010; DAI et al., 2017; LI et al., 2018).

5.3.2 Adsorption kinetic

Adsorption kinetic is expressed as the mass transfer rate of compounds contained in the fluid phase to the adsorbent, and from it, the parameters obtained by modeling can be compared to the behavior of the adsorbent obtained experimentally (QIU et al., 2009; LARGITTE; PASQUIER, 2016).

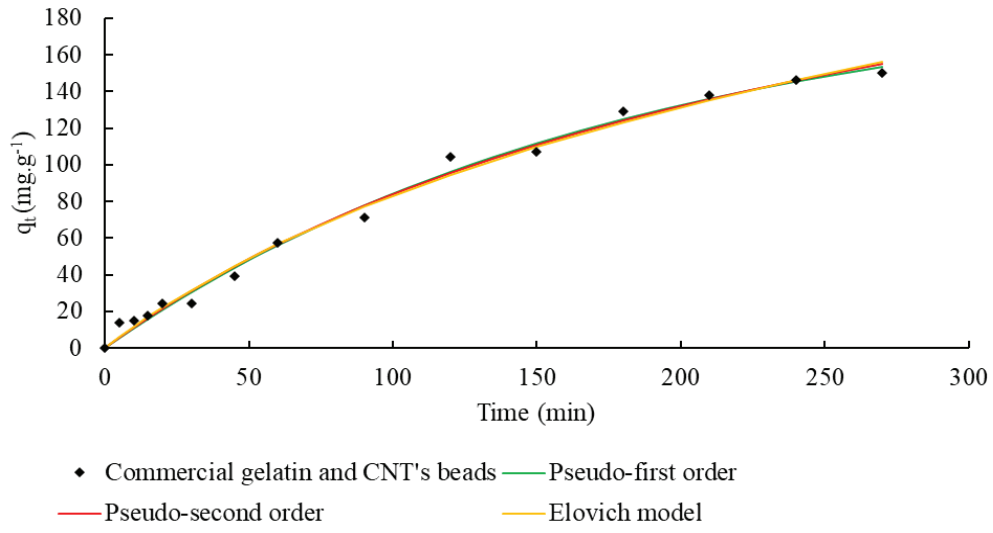
The kinetic data of the TYD adsorption (25 ºC, 120 rpm, pH 2.5, and adsorbent dosage of 0.4 $g.L^{-1}$) by the commercial gelatin/CNT's beads and RCTLW gelatin/CNT's beads are shown in Figure 2 (a) and (b), respectively.

In the adsorption of TYD (Figure 2) for both materials containing gelatin and CNT's, it's noted that the adsorption density continues to increase after 300 min, due to incomplete saturation of the adsorbent active sites by the dye.

Table 3 shows that the PFO, PSO, and Elovich models had good coefficients of determination (R^2 and $R^2_{adj.}$) to the kinetic experimental. These good fits can be illustrated by means of graphics (Figure 2), in which the curves of the models overlap with the curve of the experimental data, showing a good fit of the models to the kinetic data.

Figure 2: Kinetic adsorption of TYD (25 ºC, 120 rpm, pH 2.5, and adsorbent dosage of 0.4 $g.L^{-1}$) by (a) Commercial gelatin/CNT's beads, (b) RCTLW gelatin/CNT's beads.

a)



b)

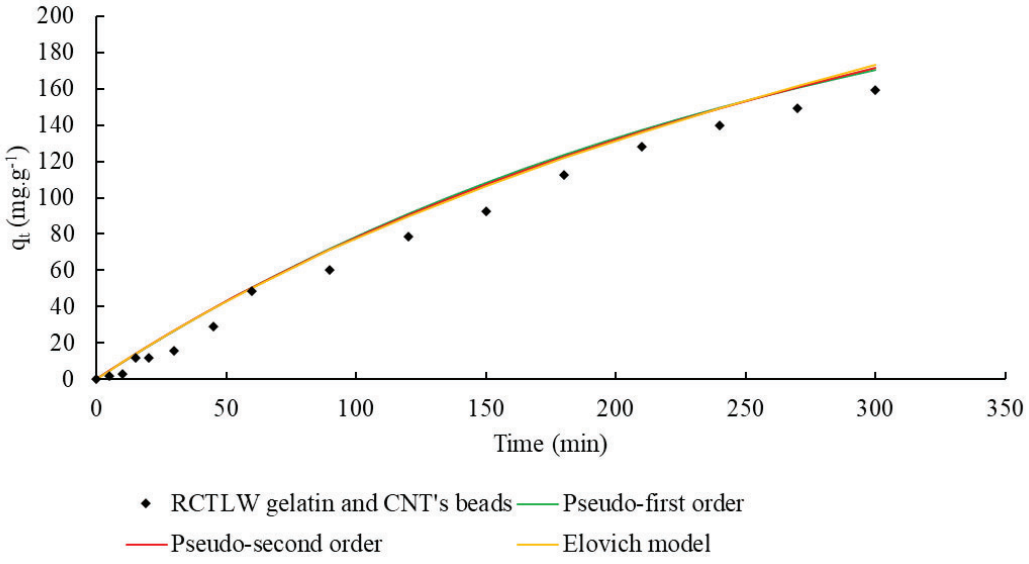


Table 3 shows the values of the parameters of the kinetic models of Pseudo-first order, Pseudo-second order, and Elovich fitted to the experimental kinetic data of adsorption of TYD by commercial gelatin/CNT's beads and RCTLW gelatin/CNT's beads.

Table 3: Kinetic model parameters for adsorption of TYD by commercial gelatin/CNT's beads and RCTLW gelatin/CNT's beads

Kinetic model/Parameter	Tartrazine yellow dye	
	Commercial gelatin/CNT's beads	RCTLW gelatin/CNT's beads
Pseudo-first order		
q_1 ($mg.g^{-1}$)	197.9	254.8
k_1 (min^{-1})	0.0056	0.0037
R^2	0.99	0.99
R^2 adj.	0.99	0.99
Pseudo-second order		
q_2 ($mg.g^{-1}$)	309.66	428.84
k_2 (min^{-1})	$1.2x10^{-6}$	$5.19x10^{-6}$
R^2	0.99	0.99
R^2 adj.	0.99	0.99
Elovich		
α ($mg.g^{-1}.min^{-1}$)	1.21	0.97
β ($g.mg^{-1}$)	0.0085	0.0055
R^2	0.990	0.987
R^2 adj.	0.989	0.986
qe experimentals ($mg.g^{-1}$)	183.90[a]	110.10[b]

[a] qe experimental calculated from the parameters of the Langmuir isotherm;
[b] qe experimental calculated from the parameters of the Freundlich isotherm.

The experimental qe were calculated taking into account the best isotherm model that fit each type of material. In this case, the Freundlich model was used for commercial gelatin/CNT's beads and the Langmuir model for RCTLW gelatin/CNT's beads. Thus, it was found that the kinetic parameters in the adsorption of TYD, the values of qt experimental of the PFO model are closer to the experimental qe calculated by Freundlich and Langmuir models, respectively. Also, it notorious the PFO model overestimated the qt for RCTLW/CNT's beads. On the other hand, the PSO model overestimated the capabilities of adsorption for both materials.

The Elovich model also shows a determination coefficient close to 0.99 for both materials, and this model involves chemisorption in the solid surface, suggesting that the adsorption of the dye onto commercial and RCTLW gelatin/CNT's beads occurred by internal and external mass transfer (PICCIN et al., 2011).

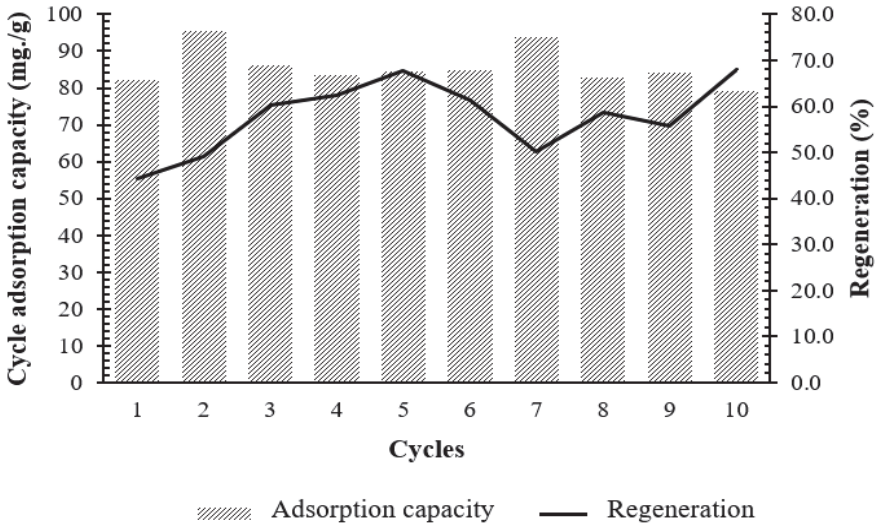
5.3.3 Desorption and reuse studies

Regeneration is used to remove the adsorbed accumulated on the surface of the material and thus recover the capacity of the absorbent. Regeneration increases the life cycle of the material, which means that less solids wastes are produced at the end of each process, making it possible a reduction in the economic and environment impact of the process (BONILLA-PETRICIOLET et al., 2017).

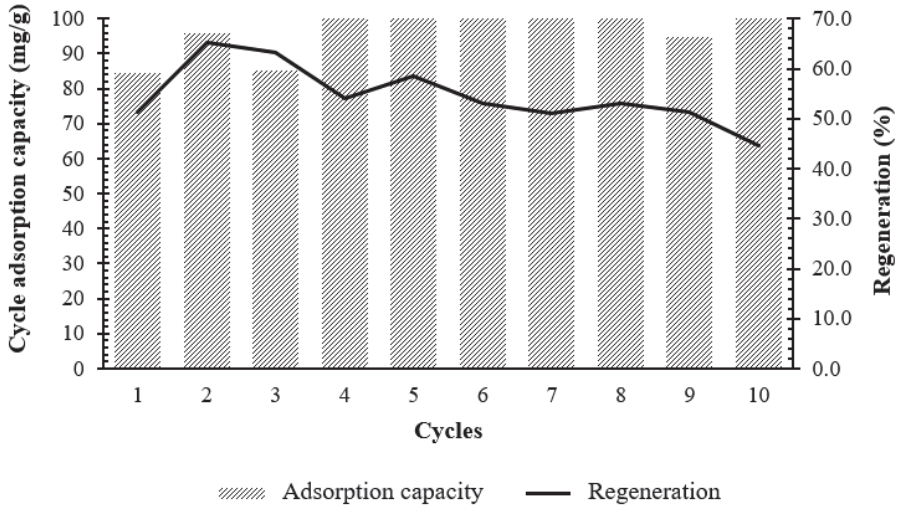
Figure 3 (a) and (b) show the results of the desorption and reuse tests of the commercial and RCTLW gelatin and CNT's beads, in the adsorption of TYD.

Figure 3: Desorption and reuse tests (25 ºC, 120 rpm, pH 2.5, and adsorbent dosage of 1.66 $g.L^{-1}$) using (a) Commercial gelatin/CNT's beads and (b) RCTLW gelatin/CNT's beads

a)



b)



The commercial gelatin/CNT's beads (Figure 3a), showed an adsorption capacity in the first cycle of 82 $mg.g^{-1}$, varying between 80 to 95 $mg.g^{-1}$ from the second to the tenth cycle. The regeneration started at 45%, and varied from the second to the tenth cycle, in a range of 45 to 68%, ended with 68% of dye regeneration. For RCTLW gelatin/CNT's beads (Figure 3b) presented an initial adsorption capacity of 85 $mg.g^{-1}$, with variations from 86 to 100 $mg.g^{-1}$, from the second to the tenth cycle. The regeneration started with 51% varying between 45 to 65% over the cycles, ending the tenth and last cycle with 45% of dye regeneration.

The use of NaOH 0.05 $mol.L^{-1}$ as an eluent for the desorption of TYD using commercial and RCTLW gelatin with CNT's beads, doesn't cause the reduction in the adsorption capacity of the composite, being possible to be used for 10 cycles. The NaOH in an aqueous solution makes the gelatin amine groups be deprotonated, causing the electrostatic interactions with the dye to break down.

Other researches evaluated the life cycle using gelatin-based adsorbent composites, for example, Chen et al. (2018) used gelatin/β-cyclodextrin composite fiber adsorbent for the adsorption of methylene blue, obtaining an adsorption efficiency of 73% for 9 cycles. Chaudhary et al. (2020), reported that gelatin grafted methyl methacrylate/graphite hydrogel composite for adsorption of methyl violet showed stability of 95.8% after 6 cycles. Priya et al. (2019) described that the sodium alginate/gelatin-based ZnS-nanocomposite hydrogel for adsorption of biebrich scarlet and crystal violet dyes presented efficiency greater than 90% after 4 cycles for both dyes.

If we compare the adsorption and regeneration capacities obtained for composites based on commercial and residual gelatin at the end of the tenth cycle (Figure 3), there are reductions of 23 and 20% in the regeneration and adsorption capacity, respectively, of RCTLW gelatin compared to commercial gelatin. However, it must take into account that the residual origin of the recovered gelatin does not imply the use of commercial gelatin with favorable characteristics for food production, addressing a more technological and environmental bias (RIGUETO et al., 2021c).

5.4 CONCLUSIONS

This work, the study of adsorption of the tartrazine yellow dye was presented through the equilibrium, kinetic and reuse tests. In the equilibrium tests, the commercial gelatin and RCTLW composite beads showed an adsorption capacity of 202.39 and 131.32 $mg.g^{-1}$, respectively, estimated by the Langmuir model. For commercial gelatin/CNT's beads, the

Freundlich model fitted better to the experimental data, indicating that the adsorption by the referred material is not limited to monolayer, whereas for RCTLW gelatin/CNT's beads, the Langmuir model better predicted the behavior of the isothermal curve, suggesting monolayer adsorption. In the adsorption kinetics, the density continued to increase after 300 min for both composite materials, with a better prediction of the pseudo-first order model.

In general, the gelatin composite beads showed a promising bet for use as an adsorbent for the tartrazine yellow dye. In comparison to commercial gelatin, even with lower capacities for adsorption and regeneration of the dye understudy, RCTLW gelatin presents a more technological and environmental bias, allowing the use of compounds of interest, such as collagen, and minimizing the solid waste discarded to the environment.

As perspectives, we emphasize the need for works that aim at studies of the economic viability of gelatins from residual sources, such as tannery wastes, for example, for applications as an adsorbent.

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6. CONCLUSÃO

Os artigos oriundos desse trabalho de dissertação apresentaram a produção, caracterização e estudos de adsorção de esferas compósitas de gelatina comercial e recuperada de resíduos de couro curtido ao cromo (III), com adição de nanotubos de carbono. A extração e a concentração da gelatina dos resíduos de couro foi realizada com êxito, empregando hidrólise alcalina e uso de membranas, respectivamente.

Comparando os materiais adsorventes com e sem adição de nanotubos de carbono, verificou-se que a adição dos mesmos não proporcionou aumento da capacidade de adsorção de diclofenaco de sódio e do corante amarelo tartrazina. No entanto, a adição dos CNT's proporciona maior afinidade de adsorção de diclofenaco para ambas as gelatinas, comportamento não observado para o corante. As capacidades de adsorção do corante amarelo tartrazina variaram de 131,32 a 263,13 $mg.g^{-1}$, enquanto que para o diclofenaco as variações foram de 17,51 a 36,35 $mg.g^{-1}$.

Na modelagem matemática, os modelos de Langmuir, Freundlich e Redlich-Peterson foram eficazes na predição do comportamento de equilíbrio dos contaminantes estudados, mostrando que na adsorção empregando as esferas de gelatina comercial e recuperada, as isotermas de adsorção do corante e diclofenaco, seguem os modelos de Freundlich e Langmuir, respectivamente. Ajuste oposto foi verificado nas esferas compósitas acrescidas de nanotubos. Os perfis das curvas isotérmicas foram modificados em função do material utilizado, sugerindo mudanças de mecanismo, onde, as interações eletrostáticas e as ligações de hidrogênio possivelmente, foram os mecanismos envolvidos na adsorção do corante e diclofenaco, respectivamente.

O estudo de reciclo mostrou que ambas as esferas podem ser utilizadas por até 10 ciclos, com capacidades de adsorção próximas a 100 $mg.g^{-1}$, e o NaOH com eluente foi eficiente para realizar a dessorção do corante adsorvido.

Como perspectivas futuras, ressalta-se a necessidade de trabalhos que abordem: i) a produção de compósitos adsorventes a base de gelatina recuperada de resíduos de couro, com adição de outros componentes biopolímeros de fontes residuais, como quitosana, por exemplo, a fim de aumentar a resistência mecânica do material, tornando prescindível o processo de reticulação; ii) estudo de viabilidade econômica para justificar a aplicação da gelatina de fonte residual; iii) estudos de adsorção empregando efluentes reais, outros contaminantes emergentes e utilizando ensaios em coluna de leito fixo.

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ANEXO A – CARACTERIZAÇÃO DO RESÍDUO DE COURO

O resíduo de couro curtido ao cromo (III) foi caracterizado com relação ao teor de umidade (ASTM D3790-2012), cinzas (ASTM D2617-2012), pH (ASTM D2810-2018), Nitrogênio Total Kjeldahl (NTK) (ABNT NBR-11065, 2007) e cromo (ASTM D2807-17a). Todas as análises foram realizadas em triplicata.

Tabela: Caracterização do resíduo de curtume utilizado na extração da gelatina

Amostra	**Umidade (%)**	**Cinzas (%)**	**pH**	**NTK (%)**	**Cromo (%)**
Resíduo de couro curtido ao cromo (III)	52,03±0,55	5,76±0,12	3,18±0,05	14,13±0,36	3,15±0,23

ANEXO B – CARACTERIZAÇÃO DA GELATINA RCCC APÓS CONCENTRAÇÃO EM MEMBRANAS

Durante a produção das esferas, as soluções das gelatinas comercial e RCCC foram caracterizadas quanto ao teor de proteínas (LOWRY, 1951), para garantir a mesma concentração no preparo das esferas. As concentrações de cálcio, sódio e magnésio também foram determinadas. As concentrações de cálcio e magnésio foram determinadas por titulação, de acordo com o método 3111B (APHA, 2012). Para a análise de sódio (método 3111B) e cromo (método 3113A), foi realizada em equipamento espectrofotômetro com absorção atômica (Shimadzu, AA-7000, Japão) (APHA, 2012).

Tabela: Caracterização química da gelatina extraída dos resíduos de couro curtidos ao cromo (III) por hidrólise térmica e alcalina (70ºC, 120 rpm, 6h), após concentração em membranas de ultrafiltração

Análise	**Gelatina RCCC antes da diafiltração**	**Gelatina RCCC após diafiltração**
Umidade (%)	94,918±0,588	96,352±0,021
pH	8,091±0,112	7,620±0,014
Condutividade ($mS.cm^{-2}$)	4,710±0,059	2,145±0,007
Proteína (%)	5,574±0,343	4,207±0,078
Cromo ($mg.L^{-1}$)	0,242±0,014	0,179±0,007
Cinzas (%)	4,172±0,739	2,319±1,033

ANEXO C – CARACTERIZAÇÃO DAS SOLUÇÕES DE GELATINA

Durante a produção das esferas, as soluções das gelatinas comercial e RCCC foram caracterizadas quanto ao teor de proteínas (LOWRY, 1951), para garantir a mesma concentração no preparo das esferas. As concentrações de cálcio, sódio e magnésio também foram determinadas. As concentrações de cálcio e magnésio foram determinadas por titulação, de acordo com o método 3111B (APHA, 2012). Para a análise de sódio (método 3111B) e cromo (método 3113A), foi realizada em equipamento espectrofotômetro com absorção atômica (Shimadzu, AA-7000, Japão) (APHA, 2012).

Tabela: Caracterização das soluções de gelatina comercial e RCCC utilizadas no preparo das esferas adsorventes

Análise	**Gelatina comercial**	**Gelatina RCCC**
Proteína (%)	8,092	8,130
Cálcio ($mg.L^{-1}$)	72,420±2,12	49,905±3,41
Magnésio ($mg.L^{-1}$)	30,310±1,45	327,910±3,81
Sódio ($mg.L^{-1}$)	<3,00	<3,00
Cromo ($mg.L^{-1}$)	0,0075±0,0007	0,546±0,0007

ANEXO D – CARACTERIZAÇÃO DA ÁREA SUPERFICIAL DAS ESFERAS POR BET

A análise de área superficial das esferas adsorventes foram determinadas por Brunauer, Emmett e Teller (1938), pela técnica multiponto (BET), em um aparelho volumétrico usando nitrogênio. Os dados de adsorção de N_2 foram medidos com um aparelho Quantachrome Quantachrome, NOVA 1200e, sob uma pressão relativa variando de 10^{-6} a 0.99.

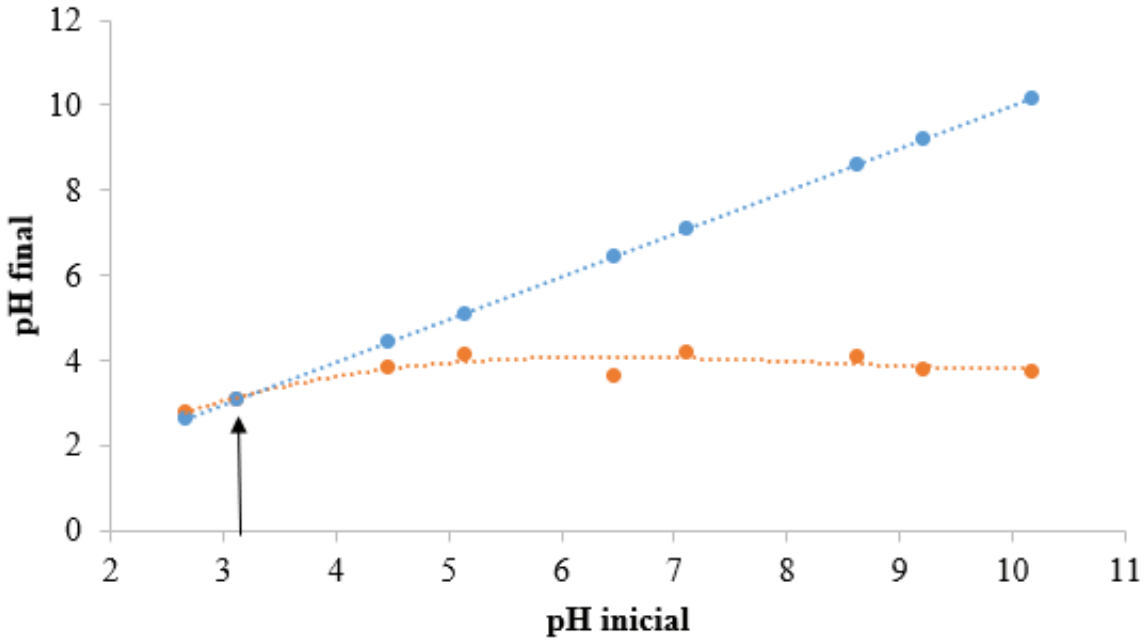
Tabela: Caracterização da área superficial das esferas de gelatina e nanotubos de carbono pelo método de BET

Amostra	**Area superficial ($m^2.g^{-1}$)**
Esferas de gelatina comercial	4,533
Esferas de gelatina RCCC	0,194
Nanotubos de carbono (CNT's)	224,949
Esferas de gelatina comercial e CNT's	0,338
Esferas delatina RCCC e CNT's	0,394

ANEXO E – CARACTERIZAÇÃO DOS NANOTUBOS DE CARBONO POR PONTO DE CARGA ZERO

O ponto de carga zero foi determinado pela adição de 20 mL de solução de NaCl a 0,05 mol.L-1 à amostra de água com um pH inicial definido (variando de 2 a 10, adicionando-se 0,1 mol.L-1 de HCl ou NaOH) em vários frascos contendo 50 mg dos nanotubos de carbono. As suspensões foram mantidas a 25 ºC em incubadora shaker (Marconi, MA-420, Brasil) a 25 ºC e 120 rpm por 48 h, a fim de garantir que atingissem o equilíbrio. O pH das soluções foi então medido usando o medidor de pH (Digimed, D-22, Brasil). O valor do ponto de carga zero é o ponto em que a curva de pHf-pHi versus pHi cruza uma linha igual a zero.

Figura: Ponto de carga zero dos nanotubos de carbono de parede multipla funcionalizados por oxidação



MATERIAL SUPLEMENTAR

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