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https://dx.doi.org/10.21577/0103-5053.20240048

J. Braz. Chem. Soc. **2024**, *35*, 9, e-20240048, 1-16 ©2024 Sociedade Brasileira de Química

Chitosan/Poly(2-(diisopropylamino)ethyl Methacrylate-Based pH-Sensitive Magnetic Composite for Application in Avermectins Adsorption in Aqueous Medium

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A new composite material with magnetic and pH-responsive properties, composed of chitosan/ poly(2-diisopropylamino)ethyl methacrylate ($Fe_3O_4/SiO_2/CS/PDPA$) was developed with the purpose of removing avermectins in aqueous media. The material was characterized by different techniques to evaluate its characteristics. The adsorption process was investigated through the optimization of some parameters, with the most favorable results at pH 8.0, using 20 mg of adsorbent and stirring for 5 min. Under such conditions, the material showed adsorption efficiency of around 80.5, 69.9, and 74.8% for eprinomectin, doramectin and ivermectin, respectively. The adsorption mechanism was investigated using the pseudo-second order kinetic model and the Langmuir-Freundlich dual site isotherm model. Thermodynamic analysis indicated that the adsorption process is exothermic and spontaneous. The material also showed good regenerative capacity, allowing several reuse cycles. The results obtained suggest that the synthesized material has potential application as an adsorbent in the removal of avermectins from aqueous samples.

Keywords: magnetic composite, poly(2-(diisopropylamino)ethyl methacrylate), chitosan, responsive polymers, antiparasitics

Introduction

Avermectins (AVMs) are macrocyclic lactones that naturally occur by *Streptomyces avermitilis* fermentation.^{1,2} Widely utilized in veterinary medicine and agriculture, they are employed to combat pests and parasites such as mites, ticks, worms, and scabies because of their insecticidal and anthelmintic characteristics.^{3,4} Their mechanism of action is hypothetical because AVMs induce neurotoxicity in invertebrates and vertebrates and because they act on glutamate receptors, possibly causing paralysis and death of the parasite.⁵ The intensive and inappropriate use of AVMs is responsible for the dissemination of these compounds in the environment.⁶ Due to their non-specific action, they act not only on parasites, but also on other species in the ecosystem, leading to undesirable effects on non-target species.⁷ In addition, they have a certain resistance to

*e-mail: lguimaraes@ufsj.edu.br Editor handled this article: Fernando C. Giacomelli (Associate) degradation, tending to accumulate, making this a matter of environmental and health concern.^{8,9}

Thus, several studies¹⁰⁻¹³ have been carried out aiming to develop methods that help in the monitoring and reduction of these pollutants in the environment. Among them, adsorption techniques stand out, which present simplicity of operation, low cost, and ability to regenerate adsorbent materials,14-17 and allow adaptations to increase contaminants removal efficiency.¹⁸ Recently, magnetic materials have been widely used in adsorption, separation, and removal of pollutants.¹⁹ Iron oxide nanoparticles, for example, are extensively researched due to their rapid artificial synthesis and their attractive chemical and magnetic properties.²⁰ The magnetic materials offer the benefit of being able to disperse in solutions or suspensions in a reversible manner using an external magnetic field, eliminating the requirement for centrifugation or filtration and thus simplifying and speeding up the process.^{21,22} However, magnetic nanoparticles such as Fe₃O₄ need coating as they are prone to corrosion, oxidation, and aggregation processes.^{23,24} Silica (SiO_2) is commonly chosen for coating because of its stability under acidic conditions, resistance to redox reactions, ability to prevent magnetic nanoparticle aggregation, and the presence of silanol groups on its surface, which enable functionalization with various chemical groups.²⁵

An alternative that can provide better adsorption capacity to the material is the functionalization of magnetic nanoparticles with polymers. Biopolymer hydrogels, or natural polymer hydrogels, are produced from biopolymers and meet sustainability requirements, being non-toxic, degradable, biocompatible, and easy to handle, in addition to offering promising applications for water treatment. A significant subset of natural polymeric hydrogels consists of hydrogels derived from polysaccharides, including hydrogels made from locust bean gum, guar gum, agar, chitosan, and various other materials.²⁶⁻²⁹

Chitosan (CS), poly- β - $(1\rightarrow 4)$ -2-amino-2-deoxy-D-glucose is a biopolymer that presents biocompatibility, biodegradability, and low cost.^{30,31} It is soluble only in acidic pH aqueous solutions, being insoluble in most organic solvents.³² The existence of functional groups, such as NH₂ and OH, in its structure, allows the occurrence of chemical changes, enabling the development of several hybrid materials in different forms and with varied applications, such as the capacity to eliminate a variety of contaminants like dyes, phenolic compounds, pharmaceuticals, metallic ions, and pesticides from wastewater.^{33,34}

Hybrid organic or inorganic nanoparticles with a controlled structure have been extensively studied.35-37 Hybrid polymers with characteristics responsive to stimuli, such as changes in pH, temperature, ionic strength, and magnetic field, may perform better in adsorption processes. pH-sensitive polymers are polyelectrolytes containing weak acidic or basic groups that release or accept protons in response to shifts in the pH of the environment.³⁸ Changes in the external pH can lead to reversible alterations in volume, solubility, conformation, and configuration of the polymeric chains, due to the occurrence of alterations involving the intermolecular interactions between them.³⁹ In this manner, hydrogen bonds, ionic interactions, and hydrophobic interactions between the polymer and the surrounding water molecules are altered, resulting in a reversible phenomenon of separation, or self-assembly through a reversible microphase.40

Polymers that carry basic fractions, such as the amine group, can be protonated and positively charged under acidic conditions, in a way that chains tend to expand due to electrostatic repulsions.⁴¹ Poly(2-(diisopropylamino) ethyl methacrylate (PDPA) is a pH-sensitive homopolymer, which has tertiary amino groups in its structure and has a pK_a of around 6.8.⁴² Due to amino group protonation, this compound shows hydrophilic behavior in aqueous solutions with a pH lower than 6.8 and becomes hydrophobic at a pH higher than the pK_a .^{43,44} Thus, in a solution with a pH value higher than its pK_a , it has a greater affinity for liposoluble molecules, such as the distinct AVMs.

Considering the significant volume of pollutants discharged into aquatic environments and the associated risks to both the environment and human health, extensive endeavors have been made to develop effective treatments. Adsorption techniques employing functionalized magnetic materials have been extensively explored and advanced. Modified magnetite nanoparticles (MNPs) using β-cyclodextrine/allyl 2,3-epoxypropyl ether (AGE) and N-vinylcaprolactam (NVC) as a thermosensitive polymer were synthesized to be used as adsorbents for the removal of diazinon from aqueous solutions, showing significant potential in adsorbing the pesticide from the International Anzali Wetland.⁴⁵ In another study, the preparation of grafted β-cyclodextrin/thermo-sensitive polymer onto modified Fe₃O₄@SiO₂ nanoparticles was investigated for the removal of fenitrothion from aqueous solutions, showing excellent pesticide adsorption capacity.²⁰ In the studies carried by Pandey et al.,28 the synthesis of hydrogel nanocomposites of carob gum-cl-polyacrylonitrile hydrogel nanocomposites (LBG-cl-PAN/IONP) integrated with magnetic iron oxide (IO) was conducted by in situ mineralization of iron ions in a hydrogel matrix for the adsorption of methylene blue and methyl violet from aqueous solution. According to the study, the material exhibited multifunctional efficacy, showing promise for both water treatment applications and antibacterial and supercapacitors.

The purpose of this study was to develop a pH-sensitive composite with a magnetic core and a CS-based coating combined with a synthetic polymer (PDPA) to remove various AVMs (eprinomectin, doramectin, and ivermectin) from aqueous media. Magnetic nanoparticles were used due to their ability for quick and efficient separation. Chitosan functionalization was chosen because of its relevant characteristics, such as biodegradability, cost-effectiveness, and favorable reactivity, allowing modifications in its polymeric structure that result in a material with improved properties. Hybrid polymers responsive to stimuli, such as pH variations, have the potential to enhance performance in adsorption processes. Therefore, PDPA was selected for possessing tertiary amino groups in its structure, becoming hydrophobic at a pH higher than its pK_a and exhibiting greater affinity for AVMs, which are liposoluble molecules.

The synthesized materials (Fe_3O_4 , Fe_3O_4/SiO_2 and $Fe_3O_4/SiO_2/CS/PDPA$) were characterized by scanning electron microscopy coupled to an energy dispersion spectrometer (SEM/EDS), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), thermogravimetric analysis (TGA), point of zero charge (PZC), and effect on material surface wettability. In the investigation of adsorption, various factors such as pH, quantity of adsorbent material, contact time, concentration, and temperature were examined. Kinetic models including pseudo-first order, pseudo-second order, Elovich, and intra-particle diffusion were used to analyze the adsorption processes of AVMs by the developed material. In addition to this, isothermal models such as Langmuir, Freundlich, Sips, single-site Langmuir-Freundlich, dual-site Langmuir-Freundlich, Redlich-Peterson, Temkin, and Hill were also applied for better understanding.

Experimental

Materials

Eprinomectin (EPRI), doramectin (DORA), and ivermectin (IVER) stock solutions were made in methanol at a concentration of 20.0 mg mL⁻¹, stored in amber bottles, and maintained at -20 °C. These solutions were then diluted with ultrapure water to produce standard solutions with concentrations ranging from 0.03 to 2.5 mg mL⁻¹. EPRI, DORA, IVER, ferric chloride hexahydrate (FeCl₃.6H₂O), ferrous sulfate heptahydrate (FeSO₄.7H₂O), chitosan (CS) of medium molar mass (degree of deacetylation of 75-85% and molar mass of 190,000-310,000 Da), 3-(trimethoxysilyl)propyl methacrylate (TMSPMA, 98%), 2-(diisopropylamino)ethyl methacrylate (DPA), and ammonium persulfate (APS) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Sodium hydroxide (NaOH) and ethanol were purchased from Synth and Dinamica (Diadema, SP, Brazil), respectively. Tetraethyl orthosilicate (TEOS) was obtained from Merck (Darmstadt, HE, Germany). Acetic and hydrochloric acids were purchased from Vetec (Rio de Janeiro, RJ, Brazil). Ammonium hydroxide (NH₄OH, 28%) was purchased from Quemis (Indaiatuba, SP, Brazil). Acetonitrile and methanol, high performance liquid chromatography (HPLC) grade, were obtained from J.T. Baker (Mexico City, MX, Mexico). Ultrapure water underwent purification and distillation through the Millipore Milli-Q Plus[®] system (Bedford, MA, USA).

Synthesis of Fe₃O₄/SiO₂/CS/PDPA composite

The synthesis was performed in three stages. In the first stage, Fe_3O_4 nanoparticles were produced by reacting $FeCl_3.6H_2O$ with $FeSO_4.7H_2O$. Subsequently, in the second

stage, the surfaces of these magnetic nanoparticles were coated with TEOS (Fe_3O_4/SiO_2). And finally, in the third stage, the modified magnetic nanoparticles were coated with CS and then proceeded to the DPA polymerization process for synthesis and coupling of PDPA in the CS structure.

Preparation of magnetic nanoparticles coated with SiO₂

In 80 mL of deionized water heated to 80 °C, a solution of 15 mmol FeCl₃.6H₂O and 10 mmol FeSO₄.7H₂O was stirred until fully dissolved. Subsequently, 50 mL of ammonium hydroxide (NH₄OH) with a concentration of 28% (v/v) were added drop by drop, causing the solution to change color from yellow to black. The mixture was then left at 80 °C for half an hour. The resulting precipitate was collected using a neodymium magnet (NdFeB, size: $50 \times 50 \times 5$ mm thick N42), washed with deionized water until reaching pH 7.0 and dried in an oven at 60 °C for 24 h.⁴⁶

To functionalize the nanoparticles with TEOS, 600 mg of Fe₃O₄ were introduced to a solution containing 60 mL of ethanol and deionized water in a ratio of 5:1 (v/v). The mixture was subjected to ultrasonic treatment for 20 min. Following this, a combination of 10 mL of NH₄OH at 28% concentration (v/v) and 4 mL of TEOS were added. The reaction proceeded at room temperature under mechanical agitation for a duration of 12 h. Subsequently, the modified magnetic nanoparticles (Fe₃O₄/SiO₂) were separated using a magnet from the reaction medium and then washed with deionized water until reaching pH level 7.0. Finally, the resulting precipitate was dried at an elevated temperature of 60 °C for a period lasting for 24 h.⁴⁶

Modification of magnetic nanoparticles with CS coupled with $\ensuremath{\mathsf{PDPA}}$

In 35 mL of acetic acid solution (1% v/v) 0.5 g of CS was dissolved. Subsequently, 0.347 g of Fe₃O₄/SiO₂ nanoparticles were added to the solution, followed by stirring for 30 min. Afterwards, the mixture was placed in an oil bath at 70 °C. The solution received 355 µL of TMSPMA and then 300 µL of DPA monomer while being stirred continuously under a nitrogen atmosphere. After 30 min, a slow addition of 2.5 mL ammonium persulfate solution (10 g L⁻¹) took place. The reaction mixture underwent vigorous magnetic stirring for about 4 h. Separation was achieved using a neodymium magnet and the particles were washed with ethanol five times (30 mL each). Finally, the material was dialyzed in water for 5 days, then lyophilized and subsequently macerated.⁴⁷

Characterization of Fe₃O₄/SiO₂/CS/PDPA composite

Scanning electron microscopy images (SEM) were captured using a Hitachi Analytical Table Top TM3000 (New York, USA) scanning electron microscope. The voltage acceleration was set at 20 kV and the instrument was equipped with an energy dispersion spectrometer (EDS). Samples were placed under a carbon tape adhered to the surface of the stub. For FTIR analysis, an PerkinElmer infrared spectrometer Spectrum GX (Waltham, USA) with KBr pellets was utilized, operating between 4000 and 400 cm⁻¹ at a resolution of 4 cm⁻¹ with 128 scans. XRD characterization of the crystalline structures employed a Shimadzu XDR 6000 diffractometer (Tokyo, Japan) using Cu K α_1 = 1.54059 Å and K α_2 = 1.54443 Å radiation. Additionally, thermogravimetric analysis (TGA) was conducted in a Shimadzu DTG-60H thermobalance (Tokyo, Japan) under nitrogen flow (50 mL min⁻¹) from 25 to 800 °C at a heating rate of 10° C min⁻¹ using an alumina sample holder.

In order to establish the point of zero charge (pH_{PZC}) for Fe₃O₄/SiO₂/CS/PDPA material, various aqueous solutions were initially modified to pH values of 2.13, 4.09, 6.10, 7.95, and 10.11 using either NaOH or HCl solutions with a concentration of 0.1 mol L⁻¹ (pH_{initial}). Subsequently, 7 mL of each solution were added to 10 mg of the material and allowed to stand for 24 h. The suspensions pH were then measured again (pH_{final}), and the Fe₃O₄/SiO₂/CS/PDPA material pH_{PZC} was calculated by identifying the point at which the initial pH intersected with the final pH curve.⁴⁸ All determinations were performed in triplicate.

The evaluation of materials wettability involved measuring the contact angle (θ) formed by a water droplet on the material surface. A $\theta \ge 90^{\circ}$ indicates hydrophobic behavior, while $\theta \le 90^{\circ}$ suggests that the material is hydrophilic.^{46,49} The images were captured using a Nikon D90 (Tokyo, Japan) camera combined with a 50 mm magnifying glass.

Chromatographic analysis of avermectins

Chromatographic analysis was conducted using an Agilent[®] HPLC system (Palo Alto, CA, USA), comprising a quaternary pump (1260 G1311B), automatic injector (1260 Hip ALS G1367E), column oven (1290 TCC G1316C), thermostat (1260 G1330B), UV-Vis detector (1260 VWD G1314F), and an Agilent OpenLAB Chromatography Data System[®] data acquisition system. Chromatographic separations of the different AVMs were performed in isocratic mode on a Phenomenex[®] Gemini C18 column (150 mm × 4.6 mm, 5 μ m), with a mobile

phase composed of methanol:acetonitrile:ultrapure water (37:50:13, v/v/v), flow rate of 1.2 mL min⁻¹, injection volume of 20 μ L, $\lambda = 250$ nm, and temperature of approximately 25 °C. Figure S1 (Supplementary Information (SI) section) shows the chromatographic separation of AVMs and Table S1 (SI section) shows the chromatographic parameters of the optimized condition.

Adsorption, desorption, and reuse studies of the $Fe_3O_4/SiO_2/CS/PDPA$ composite

Experiments were conducted to investigate the adsorption of AVMs in aqueous solutions using a horizontal shaker with controlled temperature and mechanical agitation set at 250 rpm. The concentration of the different AVMs was 0.1 mg mL⁻¹ to investigate the effect of pH, contact time, amount of adsorbent, and temperature. As for isothermal tests, AVM concentrations ranged from 0.05 to 2.2 mg mL⁻¹. To assess the impact of pH on the adsorption of AVMs by Fe₃O₄/SiO₂/CS/PDPA material, aqueous solutions of AVMs (0.1 mg mL⁻¹) were prepared at five different pH values (2.0, 4.0, 6.0, 8.0, and 10.0), adjusted with HCl or NaOH (both 0.1 M). Subsequently, 20 mg of Fe₃O₄/SiO₂/CS/PDPA and 2.0 mL of adsorbate solution were added in Falcon® tubes and kept under constant agitation at room temperature for 5 min in a horizontal shaker. The amount of adsorbent was evaluated at 5, 10, 20, and 30 mg of Fe₃O₄/SiO₂/CS/ PDPA. The influence of contact time of the AVMs with the adsorbent material, as well as the adsorption kinetics were assessed by altering the agitation time within a range of 0.5 to 10 min and the thermodynamic study in the temperatures of 25, 35, and 45 °C.

All experiments were performed in triplicate. AVMs concentration in the supernatant, magnetically separated and filtered, was determined by high performance liquid chromatography with UV-Vis detection (HPLC-UV). AVMs adsorbed were quantified by determining the disparity in initial and final concentrations of the analyte in the solutions at equilibrium. The efficiency of adsorption (A) (equation 1) and the quantity of AVMs adsorbed at equilibrium (q_e , mg g⁻¹) (equation 2) were computed: ^{50,51}

$$A(\%) = \frac{\left(C_{i} - C_{eq}\right)}{C_{i}} \times 100$$
⁽¹⁾

$$q_{e}\left(mg \ g^{-1}\right) = \frac{\left(C_{i} - C_{eq}\right) \times V}{m}$$
(2)

In the thermodynamic study, the distribution coefficient (K_d) was calculated using equation 3^{52}

$$K_{d} = \frac{\left(C_{i} - C_{eq}\right) \times V}{mC_{eq}}$$
(3)

where C_i represents the initial concentration and C_{eq} (mg mL⁻¹) the equilibrium concentration; V (mL) denotes the volume of the aqueous solution, while m (g) stands for the mass of adsorbent utilized.

In the kinetic study, the models evaluated were pseudo-first-order (PFO, equation S1), pseudo-secondorder (PSO, equation S2), Elovich (equation S3), and intraparticle diffusion (equation S4). The isothermal models studied were Langmuir (equation S5), Freundlich (equation S6), Sips (equation S7), Redlich-Peterson (equation S8), Temkin (equation S9), Hill (equation 10), single-site Langmuir-Freundlich (equation S11), and dual-site Langmuir-Freundlich (equation S12) in the SI section.53-57 Data related to kinetics and isothermal processes were analyzed using non-linear equations that are well-documented in academic literature. The most suitable models were determined through examination of the coefficients of determination (R^2) and comparison of experimental q_e values with those obtained from the equations, as well as assessment of nonlinear error metrics such as residual root mean square error (RMSE).47

In the AVM desorption assay, acetate buffer pH 4, phosphate buffer pH 7, bicarbonate buffer pH 10, acetonitrile, and methanol were used as desorption solvents. Initially, the adsorption process was carried out with optimized parameters, the material was separated using a magnet and supernatant was then eliminated. Then, in each Falcon® tube containing the adsorbed material, 2.0 mL of each desorption solvent was added. The tubes were placed on a horizontal shaker at 250 rpm for 5 min. Next, the supernatant was separated from the material, passed through a filter, and analyzed in order to determine the quantity of analyte that had been removed. Each experiment was conducted three times (n = 3), and the desorption percentage was determined using equation S13. After desorption, 2 mL of acetonitrile were added to the adsorbent and agitated for 5 min. This was followed by adding 2 mL of ultrapure water to regenerate the material, which was then stirred for 1 min. The resulting supernatants were both discarded. Subsequently, the material underwent five cycles of adsorption-desorption to assess its reusability.

Results and Discussion

Obtaining of Fe₃O₄/SiO₂/CS/PDPA composite

Initially, the processes for preparing the particles of Fe_3O_4 and Fe_3O_4/SiO_2 were carried out. Obtaining the

iron particles was given by the coprecipitation method of iron II sulfate (FeSO₄) with iron III chloride (FeCl₃), in a basic medium.⁵⁸ Then, to obtain the magnetic support (Fe₃O₄/SiO₂), modification with TEOS was performed, through which chemically stable modified magnetic particles with high magnetic performance were obtained since the magnetic properties of Fe₃O₄ were maintained.⁵⁹ Subsequently, Fe₃O₄/SiO₂ was covered with CS and PDPA, as follows: the initiator APS was thermally dissociated, generating sulfate anion radicals in the reaction medium, which attacked the CS chains and originated macro radicals, which interacted with the DPA and TMSPMA monomers, leading to the chain growth process.^{60,61} The proposed Fe₃O₄/SiO₂/CS/PDPA synthesis scheme is illustrated in Figure 1.

Characterization of Fe₃O₄/SiO₂/CS/PDPA composite

Characterization of morphology and elemental composition by SEM/EDS

Figure 2 shows particle morphologies of Fe_3O_4 (Figures 2a-2b), Fe_3O_4/SiO_2 (Figures 2c-2d), and $Fe_3O_4/SiO_2/CS/PDPA$ (Figures 2e-2f), at amplifications of 500 and 1500×. Electromicrographs showed heterogeneous surfaces with no defined shape, with some irregular clusters for all synthesized materials. However, it was noted that magnetic nanoparticle modification (Fe_3O_4) with TEOS (Figure 2c-2d) and subsequent coating with CS and PDPA (Figures 2e-2f) made the material more fragmented.

EDS analysis enabled a semi-quantitative assessment of the elemental composition of the materials (see Table 1). For Fe₃O₄, a high percentage of Fe and O was observed, in addition to very small amounts of Si, N, and Cl from the reaction medium and remaining impurities after washing, as well as the presence of C, because of the carbon tape used for fixing the materials on the setup. The material coated with SiO₂, Fe₃O₄/SiO₂, experienced a decrease in the quantity of Fe and an elevation in O, as well as an increase in Si, attributed to the TEOS coating, along with a small amount of C, N, and Cl. Relating to Fe₃O₄/SiO₂/ CS/PDPA material, there was a reduction of Fe and Si, a small variation in O percentage, and a significant increase in C content, provided by PDPA and CS structures, demonstrating the presence of organic materials under the modified magnetic particles.

Evaluation of chemical bonds and functional groups by FTIR

FTIR spectra of Fe_3O_4 , Fe_3O_4/SiO_2 , CS, and $Fe_3O_4/SiO_2/CS/PDPA$ are shown in Figure 3a. Fe_3O_4 exhibits an absorption peak at around 539 cm⁻¹ due to the stretching vibration of the Fe–O bond. The bands



Figure 1. Scheme of the synthesis of Fe₃O₄/SiO₂/CS/PDPA composite.



Figure 2. Scanning electron microscope images for Fe_3O_4 at different magnifications: (a) 500x; (b) 1500x; and Fe_3O_4/SiO_2 : (c) 500x; (d) 1500x; and $Fe_3O_4/SiO_2/CS/PDPA$: (e) 500x; (f) 1500x.

				Element / %			
Material	С	0	Si	Fe	Ν	Clb	Total
Fe ₃ O ₄	5.09a	24.87	0.12	68.38	0.90	0.63	100.00
Fe ₃ O ₄ /SiO ₂	4.09a	47.47	23.10	23.84	1.11	0.40	100.00
Fe ₃ O ₄ /SiO ₂ /CS/PDPA	23.06	42.53	15.77	14.16	4.15	0.32	100.00

Table 1. Determination of the elemental composition of the synthesized materials by EDS analysis

^aContamination (use of carbon tape for conducting the analyses); ^bimpurities. CS: chitosan; PDPA: poly(2-diisopropylamino)ethyl methacrylate.

at 1632 and 3438 cm⁻¹ are associated with angular strain and the stretching mode of the –OH group, respectively. Meanwhile, in the absorption spectrum for Fe_3O_4/SiO_2 , peaks around 1076 and 810 cm⁻¹ correspond to asymmetric and symmetric stretching vibrations of Si–O–Si. Additionally, a band observed at 943 cm⁻¹ can be attributed to Si–O stretching vibrations.⁶²

The CS spectrum revealed a band at 3350 cm⁻¹, which represents the stretching vibration of the O–H bond, superimposed on the N–H stretching band. The absorption at 2868 cm⁻¹ is attributed to the stretching of CH₃ and CH₂ groups. Additionally, the band observed at 1653 cm⁻¹ corresponds to the stretching of the C=O double bond amide group carbonyl (amide I) while that at 1585 cm⁻¹ signifies angular deformation vibrations of N–H bonds (amide II). We observed bands at 1374 cm⁻¹ due to angular deformation of CH₃ groups and at 1150 cm⁻¹ for C–N stretching vibrations. The absorptions at 1069 and 1028 cm⁻¹ correspond to the stretching of C–O and C–O–C glycosidic bonds and the band at 893 cm⁻¹ is due to C–O–C

In the Fe₃O₄/SiO₂/CS/PDPA spectrum, the absence of C=C stretching bands around 1500 to 1600 cm⁻¹, typical of the DPA monomer, can be seen, demonstrating the rupture of this double bond and the formation of a single bond between a free radical of chitosan (from thermal dissociation of the radical initiator) and a molecule of DPA, with, therefore, the radical polymerization of DPA monomers.^{66,67} Furthermore, the formation of Fe₃O₄/SiO₂/CS/PDPA can be identified by comparing its spectrum

with that of CS. This comparison suggests that PDPA may be linked to OH and NH_2 groups, as evidenced by the absence of absorption bands associated to stretching vibrations of amino and hydroxyl groups present in the CS spectrum. It is also possible to observe a more intense band between 1000 and 1200 cm⁻¹, indicating the stretching of C–O–C bonds from the ester group of PDPA. This also includes the stretching of C–O–C bonds in the ether group, a consequence of coupling between PDPA and CS. This bonding may take place through the reaction involving the double bond located at the end of the PDPA polymer chain and the OH groups of CS.⁴⁷

Verification of the presence of crystalline and amorphous structures by XRD

To perform the chemical identification and to evaluate the crystal structure and microstructure of the synthesized materials, the characterization by XRD was performed. According to Figure 3b, it is possible to observe six characteristic Fe₃O₄ peaks located between the 20 and 70° diffraction angle (20), which refer to Miller indices (220), (311), (400), (422), (511), and (440). This result is consistent with the crystalline diffraction pattern for Fe₃O₄ found in the American Mineralogist Crystal Structure Database.⁶⁸ Nevertheless, traces of maghemite, the oxidized form of magnetite, may be present due to the synthesis process not being conducted in an inert atmosphere. However, identifying these traces is currently not significant as maghemite exhibits magnetic properties similar to magnetite. The same angles are visible in the Fe₃O₄/SiO₂



Figure 3. (a) FTIR (KBr); (b) X-ray diffraction analyses; (c) thermogravimetric analyses of Fe₃O₄, Fe₃O₄/SiO₂ and Fe₃O₄/SiO₂/CS/PDPA.

and Fe₃O₄/SiO₂/CS/PDPA diffractograms, indicating that these materials preserved the crystalline structure of Fe₃O₄, assuring its magnetic properties. Furthermore, it is possible to observe that the angles were less intense, confirming the coating of Fe₃O₄ nanoparticles with SiO₂ and, later, with polymeric material. In the Fe₃O₄/SiO₂/CS/PDPA diffractogram, there is also the beginning of the formation of a halo at approximately $2\theta = 20^{\circ}$, referring to the amorphous characteristic of polymeric materials, showing the coating of the magnetic particles with the CS coupled to the PDPA.⁶⁹

Determination of the thermal degradation profile by TGA

To evaluate the thermal decomposition of the synthesized materials, TGA was performed (Figure 3c). It is possible to verify in all thermograms a mass loss event, at temperatures below 100 °C, referring to the loss of weakly adsorbed water on the surface of the materials. Both Fe_3O_4 and Fe_3O_4/SiO_2 , after heating at 800 °C, lose a small percentage of mass, 2.92, and 8.49%, respectively, due to high thermal resistance of magnetite. The percentage in the Fe_3O_4/SiO_2 thermogram does not only correlate with water release but also indicates the reduction of organic fraction content due to the functionalization of the magnetic nanoparticle with TEOS. For Fe₃O₄/SiO₂/CS/PDPA, there is a significant mass loss of approximately 63%, which corresponds to the decomposition of the polymeric material, CS, and PDPA. The results obtained by the thermal decomposition analysis validate the existence of the polymeric (organic) material encrusted with Fe₃O₄/SiO₂ particles, producing a material with an inorganic magnetic fraction together with organic polymeric material (25-800 °C). These results indicate that the majority of the Fe₃O₄/SiO₂/CS/PDPA mass is attributed to the polymeric material (CS/PDPA), comprising over 60%, while only around 37% of the mass originates from the magnetic particles, which remain stable within the temperature range analyzed (25-800 °C).46

Wettability study

The measurement of a material hydrophilicity can be examined through the contact angle formed by a drop of water, at rest, on its solid surface. Material surfaces are classified according to the obtained contact angle: superhydrophilic for angles smaller than 5°, hydrophilic for smaller than 90°; hydrophobic for those between 90° and 150° and super-hydrophobic if the angle is greater than 150° .⁴⁶ As can be observed in Figure 4, contact angles of 69.3 and 74.2° were obtained for Fe₃O₄ (Figure 4a) and Fe₃O₄/SiO₂ (Figure 4b), respectively, suggesting that both had hydrophilic surfaces. For Fe₃O₄/SiO₂/CS/PDPA (Figure 4c) the contact angle is 131.9°, indicating that the polymeric coating (CS/PDPA) resulted in a material with a hydrophobic surface, therefore, with different characteristics from its precursors.

Study of the adsorption capacity of avermectins by $Fe_{3}O_{4}/SiO_{2}/CS/PDPA$ composite

Influence of pH, $\text{pH}_{\text{PZC}},$ amount of adsorbent material, and contact time

The influence of pH on the AVMs adsorption process was evaluated using five different pH values of the medium (2.0, 4.0, 6.0, 8.0, and 10.0). As can be seen in Figure 5a, the material showed the highest percentage of adsorption at pH 8.0. The analyzed AVMs present the following pK_a values: DORA and IVER 12.47, and EPRI 12.49, therefore for pH values below 12.0 all are found in their molecular forms (100%).⁷⁰ This favored the adsorption process on Fe₃O₄/SiO₂/CS/PDPA, around 80.5% for EPRI, 69.9% for DORA and 74.8% for IVER.

The point of zero charge (pH_{PZC}) indicates the pH value at which the sum of the electrical charges present on its surface is equal to zero. It is established by identifying the pH at which the initial solution and the solution in contact with the material have similar or almost identical pH values. When the pH of the solution is below the pH_{PZC} of the material, the surface of the material exhibits a positive net charge and a negative charge when the pH is above the pH_{PZC} .^{46,71} Figure 5b demonstrates that the pH_{PZC} of Fe₃O₄/SiO₂/CS/PDPA is 7.58. Therefore, when the pH is below 7.58, the surface of the material exhibits a positive charge, whereas at pH above 7.58, the charge is negative. Thus, at pH 8.0, the Fe₃O₄/SiO₂/CS/PDPA surface still



Figure 4. Surface wettability evaluation of the (a) Fe₃O₄; (b) Fe₃O₄/SiO₂; (c) Fe₃O₄/SiO₂/CS/PDPA.



Figure 5. (a) Percentage of avermeetins adsorption on material at different pH values; (b) pH_{PZC} of Fe₃O₄/SiO₂/CS/PDPA; (c) influence of the amount of adsorbent material on the adsorption of avermeetins.

shows charge balance, tending to a negative charge, and AVMs are in their molecular forms, making it possible to deduce that van der Waals-type interactions and hydrogen bonds can occur between the adsorbent material and AVMs, as they involve intermolecular forces. Furthermore, CS $(pK_a = 6.3-7.0)^{47.70}$ and PDPA $(pK_a ca. 6.8)^{70}$ possess amino functional groups that are deprotonated in basic solutions. Therefore, CS, and PDPA exhibit hydrophobic behavior in basic solutions, where the pH value is higher than the pK_a . In other words, CS modified with PDPA potentially shows better adsorption of AVMs in a pH 8.0 solution due to the high lipophilicity of these molecules.

To study the effect of the amount of adsorbent, 5, 10, 20, and 30 mg of Fe₃O₄/SiO₂/CS/PDPA were analyzed. It is observed in Figure 5c that the amount of AVMs adsorbed increased as the amount of material also increased, remaining practically constant from 20 mg onwards. A greater quantity of material is expected to have a higher number of active sites for adsorbate molecule interaction on its surface, leading to an increase in the amount adsorbed until reaching a constant level of adsorption. Thus, it was determined that the amount of Fe₃O₄/SiO₂/CS/PDPA used in future studies would be 20 mg.

In Figure 6, which shows the graph of the experimental data of q_t (amount of AVMs adsorbed) *versus* time, it is possible to observe that the adsorption remained stable after 5 min. Before that time, adsorption occurred as a

result of the availability of active sites on the surface of Fe₃O₄/SiO₂/CS/PDPA. Therefore, when the active sites were occupied by adsorbate, the amount adsorbed reached equilibrium, remaining constant. For the three AVMs studied, equilibrium was reached within 5 min. It is possible to observe that EPRI presented the highest amount of adsorption ($q_e = 8.03 \text{ mg g}^{-1}$), followed by IVER ($q_e = 7.39 \text{ mg g}^{-1}$), and finally DORA ($q_e = 6.72 \text{ mg g}^{-1}$).

Adsorption kinetics

The study of adsorption kinetics is of utmost importance for understanding the mechanism involved in the process. The kinetic analysis included the application of four different models: PFO, PSO, Elovich, and intraparticle diffusion. The kinetic parameters of each model were analyzed and presented in Table 2, and the non-linearized forms were graphically represented in Figures S2-S5 (SI section). The most suitable kinetic model was selected based on its ability to match the experimental findings in terms of adsorption capacity at equilibrium (q_e), coefficient of determination (R^2), and statistically significant metrics such as RMSE.⁷²

According to Table 2, the PPO model presents calculated values of q_e (EPRI = 8.004 mg g⁻¹; DORA = 6.697 mg g⁻¹; IVER = 7.354 mg g⁻¹) close to the experimental values (q_{eexp}), (EPRI = 8.035 mg g⁻¹; DORA = 6.724 mg g⁻¹ and IVER = 7.387 mg g⁻¹), however, it did not show good



Figure 6. Influence of contact time on adsorption of (a) eprinomectin; (b) doramectin; (c) ivermectin on Fe₃O₄/SiO₂/CS/PDPA.

	Pseudo-first-order				Elovich				
	K ₁ / min ⁻¹	$q_e / (mg g^{-1})$	$q_{eexp} / (mg g^{-1})$	\mathbb{R}^2	RMSE	$\frac{\alpha /}{(\text{mg g}^{-1} \min^{-1})}$	β / (g mg ⁻¹)	\mathbb{R}^2	RMSE
EPRI	0.198	8.004	8.035	0.635	0.052	5.68×10^4	13.674	0.934	0.022
DORA	0.248	6.697	6.724	0.569	0.046	3.79×10^4	16.301	0.987	0.018
IVER	0.081	7.354	7.354	0.653	0.062	5.73×10^4	9.750	0.983	0.019
		Ps	eudo-second-ord	er			Intraparticl	e diffusion	
	$\frac{K_2}{(g m g^{-1} m i n^{-1})}$	$q_e / (mg \ g^{-1})$	$q_{eexp} / (mg g^{-1})$	\mathbb{R}^2	RMSE	K _{id} / (mg g ⁻¹ min ^{-1/2})	C / (mg g ⁻¹)	\mathbb{R}^2	RMSE
EPRI	4.039	8.039	8.035	0.925	0.023	0.036	7.780	0.882	0.029
DORA	1.456	6.727	6.724	0.913	0.021	0.076	6.507	0.972	0.027
IVER	0.602	7.397	7.387	0.958	0.021	0.134	7.042	0.949	0.020

Table 2. Parameters concerning the kinetics obtained from the adsorption of AVMs in Fe₃O₄/SiO₂/CS/PDPA

EPRI: eprinomectin; DORA: doramectin; IVER: ivermectin; q_e : adsorbed quantities at equilibrium and at any time; q_{eexp} : experimental values; K_1 , K_2 , K_{ia} : pseudo-first-order, pseudo-second-order, intraparticle diffusion constants, respectively; α : adsorption rate; β : desorption rate; C: constant related to the thickness of the boundary layer of the adsorbent; R^2 : correlation coefficient; RMSE: root mean square error.

adjustment to the obtained experimental data, as observed by the determination coefficients (R^2), lower than 0.653. The PSO model (see Figure S3, SI section) yielded superior fits to the measured data, achieving R^2 values exceeding 0.913 for all AVMs and q_{eexp} values even closer than the PPO model, as well as demonstrating low RMSE values. Thus, the most suitable adjustment to this model suggests that the adsorption mechanism is governed by a second-order rate equation and that chemical adsorption was the limiting step for the adsorption of AVMs by Fe₃O₄/SiO₂/CS/PDPA.⁷³

In addition to the PPO and PSO models, the analysis also included the Elovich and intraparticle diffusion models to determine the mechanism of diffusion in the adsorption process. Both models posit that the active sites on the adsorbents are varied and have dissimilar activation energies. Moreover, the adsorption process involves two distinct stages: mass transfer to the adsorbent surface and subsequent intraparticle diffusion. The initial step entails swift adsorption at the exterior sites of the adsorbent material, while the second phase is characterized by a slower adsorption process occurring at the more internal sites.53,74 After analyzing the experimental data from Elovich (Figure S4, SI section), it can be observed that the first line of the graph presents a good fit with R² values of 0.934 for EPRI, 0.987 for DORA, and 0.983 for IVER (Table 2), therefore, it can be said that adsorption takes place at the outermost sites of the adsorbent material. Additionally, it is worth noting that the α values were greater than the β values, suggesting a strong affinity between the adsorbent and adsorbate.75

According to the intraparticle diffusion model, adsorption can also be affected by the parameter associated with the boundary layer thickness (C). The higher the value of C, the more diffusion-dependent the adsorption process will be. Figure S5 (SI section) shows that the curve does not cross the origin and displays positive values of C ($C_{EPRI} = 7.780$, $C_{DORA} = 6.507$, and $C_{IVER} = 7.042$), indicating that the adsorption process may involve complex mechanisms, besides intraparticle diffusion not being the sole limiting step in the overall process.^{53,75} However, the coefficient of determination (R^2) values for the intraparticle diffusion model are lower than those of the Elovich model (Table 2), suggesting that the adsorption process takes place primarily in the outermost layers of the adsorbents.

Adsorption isotherm

Isotherm models are utilized to comprehend phenomena observed during the adsorption process, including surface properties and the affinity of the adsorbent.⁷⁶ To understand the adsorption behavior of AVMs on Fe₃O₄/SiO₂/CS/PDPA, eight isothermal models were used: Langmuir, Freundlich, Sips, Redlich-Peterson, Temkin, Hill, single-site Langmuir-Freundlich and dual-site Langmuir-Freundlich. Figure 7 shows the isotherms constructed from the non-linear fit of the experimental data for the studied models and Table 3 shows the parameters obtained by the analyzed models.

The Langmuir model describes the process of adsorption in monolayers on a homogeneous adsorbent surface, containing a finite number of adsorption sites, identical and with the same energy.⁷⁷ This model provided low K_L values (EPRI = 0.0023 Lg^{-1} , DORA = 0.0019 Lg^{-1} , and IVER = 0.0027 Lg^{-1}), which suggests little interaction between adsorbent and adsorbate, favoring the desorption. The R² values obtained were below 0.974, indicating that the Langmuir model does not correspond to the best adsorption process of AVMs on Fe₃O₄/SiO₂/CS/PDPA.



Figure 7. Adjusted isothermal models for (a) eprinomectin; (b) doramectin; (c) ivermectin.

Table 3. Nonlinear isotherm coefficients derived from the adsorption of avermectins in Fe₃O₄/SiO₂/CS/PDPA

Model	Parameter	Eprinomectin	Doramectin	Ivermectin
	$K_L / (L g^{-1})$	0.0023	0.0019	0.0027
Langmuir	Q / (mg g ⁻¹)	196.64	180.73	189.82
	\mathbb{R}^2	0.968	0.961	0.974
	$K_{\rm F} / ({\rm mg}~{\rm g}^{-1})$	3.2545	2.3499	3.9731
Freundlich	1/n	0.549	0.576	0.518
	\mathbb{R}^2	0.932	0.923	0.931
	K _s / (L mg ⁻¹)	0.0136	0.0390	0.0248
0.	Q / (mg g ⁻¹)	196.61	180.71	189.80
Sips	n	6.019	20.103	7.758
Freundlich K ₁ Freundlich K ₂ Sips Q K Redlich- Peterson K α Iemkin b _T Image: A state of the state of th	\mathbb{R}^2	0.962	0.954	0.968
	$K_{R} / (L g^{-1})$	0.295	0.239	0.0248 189.80 7.758 0.968 0.305 0.189 0.989 0.961 0.109 96.293 0.829 145.247 51.743 1.584 0.815 0.0012
	α / (L mg ⁻¹)	0.324	0.467	0.189
Redlich-Peterson	β	0.997	0.990	0.989
	\mathbb{R}^2	0.950	0.948	0.961
	$A_{T} / (L g^{-1})$	0.114	0.063	0.954 0.968 0.239 0.305 0.467 0.189 0.990 0.989 0.948 0.961 0.063 0.109 98.749 96.293 0.833 0.829 125.347 145.247 124.643 51.743 0.911 1.584
Temkin	b _T / (kJ mol ⁻¹)	102.086	0.0019 0.0 180.73 18 0.961 $0.$ 2.3499 3.5 0.576 $0.$ 0.923 $0.$ 0.0390 0.0 180.71 18 20.103 $7.$ 0.954 $0.$ 0.239 $0.$ 0.467 $0.$ 0.990 $0.$ 0.948 $0.$ 0.990 $0.$ 0.948 $0.$ 0.990 $0.$ 0.948 $0.$ 0.991 $1.$ 0.948 $0.$ 0.948 $0.$ 0.948 $0.$ 0.948 $0.$ 0.948 $0.$ 0.948 $0.$ 0.948 $0.$ 0.948 $0.$ 0.9911 $1.$ 0.847 $0.$ 0.0011 0.0 0.0039 0.0 0.0139 0.0 0.0139 0.0 0.0139 0.0 0.0139 0.0 0.0139 0.0 0.0139 0.0 0.0139 0.0 0.0139 0.0 0.0139 0.0 0.0139 0.0 0.0139 0.0 $0.109.56$ 10 2.431 26 8.549 $1.$	96.293
	\mathbb{R}^2	0.806	0.833	0.829
	$q_{\rm H} / (mg \ g^{-1})$	140.644	125.347	145.247
11'11	$K_{\rm H} / (L mg^{-1})$	52.731	124.643	0.0027 189.82 0.974 3.9731 0.518 0.931 0.0248 189.80 7.758 0.968 0.305 0.189 0.961 0.109 96.293 0.829 145.247 51.743 1.584 0.815 0.0013 258.36 1.942 0.987 0.0033 0.0063 30.83 105.11 26.394 1.481 0.902
Hill	n	0.777	0.911	1.584
	\mathbb{R}^2	0.799	0.847	0.815
	K / (L g ⁻¹)	0.0012	0.0011	0.0013
Single-site Langmuir-	Q / (mg g ⁻¹)	252.29	220.42	258.36
Freundlich	n	2.245	2.424	1.942
	\mathbb{R}^2	0.981	0.984	0.987
	$K_1 / (L g^{-1})$	0.0032	0.0039	0.0033
	$K_2 / (L g^{-1})$	0.0051	0.0139	0.0063
	$Q_1 / (mg g^{-1})$	34.32	6.10	30.83
Dual-site Langmuir-Freundlich	Q ₂ / (mg g ⁻¹)	103.76	109.56	105.11
	n_1	30.266	2.431	26.394
	n ₂	1.322	8.549	1.481
	\mathbb{R}^2	0.995	0.982	0.992

 Q, Q_1, Q_2 : constant related to maximum adsorption capacity; $K_L, K_{F^3}, K_S, K_R, K_H, K_1, K_2$: related to the affinity adsorbent-adsorbate parameters; α : Redlich-Peterson isotherm constant; β : Redlich-Peterson exponent; A_T : equilibrium binding constant of the Temkin isotherm; b_T : Temkin isotherm constant; q_H : saturation for maximum uptake of the Hill isotherm; n: constant related to the adsorption intensity or degree of adsorption.

The Freundlich model accounts for the adsorption process taking place in multiple layers, where the interaction between the adsorbent and the adsorbate happens in heterogeneous sites with varying affinities and binding energies.⁷⁸ For this model, K_F values of 3.2545 mg g⁻¹ were obtained for EPRI, 2.3499 mg g⁻¹ for DORA, and 3.9731 mg g⁻¹ for IVER and values of n greater than 1, indicating favorable adsorption conditions.⁵² However, the R² values were less than 0.932 (Table 3), presuming that this model also does not offer the most accurate description of the adsorption process.

The Sips model combines aspects of both the Langmuir and Freundlich models, proposing that the adsorbent surface can exhibit homogeneity at high concentrations of adsorbate and heterogeneity at low concentrations.⁷⁹ This model showed low K_s values (EPRI = 0.0136 L mg⁻¹, DORA = 0.0390 mg⁻¹, and IVER = 0.0248 mg⁻¹) and n values exceeding 1 (Table 3), suggesting that the adsorption process has low energy consumption. However, this model presented values of R² = 0.962 for EPRI, 0.954 for DORA, and 0.968 for IVER, indicating inadequate fitting of the experimental results to this model.

The Redlich-Peterson model is a variant of the Sips isotherm. It integrates three parameters, combining elements of both Langmuir and Freundlich isotherms, meaning it can be applied to both homogeneous and heterogeneous systems.^{55,80} This model showed β_R values close to 1.0 for the three analyzed AVMs, suggesting the possibility of converting the equation to the Langmuir equation. The R² values obtained were below 0.961, suggesting that this model does not accurately represent the adsorption process of AVMs on Fe₃O₄/SiO₂/CS/PDPA.

The Temkin model takes into account the interaction between the heterogeneous surface of the adsorbent molecules and the adsorbate molecules. It postulates that the heat of adsorption of all molecules in the layer decreases linearly with increasing surface coverage of the adsorbent.⁸¹ In contrast, the Hill model assumes that adsorption is a cooperative process where the presence of adsorbates on one adsorbent site influences multiple sites on the adsorbent. It describes the binding of multiple species on uniform substrates.⁵⁷ Both models showed R² values well below the ideal value, indicating that they do not fit this adsorption study.

The single-site Langmuir-Freundlich isotherm model shares a similar concept to Sips; however, it employs a distinct mathematical equation to assess the adsorption mechanism. Similar to the Freundlich model, the n value determines the favorability of the adsorption process. The dual-site Langmuir-Freundlich model also combines the Langmuir and Freundlich models, and can occur in

homogeneous or heterogeneous locations, however, it exceeds some limitations present in the Sips and singlesite models.53 The single-site Langmuir-Freundlich model showed n values of 2.245 for EPRI, 2.424 for DORA, and 1.942 for IVER, however, the maximum adsorption capacity between the analyzed models was not close to the values found experimentally. In addition, low K values, as well as R² values between 0.980 and 0.986, confirm that this model did not fit properly. However, the dual-site Langmuir-Freundlich model obtained a maximum adsorption capacity (Q_{max}) of 138.08 mg g⁻¹ for EPRI, 115.66 mg g^{-1} for DORA, and 135.94 mg g^{-1} for IVER, values that were very close to those determined experimentally: 125.32 mg g⁻¹ for EPRI, 110.06 mg g⁻¹ for DORA, and 128.41 mg g⁻¹ for IVER. Furthermore, the analyte showed values of $n(n_1 + n_2)$ greater than 1, indicating that the adsorption process was favorable and also the best fits with R² values of 0.995, 0.982, and 0.992 for EPRI, DORA, and IVER respectively. Therefore, this suggests that the dual-site Langmuir-Freundlich model is the most suitable for representing the adsorption process of AVMs on Fe₃O₄/SiO₂/CS/PDPA based on the experimental data.

Effect of temperature and thermodynamic studies

The adsorption of AVMs on $Fe_3O_4/SiO_2/CS/PDPA$ was analyzed at temperatures of 25, 35, and 45 °C under previously optimized conditions. As can be seen in Figure S6a (SI section), the rise in temperature promoted a small increase in the amount adsorbed from 8.14 to 8.79 mg g⁻¹ for EPRI, from 6.65 to 7.62 mg g⁻¹ for DORA, and from 7.13 to 8.12 mg g⁻¹ for IVER. The reason for this behavior is that higher temperatures lead to increased molecular mobility, enabling a greater interaction of adsorbate molecules in the active sites of the adsorbent.⁵³

The thermodynamic procedure was assessed by considering the parameters ΔG (Gibbs free energy), ΔH (enthalpy), and ΔS (entropy) which can be determined using equations S14 and S15 (SI section).⁸² Figure S6b shows the good linear fit of the graph of lnK_d vs. 1/T with $R^2 > 0.98$ for the three studied AVMs. Table 4 shows the thermodynamic parameters obtained (ΔG , ΔH , and ΔS). It is observed that all ΔG values were negative, showing that spontaneous processes occurred. Also, as the temperature increased, ΔG values decreased, leading to the conclusion that the adsorption was favored by the increase in temperature. According to the negative values of ΔH , the adsorption process can be classified as exothermic. The positive ΔS values suggest an increase in disorder at the interfaces between the liquid and solid phases throughout the adsorption process.

	Temperature / K	$\Delta G (kJ mol^{-1})$	$\Delta H / (kJ mol^{-1})$	$\Delta S / (kJ mol^{-1})$	\mathbb{R}^2
	298	-2.64			
Eprinomectin	308	-2.77	-2.29	13.73	0.99
	318	-2.91			
	298	-2.95			
Doramectin	308	-3.09	-2.60	14.14	0.99
	318	-3.23			
	298	-3.56			
Ivermectin	308	-3.72	-3.15	16.28	0.99
	318	-3.89			

Table 4. Thermodynamic parameters of avermectins adsorption on Fe₃O₄/SiO₂/CS/PDPA

 ΔG : Gibbs free energy; ΔH : enthalpy; ΔS : entropy; R²: coefficient of determination.

Evaluation of desorption and regeneration capacity

Analytes desorption enables the adsorbent regeneration, thereby restoring its adsorption capabilities and enabling reuse. This improves the cost-effectiveness of the adsorption process. Initially, the desorption studies were performed with 2.0 mL of pH 4.0, pH 7.0, and pH 10.0 buffer solutions, considering that the adsorption was pH-dependent. However, none of these solutions was efficient in the desorption of AVMs from the material, with the amounts desorbed being less than 10%, as can be seen in Figure 8a. Therefore, it was decided to use methanol and acetonitrile, which have a greater elution force. Both solvents exhibited good desorption efficiency; however, acetonitrile was a little better, desorbing 61.47% of EPRI, 66.33% of DORA, and 60.41% of IVER.

The adsorption efficiency of the material was also assessed through five consecutive adsorption-desorption cycles, employing the same adsorbent. The adsorbent was washed with acetonitrile followed by ultrapure water between each cycle to eliminate possible ions present on its surface. The findings are presented in Figure 8b, demonstrating that the adsorption capability of $Fe_3O_4/SiO_2/$ CS/PDPA remained consistent. This suggests a reversible adsorption process and indicates significant potential for utilizing the synthesized material in the adsorption of other analytes for future research purposes.⁴⁷

Comparison with other studies

There are not many works in the literature so far that carry out the development of materials for the adsorption of AVMs in an aqueous medium. However, Olu-Owolabi et al.18 use composites prepared from kaolinite and biochar from Carica papaya (KPA) and pine cone (KPC) seeds as adsorbent material to remove ivermectin from aqueous solution. The adsorbents in this research displayed two distinct peaks of adsorption, one occurring in the acidic pH range and the other in the alkaline pH range. The maximum adsorption capacities were $105.3 \,\mu g \, g^{-1}$ for KPA and $115.8 \,\mu g \, g^{-1}$ for KPC. Equilibrium in the adsorption process occurred in 180 min. Furthermore, the study also examined the potential for reusing the composites through three cycles of adsorption-desorption. It was found that both adsorbents experienced a decrease in their adsorption capabilities over successive cycles.

Nippes *et al.*⁷⁵ examined the effectiveness of a commercial organophilic clay based on bentonite for extracting ivermectin from an aqueous solution. The highest quantity of ivermectin adsorbed by the organophilic clay



Figure 8. (a) Avermeetins desorption experiments; (b) use of $Fe_3O_4/SiO_2/CS/PDPA$ in multiple adsorption-desorption cycles.

was 3.88 mg g⁻¹, with equilibrium reached within 60 min. Additionally, the adsorption process was more favorable at the natural pH of the solution, and after six reuse cycles, the adsorption capacity of the organophilic clay decreased by half. Xikhongelo et al.83 developed a mesoporous composite material by functionalizing graphene oxide with polyamidoamine-SBA-15, aimed at adsorbing metals and emerging pollutants, such as ivermectin, from aqueous solutions. The maximum adsorption capacity of ivermectin was 291.8 µg g⁻¹ and equilibrium occurred in 720 min. Polyamidoamine functionalized graphene oxide-SBA-15 mesoporous composite (PGOSBA) showed two pH optima for ivermectin, with a minor peak at pH 3.0 and a major peak at pH 9.0. Furthermore, the reusability of the material for ivermectin adsorption was demonstrated in three consecutive cycles, with an approximate reuse efficiency of 95%.

In comparison, it is noted that in the study performed here, the balance in the adsorption process occurred in just 5 min, a much shorter time than in other works. $Fe_3O_4/SiO_2/CS/PDPA$ has higher values of maximum adsorption capacity (Q_{max}) (138.08 mg g⁻¹ for EPRI, 115.66 mg g⁻¹ for DORA, and 135.94 mg g⁻¹ for IVER) at pH 8.0, and an excellent regeneration capacity, proving to be a promising adsorbent material, with the capacity to remove AVMs from aqueous medium and with the potential for carrying out future studies to evaluate its application in the removal of other pollutants with lipophilic properties.

Conclusions

The synthesis of a pH-sensitive magnetic composite composed of chitosan and poly(2-(diisopropylamino)ethyl methacrylate) (Fe₃O₄/SiO₂/CS/PDPA), aimed at removing AVMs from aqueous media, proved to be a simple and easily executable method. The adsorbent material obtained, functionalized magnetic particles linked to chitosan coupled to PDPA, was characterized by the different techniques used through analyzes involving the starting compounds, some intermediate structures, and the final material. Adsorption studies revealed that the maximum removal of the three types of AVMs occurred at pH 8.0, using 20 mg of the adsorbent. Equilibrium in the adsorption process was achieved in just 5 min, highlighting the efficiency of the synthesized material, as well as the speed and simplicity of the method. The PSO model was identified as the most suitable for explaining the observed adsorption kinetics. Regarding the isotherm models, the Langmuir-Freundlich dual-site model was the one that best fit the experimental data, standing out as the most appropriate for describing the adsorption process of AVMs in the Fe₃O₄/SiO₂/CS/PDPA

composite. Thermodynamic analysis indicated that AVM adsorption was a spontaneous ($\Delta G < 0$) and exothermic ($\Delta H < 0$) process. Finally, it is worth noting that the synthesized material demonstrated not only excellent regeneration capacity, using acetonitrile as a solvent, but also effective reusability in multiple adsorption/desorption cycles. Therefore, the effectiveness of the Fe₃O₄/SiO₂/CS/PDPA magnetic composite in adsorbing AVMs suggests that the method could be promising for treating water contaminated with various compounds in a simple and accessible manner.

Supplementary Information

Supplementary data are available free of charge at http://jbcs.sbq.org.br as PDF file.

Acknowledgments

The authors thank the Brazilian agencies CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico), FAPEMIG (Fundação de Amparo à Pesquisa do Estado de Minas Gerais) and the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) for financial support.

Author Contributions

Leila S. Teixeira was responsible for methodology, conceptualization, investigation, data curation, validation, visualization, writing original draft; Stephanne Y. B. de Carvalho for validation, formal analysis, data curation and methodology; Ana Claudia dos Santos for investigation, formal analysis, and methodology; Marcella M. C. Borges for investigation, formal analysis and methodology; Sara S. Vieira for investigation, formal analysis, data curation; Keyller B. Borges for supervision, resources, methodology, conceptualization, writing (review and editing); Luiz Gustavo L. Guimarães for supervision, resources, methodology, conceptualization, writing (review and editing).

References

- 1. Ashour, D. S.; Int. J. Antimicrob. Agents 2019, 54, 134. [Crossref]
- Cui, B.; Gao, F.; Zeng, Z.; Wang, C.; Wang, Y.; Sun, C.; Zhao, X.; Guo, L.; Shen, Y.; Liu, G.; Cui, H.; *Sci. Rep.* **2020**, *10*, 9096. [Crossref]
- Batiha, G. E.-S.; Alqahtani, A.; Ilesanmi, O. B.; Saati, A. A.; El-Mleeh, A.; Hetta, H. F.; Beshbishy, A. M.; *Pharmaceuticals* 2020, *13*, 196. [Crossref]
- Diagboya, P. N.; Mtunzi, F. M.; Adebowale, K. O.; Düring, R. A.; Olu-Owolabi, B. I.; *Colloids Surf.*, A 2022, 634, 127930. [Crossref]

- Raftery, T. D.; Volz, D. C.; *Neurotoxicol. Teratol.* 2015, 49, 10. [Crossref]
- Guo, Z.; Su, Y. F.; Li, K.; Tang, M. Y.; Li, Q.; Xu, S.; *Sci. Rep.* 2021, *11*, 4655. [Crossref]
- Vokřál I.; Podlipná, R.; Matoušková, P.; Skálová, L.; Chemosphere 2023, 345, 140446. [Crossref]
- Jensen, J.; Scott-Fordsmand, J. J.; *Environ. Pollut.* 2012, 171, 133. [Crossref]
- Salman, M.; Abbas, R. Z.; Mehmood, K.; Hussain, R.; Shah, S.; Faheem, M.; Zaheer, T.; Abbas, A.; Morales, B.; Aneva, I.; Martínez, J. L.; *Pharmaceuticals* 2022, *15*, 332. [Crossref]
- Springer, V.; Barreiros, L.; Avena, M.; Segundo, M. A.; Adsorption 2018, 24, 431. [Crossref]
- Rana, A. K.; Mishra, Y. K.; Gupta, V. K.; Thakur, V. K.; Sci. Total Environ. 2021, 797, 149129. [Crossref]
- 12. Andrunik, M.; Bajda, T.; Materials 2021, 14, 3532. [Crossref]
- Chen, H.; Chen, X.; Zhou, H.; Zhou, X.; Xu, H.; *Mater. Sci.* 2019, 25, 90. [Crossref]
- Zhang, S.; Zhang, Y.; Ding, J.; Zhang, Z.; Gao, C.; Halimi, M.; Demey, H.; Yang, Z.; Yang, W.; *J. Environ. Sci.* 2021, *106*, 105. [Crossref]
- Li, R.; Liu, L.; Yang, F.; J. Hazard. Mater. 2014, 280, 20. [Crossref]
- Gomase, V.; Doondani, P.; Saravanan, D.; Pandey, S.; Jugade, R.; Sep. Purif. Technol. 2024, 330, 125475. [Crossref]
- Pandey, S.; Kim, S.; Kim, Y. S.; Kumar, D.; Kang, M.; *Environ. Res.* 2024, 240, 117540. [Crossref]
- Olu-Owolabi, B. I.; Diagboya, P. N.; Mtunzi, F. M.; Düring, R. A.; *J. Environ. Manage.* **2021**, *279*, 111619. [Crossref]
- Qian, J.; Kai, G.; J. Pharm. Biomed. Anal. 2020, 190, 113548. [Crossref]
- Tizro, N.; Moniri, E.; Saeb, K.; Panahi, H. A.; Ardakani, S. S.; *Microchem. J.* 2019, 145, 59. [Crossref]
- Jamasbi, N.; Ziarani, G. M.; Mohajer, F.; Darroudi, M.; Badiei, A.; Varma, R. S.; Karimi, F.; *Chemosphere* 2022, 307, 135622. [Crossref]
- Guo, X.; Du, B.; Wei, Q.; Yang, J.; Hu, L.; Yan, L.; Xu, W.; J. Hazard. Mater. 2014, 278, 211. [Crossref]
- Yu, S.; Cui, J.; Wang, J.; Zhong, C.; Wang, X.; Wang, N.; *Int. J. Biol. Macromol.* 2020, *149*, 562. [Crossref]
- Sharma, R. K.; Dutta, S.; Sharma, S.; Zboril, R.; Varma, R. S.; Gawande, M. B.; *Green Chem.* 2016, *18*, 3184. [Crossref]
- Wang, Y.; Lai, Y.; Wang, S.; Jiang, W.; Ceram. Int. 2016, 43, 1887. [Crossref]
- Pandey, S.; Makhado, E.; Kim, S.; Kang, M.; *Environ. Res.* 2023, 217, 114909. [Crossref]
- Kumar, N.; Gusain, R.; Pandey, S.; Ray, S. S.; Adv. Mater. Interfaces 2023, 10, 2201375. [Crossref]
- Pandey, S.; Son, N.; Kim, S.; Balakrishnan, D.; Kang, M.; Environ. Res. 2022, 214, 114000. [Crossref]
- Pandey, S.; Son, N.; Kang, M.; Int. J. Biol. Macromol. 2022, 210, 300. [Crossref]

- Li, Y.; Qin, Y.; Liu, S.; Xing, R.; Yu, H.; Li, K.; Li, P.; *BioMed Res. Int.* 2016, 2016, ID 9805675. [Crossref]
- Oryan, A.; Sahvieh, S.; *Int. J. Biol. Macromol.* 2017, 104, 1003. [Crossref]
- Badawy, M. E. I.; Marei, A. E. S. M.; El-Nouby, M. A. M.; Sep. Sci. Plus 2018, 1, 506. [Crossref]
- Arias, J. L. O.; Schneider, A.; Batista-Andrade, J. A.; Vieira, A. A.; Caldas, S. S.; Primel, E. G.; *Food Chem.* 2018, 240, 1243. [Crossref]
- 34. Younes, I.; Rinaudo, M.; Mar. Drugs 2015, 13, 1133. [Crossref]
- Schoth, A.; Keith, A. D.; Landfester, K.; Muñoz-Espí, R.; RSC Adv. 2016, 6, 53903. [Crossref]
- Zeng, Z.; Wei, Z.; Ma, L.; Xu, Y.; Xing, Z.; Niu, H.; Wang, H.; Huang, W.; J. Mater. Chem. B 2017, 5, 6860. [Crossref]
- Kim, Y. J.; Matsunaga, Y. T.; J. Mater. Chem. B 2017, 5, 4307. [Crossref]
- Kocak, G.; Tuncer, C.; Butun, V.; *Polym. Chem.* 2017, *8*, 144. [Crossref]
- 39. Dai, S.; Ravi, P.; Tam, K. C.; Soft Matter 2008, 4, 435. [Crossref]
- Zhang, X. L.; Niu, H. Y.; Zhang, S. X.; Cai, Y. Q.; Anal. Bioanal. Chem. 2010, 397, 791. [Crossref]
- Ghaffar, A.; Yameen, B.; Latif, M.; Malik, M. I. In *Metal Nanoparticles for Drug Delivery and Diagnostic Applications*; Shah, M. R.; Imran, M.; Ullah, S., eds.; Elsevier: Oxford, 2020, p. 259. [Crossref]
- Albuquerque, L. J. C.; Sincari, V.; Jager, A.; Kucka, J.; Humajova, J.; Pankrac, J.; Paral, P.; Heizer, T.; Janouskova, O.; Davidovich, I.; Talmon, Y.; Pouckova, P.; Stepanek, P.; Sefc, L.; Hruby, M.; Giacomelli, F. C.; Jager, E.; *J. Control. Release.* 2021, *332*, 529. [Crossref]
- Peng, C.-L.; Yang, L.-Y.; Luo, T.-Y.; Lai, P.-S.; Yang, S.-J.; Lin, W.-J.; Shieh, M.-J.; *Nanotechnology* **2010**, *21*, 155103. [Crossref]
- Hu, J.; Zhang, G.; Ge, Z.; Liu, S.; *Prog. Polym. Sci.* 2014, 39, 1096. [Crossref]
- Tizro, N.; Moniri, E.; Saeb, K.; Panahi, H. A.; Ardakani, Sobhanardakani, S.; *J. Environ. Anal. Chem.* 2020, 103, 123. [Crossref]
- de Oliveira, H. L.; Teixeira, L. S.; Dinali, L. A. F.; Simões, N. S.; Borges, K. B.; *Microchem. J.* 2019, *150*, 104162. [Crossref]
- Borges, M. M. C.; Pires, B. C.; Vieira, S. S.; Borges, K. B.; Guimarães, L. G. L.; *React. Funct. Polym.* 2021, *168*, 105050. [Crossref]
- Ai, L.; Zhang, C.; Liao, F.; Wang, Y.; Li, M.; Meng, L.; Jiang, J.; *J. Hazard. Mater.* 2011, *198*, 282. [Crossref]
- Lu, Z.; Hanif, A.; Lu, C.; Sun, G.; Cheng, Y.; Li, Z.; J. Appl. Polym. Sci. 2018, 135, 46177. [Crossref]
- Chaari, I.; Medhioub, M.; Jamoussi, F.; Hamzaoui, A. H.; *J. Mol. Struct.* 2021, *1223*, 128944. [Crossref]
- Alnajrani, M. N.; Alsager, O. A.; Sci. Rep. 2020, 10, 794. [Crossref]

- El Hassani, A. A.; Tanji, K.; El Mrabet, I.; Fahoul, Y.; El Gaidoumi, A.; Benjelloun, A. T.; Sfaira, M.; Zaitan, H.; Kherbeche, A.; Surf. Interfaces 2023, 36, 102647. [Crossref]
- Pires, B. C.; Dutra, F. V. A.; Borges, K. B.; *Environ. Sci. Pollut. Res.* 2020, 27, 6488. [Crossref]
- Mohammad, S. G.; El-Sayed, M. M. H.; *Chem. Eng. Commun.* 2020, 208, 1069. [Crossref]
- Chu, K. H.; Hashim, M. A.; Santos, Y. T. C.; Debord, J.; Harel, M.; Bollinger, J. C.; *Chem. Eng. Sci.* **2024**, 285, 119573. [Crossref]
- Khan, A. A.; Naqvi, S. R.; Ali, I.; Arshad, M.; AlMohamadi, H.; Sikandar, U.; *Chemosphere* **2023**, *316*, 137826. [Crossref]
- Rajahmundry, G. K.; Garlapati, C.; Kumar, P. S.; Alwi, R. S.; Vo, D. N.; *Chemosphere* **2021**, *276*, 130176. [Crossref]
- Chen, F. F.; Xie, X. Y.; Shi, Y. P.; J. Chromatogr. A 2013, 1300, 112. [Crossref]
- Hu, C.; Deng, J.; Zhao, Y.; Xia, L.; Huang, K.; Ju, S.; Xiao, N.; Food Chem. 2014, 158, 366. [Crossref]
- Kurdtabar, M.; Koutenaee, R. N.; Bardajee, G. R.; J. Polym. Res. 2018, 25, 119. [Crossref]
- Torres, K. G.; Almeida, R. R.; Carvalho, S. Y. B.; Haddad, J. F.; Leitão, A. A.; Guimarães, L. G. L.; *Mater. Today Commun.* 2020, 24, 101252. [Crossref]
- Dinali, L. A. F.; Oliveira, H. L.; Teixeira, L. S.; Silva, A. T. M.; D'Oliveira, K. A.; Cuin, A.; Borges, K. B.; *Microchem. J.* 2020, *154*, 104648. [Crossref]
- Sathiyaseelan, A.; Shajahan, A.; Kalaichelvan, P. T.; Kaviyarasan, V.; Int. J. Biol. Macromol. 2017, 104, 1905. [Crossref]
- de Carvalho, S. Y. B.; Almeida, R. R.; Pinto, N. A. R.; Mayrinck, C.; Vieira, S. S.; Haddad, J. F.; Leitão, A. A.; Guimarães, L. G. L.; *Int. J. Biol. Macromol.* **2021**, *166*, 902. [Crossref]
- Wu, J.; Niu, Y.; Jiao, Y.; Chen, Q.; *Int. J. Biol. Macromol.* 2019, 123, 291. [Crossref]
- Yilmaz, E.; Yalinca, Z.; Yahya, K. I.; Sirotina, U.; *Int. J. Biol. Macromol.* 2016, 90, 68. [Crossref]
- Karaman, M.; Çabuk, N.; *Thin Solid Films* **2012**, *520*, 6484. [Crossref]

- Crystallography Open Database (COD), http://www. crystallography.net/cod/, accessed in March 2024.
- Zhang, M.; Cushing, B. L.; O'Connor, C. J.; *Nanotechnology* 2008, 19, 085601. [Crossref]
- 70. Chemizalize, https://chemicalize.com/, accessed in March 2024.
- Bakatula, E. N.; Richard, D.; Neculita, C. M.; Zagury, G. J.; *Environ. Sci. Pollut. Res.* 2018, 25, 7823. [Crossref]
- Nayak, A. K.; Pal, A.; J. Environ. Manage. 2018, 217, 573. [Crossref]
- Kaur, R.; Goyal, D.; Agnihotri, S.; *Carbohydr. Polym.* 2021, 262, 117906. [Crossref]
- Jaafari, J.; Barzanouni, H.; Mazloomi, S.; Farahani, N. A.; Sharafi, K.; Soleimani, P.; Haghighat, G. A.; *Int. J. Biol. Macromol.* 2020, *164*, 344. [Crossref]
- Nippes, R. P.; Macruz, P. D.; Coslop, T. F.; Molinari, D.; Scaliante, M. H. N. O.; *Clay Miner.* 2022, *57*, 21. [Crossref]
- Wang, Z.; Kang, S. B.; Won, S. W.; *Colloids Surf.*, A 2022, 647, 128983. [Crossref]
- Lei, C.; Wang, C.; Chen, W.; Hea, M.; Huang, B.; *Sci. Total Environ.* 2020, 733, 139316. [Crossref]
- Khosravi, R.; Moussavi, G.; Ghaneian, M. T.; Ehrampoush, M. H.; Barikbin, B.; Ebrahimi, A. A.; Sharifzadeh, G.; *J. Mol. Liq.* 2018, 256, 163. [Crossref]
- Prajapati, A. K.; Mondal, M. K.; J. Mol. Liq. 2020, 307, 112949. [Crossref]
- da Cunha, R.; Silva, C. F.; dos Santos, A. C.; Teixeira, L. S.; Dinali, L. A. F.; Batista, W. V. F. C.; Nascimento Jr., C. S.; Borges, K. B.; *Surf. Interfaces* **2023**, *43*, 103534. [Crossref]
- Araújo, C. S. T.; Almeida, I. L. S.; Rezende, H. C.; Marcionilio, S. M. L.O.; Léon, J. J. L.; Matos, T. N.; *Microchem. J.* 2018, *137*, 348. [Crossref]
- Tran, H. N.; Lima, E. C.; Juang, R. S.; Bollinger, J. C.; Chao, H. P.; *J. Environ. Chem. Eng.* **2021**, *9*, 106674. [Crossref]
- Xikhongelo, R. V.; Mtunzi, F. M.; Diagboya, P. N.; Olu-Owolabi,
 B. I.; Düring, R. A.; *Ind. Eng. Chem. Res.* **2021**, *60*, 3957.
 [Crossref]

Submitted: December 7, 2023 Published online: April 5, 2024