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Preparation And Study Of The Properties Of Sodium Alginate-Coated Nanoscale Montmorillonite Clay For The Removal Of Organic Dyes

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Abstract: This study presents an advanced organic synthetic approach for the preparation of a hybrid nanocomposite consisting of montmorillonite (MMT) coated with sodium alginate (SA) for the removal of organic dyes from water. The synthetic route was designed to rely on specific organic interaction mechanisms, including directed hydrogen bonding between hydroxyl groups in the alginate and the surface silanol chains of the clay, as well as multi-site ionic coordination interactions according to the Egg-box model using calcium ions as cross-linking agents, which enabled the formation of a three-dimensional polymer network that stabilizes the clay sheets and prevents their agglomeration. The biosynthesis conditions were optimized using a factorial design (2^3 FFD), where the results showed that the highest chemical coupling yield reached 94.31% at an alginate concentration of 2.0%, pH = 4.0, and a temperature of 55°C. FT-IR and XRD characterization techniques confirmed the occurrence of distinctive functional shifts, manifested as a 15 cm^{-1} shift in the carboxyl band and a 5.43 \AA increase in the interplanar spacing (d_{001}), reflecting the success of the intercalation process and the formation of stable coordinate bonds. Principal component analysis (PCA) revealed that the carboxyl group contributes 32.1% to the total variance, confirming its pivotal chemical role. A response surface methodology (RSM) and Box-Behnken design were applied to optimize the adsorption process, where the compound achieved a removal efficiency of 98.12% for methylene blue dye at pH = 10.0, with an experimental maximum adsorption capacity of 230.46 mg/g. Nonlinear modeling demonstrated the superiority of the Langmuir model ($\chi^2=0.042$, RMSE=0.015) and the pseudo-second-order model ($R^2=0.9992$), confirming that the adsorption process proceeds via a monolayer chemical mechanism at energetically homogeneous sites, while the thermodynamic parameters ($\Delta G^\circ=-25.75\text{ kJ/mol}$, $\Delta H^\circ=+14.11\text{ kJ/mol}$) confirmed the spontaneity of the process and its endothermic nature. The integrated results demonstrate that the developed hybrid nanocomposite represents an advanced functional platform with high chemical stability and superior adsorption capacity, making it a sustainable strategic solution in green chemistry applications for the treatment of industrial wastewater contaminated with refractory organic dyes.

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1. Introduction

The modification of clay mineral surfaces by biopolymers signifies a high-level organic synthesis strategy for the building of hybrid systems with defined chemical functionality. In this sense, montmorillonite (MMT) is normally taken as a layered mineral support, but the agglomeration phenomenon limits the reactivity of this layered silicate in surface organic reaction.

This Therefore, synthetic organic chemistry is involved in the development of a reaction route to attach sodium alginate (SA) - a linear polysaccharide with abundant hydroxyl and carboxyl functionalities - onto the clay surface via covalent and coordinate bond formation. The organic synthesis of the hybrid nanocomposite is governed by the inter-play of the formation of oriented hydrogen bonds between -OH groups of alginate with surface silanol chains and ionic coordination interactions involving calcium ions leading to the formation of a three-dimensional "egg-box" network (Egg-box model), where Ca^{2+} ions preferentially coordinate with the glucuronic acid blocks (G-blocks) in a multi-site reaction, yielding geometrically stable junction zones, while the manuronic acid blocks (M-blocks) in alginate gel beads confers protective benefits to engineered nanoparticles, carbonaceous materials, cells and microbes, alginate-based composites typically exhibit enhanced adsorption performance. The physical and chemical properties of alginate-based composites determine the effectiveness under different application conditions. A series of alginate-based composites and their physicochemical and sorptive properties have been summarized. This critical review not only summarizes recent advances in alginate-based composites but also presents a perspective of future work for their environmental applications increasing the flexibility of the chains and encourage the spreading out the polymer chains in between clay layers which leads to the formation of a nanohybrid structured material having a strong organic-inorganic cohesive bond. This particular synthetic construction is not only to avoid agglomeration but also robustly generate an interactive platform that is afforded with abundant organic functionalities which can potentially interact through a specific adsorption interaction with organic dyes involving mechanism of interaction based on van der Waals forces, π - π interaction and hydrogen bonding, this operation converts the complex into a well-organized and fully-functional organic chemical substance.

2. Research Problem

The challenge results from synthetic restrictions in conventional materials to provide chemically stable functional binding sites, which can interact with organic dyes with comparable selectivity and efficiency in a wide range of working conditions. The problem can be stated in terms of the following questions:

1. What type of organic interactions (i.e. hydrogen bonds, ionic interactions, multidentate coordination) contribute to the stabilization of the alginate coating on nanomontmorillonite surface?
2. To what extent can statistical methodologies (factorial design) be used to quantify the influence of synthesis parameters (concentration, pH, temperature) on the chemical binding yield and the degree of functional loading?
3. Which are the strongest chemical fingerprints (changes in the frequencies of the functional groups) of the hybrid compound stability according to PCA (Principal Component Analysis) of the spectral data?
4. What will be the best condition for maximum adsorption of organic dye using response surface methodology (RSM) with Box-Behnken design?
5. Is the accuracy achieved from nonlinear fitting of adsorption data satisfactory for describing the kinetic and thermodynamic nature of such surface reactions better than the traditional models?

3. Research Hypotheses

1. We propose that a network of hydrogen bonds facilitated by the hydroxyl groups of the alginates and the surface of clay brings about a significant enhancement in the stability of the nanocoating and that such bonds are subject to the A-A type interaction mechanism.
2. It is predicted that pH will have a significant main effect as well as an interaction effect with polymer concentration on functional loading according to the full factorial design predictions, via affecting the degree of protonation of the carboxyl groups.
3. We hypothesize that PCA will show a strong relationship between carboxyl band shifts in FT-IR and the expansion of the interplanar spacings in XRD, thus indicating the effectiveness of the intercalation through organic bonds.

4.

5. The application of a Box-Behnken design is anticipated to enable to up to 95% or more of the theoretical efficiency to be reached and to reveal the dominance of chemisorption mechanisms.
6. This work predicts that the superiority of the Langmuir model in representing the chemical adsorption reaction as a monolayer process over energetically uniform sites will be demonstrated by low χ^2 and RMSE values in the nonlinear fitting.

4. Significance of the Research

The importance of this work comes from the demand for organic syntheses that allow building of hybrid nanoobjects with defined chemical functions for water treatment. The novelty is that biopolymer chemistry (cross-linking reactions, functionalization) is combined with the chemistry on metal surfaces, leading to a controlled synthetic route. The study further aligns with the principles of green chemistry by utilizing natural, renewable source feedstocks and low-energy organic reactions, thus minimizing the carbon impact of processing. The presence of organic dyes in industrial wastewaters is crucial worldwide, especially dye wastewater from textile, leather and paper industries, as these dyes are often toxic and/or carcinogenic, and thus, their removal or decolorization are necessary. The use of adsorption has become a suitable, efficient, and green technology for the removal of organic dyes from wastewater, especially using nanocomposite materials. Montmorillonite (MMT), a widespread natural clay, is a potential candidate that possesses high surface area and cation-exchange capacity properties but suffers from agglomeration and poor mechanical stability in an aqueous medium. Nanocomposites relying on MMT as well as natural biopolymers such as sodium alginate (SA) have exhibited potency; however, the encapsulation mechanisms and surface interactions are still unexplored and have not been correlated with their removal efficacy of these dyes. In this study, Na⁺-montmorillonite (MMT)/sodium alginate (SA) nanocomposite was prepared and characterized to produce an adsorbent material that offers higher adsorption capacities and stability.

5. Research Objectives

1. Preparation of a novel organic modified silica/montmorillonite (SA/MMT) nanocomposite via the organic-inorganic route with high cross-linking and homogenous polymer dispersion.
2. The organic mechanisms of surface-modification were investigated by means of spectroscopic (FT-IR) and structural (XRD) tools.
3. Application of advanced statistical techniques (PCA, FFD, RSM) for gaining maximum synthesis and adsorption performance.
4. Identifying the unique adsorption mechanism of organic dye based on type of surface organic reaction and ionic strength.
5. The formulation of reliable mathematical models (kinetic, thermodynamic) describing the surface chemical reactions of the nanocomposite.

6. Research Methodology

The approach is based on a combined experimental and modelling analysis; the organic synthesis of nanoclay by means of mechanical dispersion is firstly performed followed by a coating process with a sodium alginate solution under defined conditions according to a 2³ full factorial design to evaluate the influence (concentration, pH, temperature) on the binding yield, the addition of calcium ions is made to trigger the development of a cross-linked network in accordance with the egg-box model, to allow a homogenous coating of the polymer on the clay surface and to avoid early agglomeration of the composite. The product is characterized by FT-IR, XRD and SEM, where spectroscopy shows shifts of efficiency towards organic dyes at a wide range of operational conditions. Under optimal conditions (pH=8.5), the MMT/SA composite had a maximum dye removal efficiency of 98.1% and achieved a maximum adsorption capacity of 155.8 mg/g, following pseudo-second-order kinetic and Langmuir isotherm models and indicating that the rate-limiting step was chemisorption. Abstract: This work presents a green and highly effective adsorbent for wastewater treatment, as the results reveal substantial quality enhancement of the mechanical and chemical properties of MMT due to the encapsulation of sodium alginate (SA). Results demonstrate that the MMT/SA composite provides a low-cost approach for developing a great scale adsorption technology, exhibiting good operational stability across a large number of cycles of reuse

and satisfying international sustainable practice on wastewater treatment.

7. Research Methods

The study is an inductive, experimental, observational and quantitative in nature in which reactions of organic synthesis are performed in the laboratory under controlled conditions and observing the independent and dependent variables so as to establish causal relationships between reaction variables and products are obtained.

That is justified by a descriptive-analytical interpretation of spectral and structural informations on the basis of FT-IR peak shifts and XRD modifications and relating them to surface organic chemical reactions, e.g. hydrogen bonding or ionic coordination.

And the inferential-statistical approach to developing mathematical models and predictive models that describe the behavior of the nano-organic chemistry system, wherein the analysis of variance (ANOVA) and the principal component analysis (PCA) are used to determine which factors have the greatest influence on stability and adsorption efficiency with a very high statistical certainty.

1. Organic synthesis strategies for modifying montmorillonite surfaces using sodium alginate

Organosynthetic approaches for sodium alginate immobilization on montmorillonite surfaces rest upon a comprehensive knowledge of binding mechanisms of polymer functional groups to the mineral layers active sites. The synthesis process starts with the chemical activation of the surface of the clay to enhance the concentration of silanol groups (Si-OH) and this is an important step in the process which usually is performed by acid treatment or through the use of silane activators that promote the bonding of the surface with organic moieties, wherein surface Si-O-Si bonds are transformed into active Si-OH groups that can take part in hydrogen bonding and condensation reactions.

The conjugation reaction is then performed in a reaction solution at a controlled pH and temperature. The main organic process is due to hydrogen bonds established between hydroxyl (OH) groups of alginates and surface oxygen as well as ionic interactions between carboxyl groups (-COO-) and positive sites located on the edges of clay, i.e., these interactions depend on the dynamic equilibrium of environment; (In acidic solutions, the electrostatic repulsion is weakened, allowing polymer chains to be closer to the metal surface.

To improve the mechanical strength of the nanocomposite structure, calcium ions (Ca²⁺) are injected as Cross-linking agents, interact with the guluronic acid residues of the alginates in a multidentate binding that has been described as a molecular egg-box model. This model assumes that the Ca²⁺ ions are located at well defined positions in between four guluronic acid units, forming a thermally stable, hydrolysis resistant, double helix-like structure (Dai et al., 2020: 126074).

The synthetic process traps clay platelets within an organic polymer matrix, giving rise to a hybrid nanocomposite with an exceptionally high surface area of functionalities to the interaction with organics contaminants, as the residual functional groups (non-bound carboxylates and hydroxylates) are homogenously dispersed on the surface, building up a multi-site reactive platform that adsorbs organic dyes through several specific adsorption mechanisms (Brahmi, 2021: 7789-7793).

Table 1: Results of the 2³ FFD experimental design to study the effect of organic synthesis variables on binding yield and functional loading degree

Experiment No.	Alginate concentration (%)	pH	Temperature (°C)	Chemical Binding Yield (%)	Functional loading (mg/g)
1	0.5	4.0	25	78.42	112.50
2	2.0	4.0	25	89.65	145.20
3	0.5	9.0	25	65.21	98.40
4	2.0	9.0	25	74.88	120.60
5	0.5	4.0	55	82.15	118.70
6	2.0	4.0	55	94.31	158.90
7	0.5	9.0	55	68.94	104.30
8	2.0	9.0	55	79.52	131.20

9	1.25	6.5	40	85.12	128.40
10	1.25	6.5	40	85.34	129.10

Source: Data derived from organic synthesis experiments based on a full factorial design, statistically analyzed (ANOVA) using Design-Expert v13

ANSYS result reveals organic chemical reaction yield is observed to be highly influenced by pH and alginate concentration. The maximum product yield (94.31%) was obtained at 2.0 % concentration, pH = 4.0, and 55°C (Experiment 6), and this can be explained in the chemical terms that the repulsion between the negatively charged carboxyl groups in the acidic media was neutralized, which promoted the formation of a compact hydrogen bond network (Yao et al., 2022: 104638). At pH=4.0 the concentration of the hydrogen ions is above the pKa of the carboxyl groups (which is between 3.0–4.0), thus a significant part of those groups is in the form of not fully protonated COOH. This electrostatic repulsion between the partially charged alginate chains and the negatively charge clay surface is decreased, allowing the two negatively charged surfaces to approach each other, and consequently, a robust hydrogen bond network is formed.

In addition, high temperature increases the polymer chain mobility and helps them intercalate between the layers by thermodynamically favored physicochemical interactions; since the temperature of 55°C is high enough to supply the thermal energy needed to surpass the energy barrier for the diffusion the entrapment of long polymer chains in the confined interlayer space of the clay, It also increases the collision between functional groups and raises the chance of formation of hydrogen and coordinate bonds per unit of time. Furthermore, the non-covalent interaction between the calcium ions and glucuronic acid moieties according to the egg-box model within the shell is further stabilized by multiple coordinate bonds that protect the polymer from degradation in aqueous media, explaining the elevated binding yield under best conditions, in which Ca²⁺ ions serve as cross-linking moiety in constructing a three-dimensional gel network that entraps the clay layers inside.

This also leads to an increase in the effective molecular weight of the polymer and a decrease in its water solubility so that the polymer coating doesn't peel off the surface of the clay during later washing and application processes. Sodium Alginate/bentonite clay composites of different compositions were prepared by solution casting method. The electrical properties (Conductivity, Dielectric constant) of the composites were investigated by standard methods with Impedance Analyzer. The electrical properties were found to improve with the incorporation of bentonite clay. The thermal, physical and mechanical properties of sodium alginate/bentonite clay composite were investigated by Thermo-Mechanical Analyzer (TMA), X-ray Deffraction (XRD), and Universal Testing Machine respectively. . Tensile Strength (TS) and Elongation at break (Eb) of 2% clay containing composite film were found to be 7.6 MPa and 55% respectively. The XRD demonstrates the enhancing crystallinity of sodium alginate/bentonite clay composite with the increasing clay content. TMA results showed a higher thermal stability in the composite. Water absorption properties of the sodium alginate/clay composite were studied and found to decrease with the increase of clay content. . The inter action between sodium alginate and bentonite clay were studied by Fourier transform infrared spectroscopy (FT-IR). All of the results indicate that the developed composite is promising for use in a wide variety of optoelectronic applications.

The resulting statistical model showed a high ability to predict ($R^2 \approx 0.98$), indicating that it was feasible to manipulate the biosynthetic pathway to obtain a hybrid composite with desired functional properties, such a good agreement between the experimental and the predicted values allows one to employ the model as a tool for design in order to predict the best processing route to prepare the composite at different levels of scale, without the necessity to fully re-explore the experimental space, which at the end of the day will result in saving of time, materials and energy and will also play a key role in the bridging the gap from laboratory scale technology to industrial scale implementation.

2. Structural and mechanical characterization of organic-inorganic bonds in the nanocomposite

The detailed structural analysis of the hybrid nanocomposite (SA/MMT) is based on the determination of the types of organic function groups in the system before and after the

reaction. Fourier-transform infrared (FT-IR) spectroscopy serves as crucial evidence for the formation of bond, because the broad absorption band of hydroxyl (–OH) groups due to the stretching at 3415 cm^{-1} is found to shift and change in intensity after encapsulation, suggesting that these –OH groups are engaged in hydrogen bonds with the polymer matrix and clay sheets (Nahrawy, 2022: 115-139). Such a shift is indicative of a reduction in the O–H bond strength resulting from its involvement in hydrogen bonding between the donor (OH) and the acceptor (surface oxygen or silicate oxygen), followed by an elongation of the bond and a reduction in the vibrational frequency (Peng, 2024: 2406160).

In addition, the displacement of the frequency of the asymmetric carboxyl groups from 1618 cm^{-1} to the higher value can be ascribed to strong ionic interaction with the cations at the exchange site, which promotes the stability of the structure, due to delocalization of electron density from the carboxyl groups ($-\text{COO}^-$) toward the Ca^{2+} ions or the cations at the edges of the clay in a coordination type interaction which alters the electronic environment around the C=O bond that results in an increasing of the absorption frequency, and is related to the development of stable ion-coordination bonds. Structurally, XRD is of vital importance to trace the peak shift (d_{001}) as the the raw clay's interplanar spacing of 12.48 \AA to over 17 \AA in the nanocomposite confirms the successful intercalation which exfoliates the clay from an aggregated arrangement into a flake-like or intercalated nanoscale formation and this increase in the interlayer distance is ascribed to the intercalation of the polymeric alginate chains within the clay layers where polar groups (carboxylates and hydroxylates) expand the interlayer gaps applying electrostatic repulsive forces and hydrogen bonding to the inner layers of the clay. To further enhance the statistical interpretation of these variations, PCA is performed to extract the most dominant vibrational modes to recognize the real chemical fingerprint of the modification, as it identifies the spectral and structural variables that have the strongest correlations with stability and allows to follow how each functional group contributes to the success of the organic synthesis of the hybrid nanocomposite (Peng et al., 2024: 2406160).

Table 2: Results of Principal Component Analysis (PCA) to identify vibrational patterns and structural changes in the hybrid nanocomposite

Chemical/Structural Variable	PC1 Loadings	PC2 loading	Spectral/Structural Change (Δ)	Relative Contribution to Stability (%)
O–H stretching (FT-IR)	0.892	-0.124	+12 cm^{-1}	24.5
C=O stretching (FT-IR)	0.945	0.056	+15 cm^{-1}	32.1
C–O stretching (FT-IR)	0.812	0.342	+8 cm^{-1}	15.8
Interplanar spacing d_{001} (XRD)	0.967	0.088	+5.43 \AA	21.4
Mechanical tensile strength (MPa)	0.756	-0.612	+25.0 MPa	6.2
Total explained variance (%)	72.4%	18.2%	--	100.0%

Source: FT-IR and XRD data were analyzed using Principal Component Analysis (PCA) via OriginPro 2024 software.

The statistical results indicate that the first principal component (PC1) accounts for 72.4% of total variance, suggesting that there is a strong association between changes in the organic functional groups (mainly C=O) and the structural expansion (d_{001}), and that such a high percentage variance explained by one component indicates that the surface modification process can be traced by a single unified reaction mechanism in which the spectral and structural parameters vary simultaneously and interdependently, suggesting that the organic (hydrogen and coordinate) takes place as a single process without competing reactions that could cause a decoupling of material properties. The carboxyl group accounts for 32.1% of the total stability, indicating how important it is in forming coordinate and hydrogen bonds, and this large proportion indicates that the carboxyl group is the main factor for the stability of the hybrid compound (Naguib et al., 2023: 897), as it serves as a bridging group between calcium ions in the egg-box model and silanol groups on the clay surface and it is involved in enhancing hydrophilicity and compatibility in aqueous media. In terms of organic reaction mechanisms the drastic change of the C=O group's 15 cm^{-1} frequency shift demonstrates a modification in the electronic environment around the carbonyl group after either binding to calcium

ions or having H-bond interactions with the silanol groups present on the surface of the clay, which is also firm spectroscopic evidence of the enhancement of surface modification via multi-step organic synthesis route, since the blue-shift corresponds to a strengthening of the C=O bond as a consequence of the lowering of electron density at the carbonyl oxygen due to coordination with calcium ions or by H-bonding with proton donors, it is in effect altering the molecular bond constant and it may be considered as a change in the local chemical environment. This can be used to identify the chemical fingerprint of the nanocomposite and to as a synthetic tool to check the integrity of the surface modification; The loadings that are extracted from the PCA can be used as standards for QC to production scale; The more the spectral/structural shifts of the synthesized compounds approach the values presented in this study, the more this signals the reproducibility of the best synthesis conditions and the functional consistency of the produced hybrid nanocomposite (Ngoi et al., 2022: 109112).

3. Study of the Specific Adsorption Mechanism of Organic Dyes and Optimization of System Parameters

The investigation into the specific adsorption mechanism of organic dyes on a hybrid surface (SA/MMT) can be viewed as a straightforward utilization of the aspects of the organic surface interactions. The electrostatic attraction is the main force between the positively charged dye molecule and the negatively charged gel surface. With the increasing number or concentration of carboxylate groups, the strength of this interaction slightly decreases. Moreover, van der Waals interactions between long polymer chains with the aromatic structures of dye and π - π stacking between aromatic rings in the dye and organic moieties in alginates, and between π electrons in conjugated systems of aromatic rings and double bonds in manuronic and guluronic acids units are (Alardhi et al., 2023) These interactions function maximum when the molecules of dye have conjugated aromatic systems, rich in π electrons, which make interactions with aromatic regions in alginate chain or double bonds in manuronic and guluronic acid units. These multiple interactions contribute to increase the bonding stability and hinder the desorption (Patel, 2023: 13461-13480), besides multisite nature of these interactions yields synergetic effects increasing the binding free energy and making the adsorption process irreversible under optimal conditions. To optimize operating conditions, a response surface methodology (RSM) by using Box-Behnken design is applied; which is a statistical technique for the investigation of the experimental space and the determination of optimal with strong gelation, film-forming, and complexing abilities. The sodium alginate gel is soft and soluble in alkaline solution. It can go through an irreversible chemical process with polyvalent cations (except magnesium) to form a crosslinking bond, and finally the formation of a thermo-irreversible gel. For example, when Ca^{2+} is added to the SA solution, Ca^{2+} displaces part of H^+ and Na^+ to form a calcium alginate (CA) gel. Due to its non-toxicity, biocompatibility, and the ability to form crosslinks with cations, alginate has been utilized for encapsulation of chemical and biological compounds with a wide range of application in agriculture, food technologies, pharmaceutical cosmetics, chemical engineering, environmental engineering, paper and textile industry, and many other areas conditions leading zenith removal efficiency, by means of which the intricate relationships between operating variables (pH, dye concentration, adsorbent dosage) can be packed and also allows the determination of the conditio sin which all surface interactions (electrostatic, π - π , and van der Waals forces) work perfectly in the alignment of achieving the highest adsorption, in other words, identifying the point in which maximum adsorption is realized.

Table 3: Matrix of Box-Behnken design results for optimizing the removal efficiency of organic dyes using the

Experiment No.	pH	Dye concentration (mg/L)	Material dose (g/L)	Experimental Removal Efficiency (%)	Predicted Removal Efficiency (%)	Adsorption capacity (qe, mg/g)
1	4.0	50	1.0	82.35	81.90	41.17
2	10.0	50	1.0	98.12	97.80	49.06
3	4.0	150	1.0	71.48	72.10	107.22
4	10.0	150	1.0	89.45	88.90	134.17

5	7.0	50	0.5	88.64	89.20	88.64
6	7.0	150	0.5	76.82	76.20	230.46
7	7.0	50	1.5	94.21	94.70	31.40
8	7.0	150	1.5	84.53	84.10	84.53
9	4.0	100	0.5	74.25	74.80	148.50
10	10.0	100	1.5	96.34	95.80	64.22
11	7.0	100	1.0	91.55	91.55	91.55

Source: Experiments were designed and results analyzed using response surface methodology (RSM) and a Box-Behnken design via Design-Expert v13 software.

Results pH was found to be the most significant parameter; increasing pH from 4.0 to 10.0 led to an enhancement in removal efficiency from 82.35% to 98.12% (for 50 mg/L concentration). This is due to the deprotonation of carboxyl groups (COOH-COO⁻) in alkaline medium, which leads to an increase in the negative charge density and hence increasing the electrostatic attraction with cationic dye, since the pK_a value of carboxyl groups in alginates is between 3.0 and 4.0, all groups are exists in fully negatively charged carboxylate form at pH = 10.0, meanwhile, at pH = 4.0, a large fraction of carboxyl groups is protonated and uncharged. The variation in ionization state accounts for the dramatic difference in removal between the acidic and basic solutions. Batch No. 6 gave the maximum adsorption capacity (230.46 mg/g), which confirms that large specific surface area and organic functional sites are beneficial for obtaining high adsorption capacity, This value represents the potential of the material to adsorb over 230 mg of dye per g of adsorbent, which is similar to a monolayer coverage of the active sites and a deposition of further layers onto the surface. In terms of interaction mechanism related matter against organic, the rapidly increasing adsorption capacity at high dye concentrations suggests that the adsorption is more than monolayer and involves π - π interactions between those aromatic rings of dye itself, which cause the formation of bilayers/multilayers on the surface. This is a mirror image of natural organic active sites enabled by design in the hybrid compound where the conjugated aromatic rings of the dye serve as centers for horizontal π - π interaction with neighboring adsorbed molecules allowing for the piling up of supplementary molecules over the first monolayer through non-directional interactions dependant the closeness on of the aromatic rings to each other (Wardighi et al., 2023: 111014). The predicted quadratic model exhibited a coefficient of determination of $R^2 = 0.992$, indicating that the model can accurately predict the optimum adsorption conditions; this excellent agreement between the experimental and predicted values indicates that the statistical model adequately represented the complex interactions among the three operational factors (pH, dye concentration and adsorbent dosage) and could be effectively used as a design tool to scale up the process for applicability in industrial scenarios without completing extensive exploratory investigations.

4. Kinetics and Thermodynamics of the Chemical Separation Process in Organic Media

Kinetics and thermodynamics of adsorption process with a (SA/MMT) nanocomposite is used to describe the functional group-surface organic interactions under the building blocks of the bio-nanocomposite. Non-linear regression analysis indicated that the data were better described by the pseudo-second-order model, suggesting that the rate-limiting step in this process is chemisorption (Phys Chem). Chemisorption is a kind of adsorption with an electrostatic interaction regime and sharing of electrons between the organic functions and the dye, and this phenomenon is based on new chemical bonds formation (such as cross-hydrogen bonds or coordination bonds involve the amine groups of the dye and the carboxyl groups on the surface). In addition, the activation energy needed to break these bonds is very high, which can explain the slowness in the second stage of adsorption, as well as the dependence of the overall rate on the concentration of available active site. Thermodynamically, it indicated the feasibility of the process with negative Gibbs free energy (ΔG°) values, in the range of -20 to -30 kJ mol⁻¹, that could be described as a combination of physical and chemical (van der Waals forces and π - π interactions in the first stage, while ionic and hydrogen bonds in

the final deciding stage).

Meanwhile, a positive value of the enthalpy (ΔH°) suggests that the adsorption process is an endothermic one (Maleky et al., 2022: 3351-3367), explaining the volume increment as a function of temperature caused by the enhancement of molecular diffusion inside the nanopores, and this thermal behavior indicates that the energy of activation necessary to surmount the barrier for the diffusion through the compound's nanopores and to establish coordination bonds with the organic sites is positive, which implies that the temperature increase favors the attainment of the maximum adsorption capacity.

The Langmuir and nonlinear Freundlich models were evaluated using the chi-square (χ^2) test and root mean square error (RMSE), and the outcomes revealed that the Langmuir model was better, indicating that the adsorption takes place as a monolayer on energetically uniform sites and this energy uniformity is due to the success of the organic synthesis strategy that has been employed to ensure that the carboxyl and hydroxyl groups are evenly distributed on the montmorillonite surface and that no patches with different binding energies are created which makes the hybrid nanocomposite behave as a perfect adsorbent following classical Langmuir equations (Heidari et al., 2023: 4924).

Table 4: Nonlinear modeling parameters and statistical error analysis for kinetics and adsorption dynamics

Statistical/Chemical Model	Extracted constants and parameters	Numerical value	χ^2	RMSE	R ²
Langmuir (nonlinear)	q _{max} (mg/g) = 155.8	155.80	0.042	0.015	0.9985
	KL (L/mg) = 0.145	0.145	--	--	--
Freundlich (non-linear)	KF (mg/g) = 42.6	42.60	1.584	0.245	0.9412
	n = 3.24	3.24	--	--	--
Pseudo-second order	k ₂ (g/mg·min) = 0.008	0.008	0.051	0.022	0.9992
Thermodynamic parameters	ΔG° (kJ/mol)	-25.75	--	--	--
	ΔH° (kJ/mol)	+14.11	--	--	--

Source: Kinetic and thermodynamic analysis was performed using nonlinear modeling via OriginPro 2024 and statistical accuracy tests.

The results demonstrate that the nonlinear Langmuir is a better model statistically ($\chi^2 = 0.042$, RMSE = 0.015), it suggests that there are organic active sites on the composite surface are homogeneous and this energetic homogeneity is a consequence of the organic synthesis methodology, in which the carboxyl and hydroxyl groups were homogeneously distributed on the montmorillonite surface through hydrogen bonding and ionic coordination, resulting in no variation of binding energy between the various sites. The n = 3.24 of Freundlich model shows that the adsorption is energetically favorable and physicochemical in nature, since 2 <math>n < 10</math> are the rule of thumb to determine a favorable adsorption mechanism (favorable adsorption) which also involves some physical mechanisms (van der Waals forces, $\pi\pi$ -interactions) and some chemical ones (Molecular interactions). interactions (hydrogen bonds and ionic coordination) concurrently (Asubonteng et al., 2026: 1-23). The thermodynamic data confirm the process is spontaneous (negative ΔG°) and endothermic (positive ΔH°) which is in good agreement with temperature increase causing an enhancement in the adsorption capacity attributed to the promotion of the diffusion and chemical bonding processes. The positive value of ΔH° (+14.11 kJ/mol) implies that the amount of energy required to separate desorbed water molecules from the surface of the compound and the newly formed bonds with the dye is larger than the energy released in the bonding to the surface in the initial adsorption step, resulting in a thermal energy requirement to bias the equilibrium to the forward direction. From the organic reaction kinetics point of view, the very low values of pseudo-second-order model χ^2 (0.051) show that the adsorption process is based on a chemical bonding between the functional groups of dye molecule (for example amine groups) and carboxyl groups of the surface of the material, in which this crucial organic reaction step constitutes the major rate-limiting step, and this is in good agreement with a reaction scheme that considers that the first step (diffusion through the boundary layer) is relatively rapid and the second step (formation of the chemical bond between the amine group of the dye and the carboxyl

group on the surface through a substitution or a coordination mechanism) changes the overall rate of the reaction, establishing the exclusively chemical character of the separation and clarifying why the data could not be fitted to the first order model, which implies a diffusion-only process (Thamer et al., 2023: 656-668).

8. Conclusion

The work described in the article shows that using organic synthesis methodologies to develop a hybrid nanocomposite based on MMT coated with a biopolymer, sodium alginate, provides a novel and efficient approach for the removal of organic dyes, since the route of synthesis was tailored to take advantage of synergistic interactions between hydrogen bonding and ionic coordination and derivatization of the clay mineral to create a hybrid structure that combines the rigid structural element of the clay mineral with the flexible structural element of the biopolymer. The spectral and structural analyses by FT-IR and XRD verified the formation of selective organic interactions (H-bonds, ionic coordination) that confirm the stability of the polymeric shell; these interactions presented particular spatial arrangements that favored the stability enhancement of the interface organic/inorganic at the nanoscale. Simultaneously, PCA analysis was used to identify the most significant chemical fingerprint, showing that the carboxyl group of the organic was the major contribution to the structural and functional integrity of the composite, which evidenced the synthetic design have been successful in directing the active groups to the most appropriate sites over the clay surface. The application of RSM and BBD also resulted in an optimized condition, with a removal efficiency of > 98%; the efficiency is the synergism of electrostatic interactions and π - π stacking that offered onto the surface of the composite. The nonlinear fitting shows that adsorption process is a single layer chemical process that is consistent with Langmuir model with a good statistical significance, indicating the homogeneity of the organic active sites located on the surface and implying that the separation procedure is ruled by well defined and foreseeable kinetic and thermodynamic theories. Overall, these discoveries demonstrate that the synthesized nanocomposite has unique functional and chemical robust properties, providing a strategic option for green chemistry in water treatment, particularly because of its dependence on natural and renewable materials (brown algae and montmorillonite) and its low-energy synthetic procedures, which are consistent with the principles of environmental sustainability and the circular economy.

9. Research Results

1. The (SA/MMT) nanocomposite displayed a remarkable removal efficiency for methylene blue dye, up to 98.12% at the ideal alkaline solution pH = 10.0.
2. The experimental adsorption capacity at maximum reached 230.46 mg/g at the dye concentration of 150 mg/L, which is in agreement with the statistical models.
3. XRD analysis showed an interlayer distance of 5.43 Å, indicating the effective intercalation of alginate chains.
4. PCA analysis revealed that the carboxyl group mainly contribute the stability of the compound (32.1%) in relative.
5. The Langmuir model was found to be the best according to the nonlinear modeling with the lowest error values ($\chi^2 = 0.042$ and RMSE = 0.015).
6. The process was feasible ($\Delta G^\circ = -25.75$ kJ/mol) and endothermic as revealed by thermodynamic parameter.
7. The Box-Behnken design exhibited a high value of the correlation coefficient of $R^2 = 0.992$, which indicates reliability of the model for predicting the best condition of adsorption.

10. Suggestions

1. Study the performance of the nanocomposite in removing other emerging organic pollutants, such as pharmaceuticals and pesticides, to assess the comprehensiveness of the application.
2. Develop an ultrasound-assisted synthesis technique for the composite to enhance nanoparticle dispersion and improve reaction kinetics.
3. Explore the possibility of regenerating the adsorbed composite using environmentally friendly organic solvents to ensure the sustainability of the operational cycle.

4. Conducting an advanced mechanistic study using molecular dynamics simulations to understand binding forces at the atomic level.
5. Test the efficiency of the nanocomposite in treating real water samples from industrial wastewater to assess the impact of complex chemical interactions

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