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RESEARCH ON THE SYNTHESIS OF AN ADSORBENT FROM INDIAN BENTONITE MODIFIED WITH OCTYLTRIPHENYL PHOSPHONIUM BROMIDE (OTPB): STRUCTURAL CHARACTERIZATION AND EVALUATION OF METHYLENE BLUE REMOVAL EFFICIENCY IN AQUEOUS MEDIA

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ABSTRACT

This study presents the synthesis and characterization of a novel organoclay derived from Indian bentonite via an ion-exchange reaction with octyltriphenyl phosphonium bromide (OTPB) as the modifying agent. Modern analytical techniques, including XRD, FT-IR, SEM, and TGA, were employed to elucidate the structural transformations and thermal properties of the material. XRD results confirmed a significant increase in the basal spacing d001 from 10.862 Å to 14.030 Å, providing evidence of the effective intercalation of phosphonium cations. The adsorption capacity for methylene blue (MB) was investigated in detail through operational parameters such as pH, contact time, and initial concentration. The results indicate that the adsorption process follows the Langmuir isotherm model, with a maximum adsorption capacity qmax of 142.86 mg/g, several times higher than that of raw bentonite. This research affirms the significant potential of utilizing phosphonium salts to upgrade natural clay minerals into high-performance materials for environmental remediation.

Keyword: Indian bentonite, Organoclay, Phosphonium modification, Methylene blue, Adsorption

1. INTRODUCTION

The rapid development of industries such as textiles, leather, and paper has led to severe environmental consequences due to the discharge of large volumes of wastewater containing organic dyes. Among these, Methylene blue (MB)-a common cationic dye-is considered a primary pollutant due to its stable aromatic structure, which is highly resistant to degradation under natural conditions. The presence of MB in aquatic environments not only causes aesthetic pollution by reducing light transparency and inhibiting the photosynthesis of aquatic flora but also poses toxic risks to the ecosystem and human health. In response to this situation, searching for effective, low-cost, and environmentally friendly treatment methods is an urgent requirement. Among current techniques, adsorption onto natural minerals has emerged as an optimal solution due to its operational simplicity and high reusability. Specifically, Indian Bentonite, primarily composed of the mineral montmorillonite, has become a focal point of research due to its unique layered structure, high specific surface area, and high cation exchange capacity (CEC) of 98 meq/100g, making it an ideal adsorbent precursor.

However, a major barrier to using natural bentonite for treating organic compounds is its inherent hydrophilicity and the negative surface charge caused by isomorphous substitution within the crystal lattice. This leads to water molecules being easily trapped within the interlayer galleries, preventing the access of hydrophobic organic pollutants or bulky dye molecules. To overcome this limitation, this study focuses on the surface modification of bentonite using octyltriphenyl phosphonium bromide (OTPB) to produce an "organoclay" material. The ion-exchange process between inorganic cations (Na^+, Ca^{2+}) and the organic $OTPB^+$ cations not only expands the layered structure-evidenced by the increase in d_{001} basal spacing from 10.862 Å to 14.030 Å-but also completely transforms the surface nature from hydrophilic to organophilic. The intercalation of long octyl chains and bulky phenyl rings into the clay interlayers creates an ideal hydrophobic environment, significantly enhancing electrostatic interactions and

generating auxiliary $\pi - \pi$ interactions between the adsorbent and the MB dye molecules.

The novelty and highest scientific value of this research lie in the selection of a phosphonium derivative as the modifying agent instead of the conventional quaternary ammonium salts, which typically exhibit lower thermal stability. Quaternary phosphonium compounds are known for their superior thermal stability and structural integrity under harsh environmental conditions. This ensures that the modified material not only achieves an impressive maximum adsorption capacity (142.86 mg/g) but also maintains stable treatment efficiency. The synergy between the iron-rich Indian Bentonite and the OTPB agent creates an organic-inorganic hybrid material with superior structural characteristics. This opens broad prospects for practical applications in industrial textile wastewater treatment, contributing to the sustainable and effective resolution of environmental pollution.

2. MATERIALS AND METHODS

2.1. Materials

The selection of raw materials plays a decisive role in the performance and feasibility of the entire fabrication process. In this study, Indian bentonite (Bent-An) was selected as the precursor, not only due to its abundant reserves but also because of its ideal structural characteristics for ion-exchange reactions. With montmorillonite as the dominant mineral phase featuring a stable 2:1 layered structure, Bent-An possesses an impressive cation exchange capacity (CEC) of 98 meq/100g. This core technical parameter provides the necessary foundation for the penetration of bulky organic cations into the clay interlayers. The chemical composition analysis via X-ray Fluorescence (XRF), presented in Table 1, indicates that the alumino-silicate system is predominant, with SiO_2 (53.40%) and Al_2O_3 (15.20%) content. The characteristic presence of iron oxides (Fe_2O_3) at 13.50% not only imparts distinct physical properties but also contributes to the complexity and diversity of adsorption sites on the material surface.

Table 2.1. Chemical composition of Indian bentonite (Bent-An)

Oxide	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	MKN
(%) Weight	53.4	15.2	13.5	2.41	3.12	2.15	0.38	1.02	8.62

In addition to the substrate, auxiliary chemicals were strictly selected to ensure experimental precision. The modifying agent, octyltriphenyl phosphonium bromide (OTPB), was used at high purity (>98%) to minimize undesirable side reactions. For the target adsorbate, standard-grade methylene blue (MB) was utilized as the benchmark to evaluate the treatment capacity of the material, owing to its characteristic cationic structure and its prevalence in industrial wastewater.

2.2. Synthesis procedure for organoclay

To thoroughly convert the nature of Bentonite from hydrophilic to organophilic, the modification process was established through four interconnected and logically sequential stages:

First, the swelling stage is considered a critical preliminary step. Stirring 1.0g of Bent-An in distilled water for 24 hours is a calculated scientific approach to maximize hydration forces, helping the clay layers delaminate and expand to their fullest extent. This creates the necessary "open space" for large organic cations to easily penetrate the exchange sites within the crystal lattice. Following this preparation, the ion-exchange stage was implemented by introducing an OTPB solution (equivalent to 100% of the CEC) into the system. Here, a systematic substitution occurs: the bulky $OTPB^+$ organic cations, which possess a higher affinity, displace the small inorganic cations (Na^+, Ca^{2+}) from the interlayer galleries, thereby establishing a new organic structure for the material.

The stability of this process was reinforced during the reaction stage. Maintaining a constant temperature of 50°C for 4 hours under strict pH control not only accelerated the reaction kinetics of the exchange but also ensured the durability of the newly formed bonds. Finally, the purification step served as the final quality control measure. The product was washed with an ethanol/water mixture to completely remove impurities and excess Br^- ions. The total disappearance of Br^- ions after washing and drying serves as evidence that the resulting material is pure organoclay, ready for advanced adsorption applications.

3. RESULTS AND DISCUSSION

3.1. Material Structural Characterization

3.1.1. XRD Analysis and Intercalation Mechanism

In the study of clay minerals, X-ray diffraction (XRD) results serve not only as technical data but as the most direct and compelling experimental evidence confirming the transformation of the layered structure. For the raw Indian Bentonite (Bent-An) sample, the characteristic reflection peak for the d_{001} plane appears distinctly at a specific $2\theta = 8.14^{O}$angle, corresponding to a basal spacing of 10.862 Å. This value reflects the natural hydrated state of the montmorillonite mineral, where small inorganic cations are surrounded by water molecules within the interlayer galleries.

A structural turning point is clearly demonstrated following the organic modification process, as this diffraction peak shifts significantly toward a lower scanning angle ($2\theta = 6.30^{O}$), corresponding to a value of d = 14,030 Å.. The absolute increase in interlayer spacing by 3.168 Å carries significant scientific implications: it confirms that the bulky phosphonium cations successfully penetrated and occupied positions within the interlayer space. This expansion is entirely compatible with the geometric dimensions of the Octyltriphenyl Phosphonium radical when arranged in a tilted orientation between the silicate platelets. This lattice expansion not only demonstrates the efficiency of the synthesis protocol but also creates a more accessible internal volume, establishing the prerequisite for "trapping" large-sized organic dye molecules.

The XRD patterns of Bent-An and the synthesized organoclay are presented in Figure 3.1 and Figure 3.2.

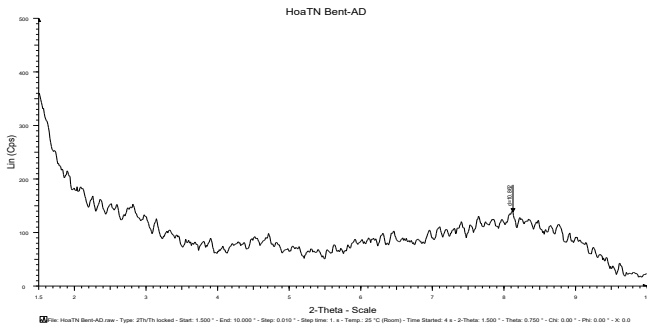

Figure 3.1. XRD pattern of Bent-An

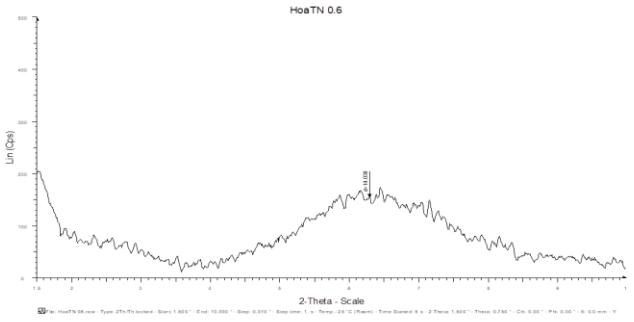

Figure 3.2. XRD pattern of the synthesized organoclay

3.1.2. FT-IR Analysis and Functional Group Interactions

Complementing the XRD results, Fourier-Transform Infrared (FT-IR) spectroscopy provides a detailed insight into the presence and interaction of chemical functional groups on the silicate matrix. In the organoclay spectra, the appearance of intense absorption bands at 2928 cm^{-1} and 2855 cm^{-1} is characteristic of the symmetric and asymmetric C-H stretching vibrations of the long alkyl chains from the OTPB agent. Notably, the absorption peak at 1438 cm^{-1} confirms the existence of the P-Phenyl bond, a core component of the phosphonium salt. The fact that these peaks maintain a stable intensity after thorough washing indicates that the organic agent is not merely superficially adsorbed via physical adhesion but is sustainably integrated into the material structure through ion-exchange interactions, establishing the organophilic nature of the organoclay.

3.1.3. SEM Morphology and TGA Thermal Stability

The fundamental transformation of the material is further evidenced by changes in surface morphology and thermal stability:

- Morphology (SEM): Scanning Electron Microscopy images reveal a stark contrast; while the original Bent-An exists as dense, flat, and compact plate-like aggregates, the modified organoclay possesses a coarse, porous surface with a clearly defined system of channels and fissures. This structure significantly increases the effective contact area, facilitating the

diffusion of adsorbates deep into the material.

- Thermal Stability (TGA): Thermogravimetric analysis curves confirm that the organoclay exhibits reliable thermal stability, remaining stable up to a threshold of 200°C. The intense mass loss phase observed between 200 – 500°C corresponds to the pyrolysis of the carbon chains and aromatic rings of the OTPB. This allows for the precise quantification of the actual intercalated organic content and reaffirms the superior thermal stability of phosphonium derivatives.

3.2. Evaluation of methylene blue Adsorption Efficiency

3.2.1. Kinetics and Influence of Factors

The adsorption process of methylene blue (MB) onto the organoclay follows a distinct kinetic pattern characterized by two successive stages. During the first 30 minutes, the adsorption rate is extremely rapid due to the strong electrostatic attraction between the negatively charged material surface and the MB^+ cations. Subsequently, the process transitions to a slower phase and reaches equilibrium at 75 minutes, as MB molecules must diffuse deep into the expanded interlayer galleries. Experimental results in Table 2 show that the dye removal efficiency reaches an impressive 99.1% at equilibrium.

Table 3.1. MB adsorption kinetics of Bent-An and the organoclay

Time (minutes)	15	30	45	60	75	90
q (mg/g) Organoclay	11.62	26.48	62.44	72.84	79.30	79.30
Percentage yield (%)	14.50	33.10	78.00	91.00	99.10	99.10

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The efficiency of the process is also strictly dependent on the medium pH. Experimental data indicate that the removal efficiency increases sharply as the pH is raised from 3 to 9. In alkaline media, deprotonation increases the negative charge density on the clay surface, thereby strengthening the electrostatic interaction with the MB^+ cations and optimizing the solution purification capacity.

3.2.2. Langmuir Isotherm Model and Adsorption Mechanism

The high correlation of the experimental data with the Langmuir model (R^2 = 0.9991) provides scientific evidence that the MB adsorption process occurs via a monolayer mechanism on homogeneous active sites. Notably, the maximum adsorption capacity (q_{max}) reached 142.86 mg/g, approximately 6 times higher than that of raw bentonite, demonstrating a remarkable improvement in processing capacity after modification.

The adsorption mechanism is not limited to traditional electrostatic attraction but involves a complex combination of multiple interactions. The presence of phenyl rings in the OTPB structure induces strong $\pi - \pi$ stacking with the aromatic rings of the MB molecule. Concurrently, the hydrophobic octyl chain acts as an in-situ organic solvent, accelerating the partition of the dye from the aqueous phase. It is the synergy between the expanded layered structure and the hydrophobic properties that grants the organoclay its superior advantage in treating color pollution.

4. CONCLUSION

Based on the experimental results of the synthesis process, modern structural characterization, and practical treatment evaluations, this study draws the following key conclusions. Firstly, the work confirms that the modification of Indian Bentonite with Octyltriphenyl Phosphonium Bromide (OTPB) is a breakthrough and effective technological solution for creating an intelligent adsorbent. The combination of a significantly expanded layered structure (from 10.862 Å to 14.030 Å) and the transformation of the surface to an organophilic nature establishes a multi-layered adsorption mechanism. The material not only utilizes traditional electrostatic forces but also maximizes $\pi - \pi$ interactions and hydrophobic effects, enabling the removal of Methylene Blue with near-absolute efficiency (99.1%) under optimized conditions.

Furthermore, the use of a phosphonium derivative has demonstrated superior advantages in terms of thermal stability and structural integrity compared to conventional quaternary ammonium agents, ensuring the sustainable operation of the

material in complex treatment environments. With an impressive maximum adsorption capacity of 142.86 mg/g-nearly six times that of the precursor-OTPB-modified organoclay moves beyond laboratory scale and opens vast prospects for implementation in large-scale industrial textile wastewater treatment systems. With a simple fabrication process, low raw material costs, and outstanding purification efficiency, this research provides a solid scientific foundation and a promising practical solution, contributing to the mitigation of water pollution and the advancement of a sustainable green industry.

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