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Lanthanum (III) encapsulated chitosan-montmorillonite composite for the adsorptive removal of phosphate ions from aqueous solution

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ABSTRACT

In the present work, lanthanum (III) encapsulated chitosan-montmorillonite composite (La-CS-MMT) was prepared as an adsorbent for the effective removal of phosphate ions from aqueous solution. Characterization of the adsorbent using FT-IR, XRD, SEM with EDX, TGA and DTA techniques were carried out. Batch adsorption experiments were carried out to optimize the effects of various operating parameters viz., shaking time, initial concentration of phosphate ions, dosage, competitor co-existing ions, pH and temperature. Phosphate ions adsorbed effectively on La-CS-MMT composite through hydrogen bonding and by outer-sphere complex formation mechanism. Freundlich isotherm model fit well with the equilibrium isotherm data. The experimental values of ΔG°, ΔS° and ΔH° revealed that the nature of adsorption was feasible, spontaneous and exothermic. The kinetic study was well fitted with pseudo-second-order model. Regeneration study of the spent La-CS-MMT-P composite was carried out upto five cycles and found that about 70% of adsorption efficiency was retained.

1. Introduction

In nature, phosphate is originated from many phosphate minerals and played a vital nutrient for the augmentation of plants and other micro and macro-organisms. Phosphate utility in agriculture causes staid water pollution through runoff into water bodies producing eutrophication [1] which leads to depletion of dissolved oxygen. Abundance growth of aquatic plants and algae create the blemishes on the ecosystem by disturbing the eco-balance of organisms subsisting in water bodies. The maximum permissible limit of phosphate ions to overcome eutrophication in water is 0.1 mg L^{-1} [2] and hence it is necessary to remove phosphate.

Various removal technologies are developed by physicochemical and biochemical methods to remove phosphate ions from water and wastewater such as ion-exchange [3], biological method [4], electrocoagulation process [5], chemical precipitation [6], membrane process [7], adsorption method [8] etc. Among those techniques adsorption is established as most efficient method because of its cost-effectiveness, ease operation, simplicity, high efficiency, reusability of adsorbent, less production of sludge etc.

Recently different adsorbents were prepared for phosphate ions removal using activated carbon [9], silica [10], fly ash [11], calcined eggshell [12], slag [13], cellulose [14], alginate [15], chitosan [16], trimetal oxide [17], graphene oxide [18], layered double hydroxides [19], La-modified tourmaline [20] etc. It has been justified that lanthanum loaded adsorbents are found to be highly efficient to remove phosphate ions when compared with other metals because La^{3+} ions which has a higher affinity for oxyanions like phosphate, as it behaves as hard Lewis acid character and a higher number of coordination [21,22].

Chitosan is one of the imperative natural adsorbent used by a lot of researchers as it has reactive functional groups like hydroxyl (—OH) and amine (—NH_2) which acts as sites for coordination to form complexes with various metal ions. It is most widely used due to its remarkable properties such as nontoxicity, bio-compatibility, easy availability, low cost, antibacterial properties etc. Montmorillonite is a natural clay mineral with 2:1 ratio of tetrahedral Si^{4+} ions and octahedral sheets of Al^{3+} ions. It is a spectacular supporting material and prominent adsorbent having high surface area, mechanical, chemical stability and less expensive. Chemically, it is represented as $(Na,Ca)_{0.33}$ $(Al,Mg)_2$ (Si_4O_{10}) $(OH)_2 \cdot xH_2O$.

Recently many literature studies have been based on the modification of clay particles using polyhydroxy – metal ions to exchange the ions in the clay particles, named as pillared intercalated particles. Much of these pillared clay acts as a promising material for phosphate elimination [23]. In addition, Darder et al. reported chitosan-montmorillonite nano composites used as anion detectors, when it was incorporated in potentiometric sensors [24]. In general, montmorillonite present in the adsorbent could potentially used for phosphate adsorption [25] to remove contaminants from water and wastewater but the removal efficiency was found to be less. By keeping these ideas La^{3+} ions encapsulated with chitosan-montmorillonite, which has a greater affinity towards phosphate was prepared. The biopolymer clay composite undergoes formation of intercalated lamellar structures due to the

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entrapment of montmorillonite particles in the polymeric matrix network and the La^{3+} ions undergoes chelation with chitosan. In addition to that it might interact with clay by exchanging Al^{3+} ions by La^{3+} ions and the hydroxyl groups on the surface of clay to under chelation as well as protonation. Thus after treated with La^{3+} ions the removal percentage of phosphate ions was increased when compared to chitosan-montmorillonite (CS-MMT) composite.

The main objective of the present study is to prepare the adsorbent lanthanum (III) encapsulated chitosan-montmorillonite composite (La-CS-MMT) with relatively low cost for removing the phosphate ions. Characterization studies with FTIR, XRD, SEM with EDX, TGA and DTA were carried out. Different operating parameters viz., shaking time, initial concentration of phosphate ions, dosage, co-existing ions, pH and temperature studies were optimized. Isotherm and kinetic studies were investigated to realize the mechanism and to determine the best fit of isotherm and kinetic models.

2. Materials and methods

2.1. Chemicals used

Chitosan (85% deacetylated) was supplied by Pelican Biotech and Chemicals Labs, Kerala (India). Montmorillonite (Supplied by Sigma Aldrich, Germany), KH_2PO_4 (98%) (Supplied by Merck), glutaraldehyde (25%), $LaCl_3 \cdot 7H_2O$ (99%), CH_3COOH (99.5%), NaOH (98%), were obtained from Merck, New Delhi. All other reagents and chemicals were of analytical grade and the experimental solutions were prepared using double distilled water.

2.2. Preparation of La-CS-MMT

About 10 g of chitosan was homogeneously dissolved in 2% of glacial acetic acid. A known amount of 5 g of montmorillonite was mixed with above solution under continuous stirring for about 6 h. The pale brown precipitate of CS-MMT was obtained after adding 0.1 M NaOH solution. The precipitate was washed using double distilled water till the neutral pH was attained. To the wet precipitate, about 2.5 wt% of glutaraldehyde solution was added and maintained at 4 °C for about 12 h to attain crosslinking. Then it was washed with double distilled water until the pH was neutral. Finally, it was treated with 5% (*W/V*) of the $LaCl_3.7H_2O$ solution for about 24 h followed by washing with double distilled water and allowed to dry in hot air oven for 6 h at 60 °C to obtained La-CS-MMT composite.

2.3. Batch experiments

Batch equilibrium method was conducted for adsorption studies where 50 mL of 100 mg L^{-1} phosphate ions solution and 0.1 g of La-CS-MMT composite were taken in a 250 mL stopper conical flask. The reaction mixture was shaken on a mechanical shaker at a speed of 120 rpm at 303 K for a fixed shaking time. After adsorption, the concentration of the supernatant solution was determined by vanadomolybdophosphoric acid method, measured at a wavelength of 400 nm using UV–Vis spectrophotometer [26]. The adsorption capacity of the adsorbent varies with shaking time. The time at which the adsorbent attain saturation was fixed as equilibrium time. The effect of shaking time was observed at 5–40 min. The concentration of the adsorbate solutions were varied between 50 and 300 mg L^{-1} in order to find the maximum adsorption capacity of the adsorbent. The adsorbent dose was varied from 0.025 to 0.2 g of La-CS-MMT composite depending upon the adsorption ability of the adsorbent. The pH is the important parameter which influences the nature of adsorbent and also adsorbate. Thus pH studies were carried out by altering it from 2 to 12 using respective 0.01 M HCl/NaOH solution. The interference of other ions commonly found in aqueous solution like HCO_3^-, Cl^-, SO_4^{2-} and NO_3^- ions were studied. The spent La-CS-MMT composite was regenerated using respective 0.1 M NaOH solutions and carried out up to five cycles. Isotherms and kinetic studies were determined using various concentrations at 303, 313 and 323 K and the value of q_e was calculated by Eq. (1) and the percentage removal was calculated by Eq. (2).

$$\text{Adsorption capacity,} \quad q_e = \frac{(C_i - C_e)}{m} V \ \text{mg/g} \tag{1}$$

$$\text{Percentage anion removal} = \left(\frac{C_i - C_e}{C_i}\right) 100 \tag{2}$$

where, the volume of adsorbate solution is represented as *V* (L), the initial phosphate ions concentration is indicated as C_i, (mg L^{-1}), the equilibrium concentrations as C_e (mg L^{-1}) and the mass of the La-CS-MMT as m (g).

2.4. Analytical instrumental techniques

To identify the functional groups present in the prepared La-CS-MMT composite before and after adsorption were characterized by Fourier transform infrared spectrometer (FT-IR) by KBr pellet technique in the range of 4000 to 400 cm^{-1} using JASCO-460 plus model, Japan. The crystalline phases of La-CS-MMT and La-CS-MMT-P composite were determined by X-ray diffraction method (XRD) at 25 °C using Cu-Kα radiation by X'per PRO model-PANalytical, Netherland. Scanning electron microscope (SEM) analysis, the surface of the adsorbent was characterized by using Vega 3 Tescan model and with energy dispersive X-ray analyzer (EDX), the elements present in the adsorbent before and after adsorption was qualitatively examined and localized by using Bruker Nano GMBH, Germany. Thermal stability of the La-CS-MMT composite was studied with thermo-gravimetric analysis (TGA) and differential thermal analysis (DTA) using TG-DTA 6200 instrument of SEIKO model. Phosphate ions were analyzed using Spectroquant Pharo 300, UV–Vis spectrophotometer, Merck, Germany. The pH adjustments were carried out by using Expandable ion analyzer, Orion EA940, USA, with pH electrode.

2.5. Measurement of pH at zero point charge (pH_{zpc})

The pH drift method [27] was used to measure the pH_{zpc} of La-CS-MMT composite. The pH of the electrolyte was adjusted by addition of 0.01 M HCl/NaOH solution between 2 and 12. For about 0.15 g of the La-CS-MMT composite was added to 0.01 M NaCl of 50 mL solution. After stabilizing the pH, the final pH was examined after 24 h. The graph of initial pH versus final pH would give pH_{zpc} which is the point at which initial pH and final pH are found to be equal.

3. Results and discussion

3.1. Spectral characterization

3.1.1. FT-IR spectra

The FT-IR spectra of chitosan (CS), montmorillonite (MMT), lanthanum chloride ($LaCl_3 \cdot 7H_2O$), lanthanum entrapped chitosan montmorillonite (La-CS-MMT), phosphate ions adsorbed lanthanum entrapped chitosan montmorillonite composite (La-CS-MMT-P) are represented in Fig. 1. The peaks assigned for CS as the broad band at 3432 cm^{-1} due to vibrations of —OH and $-NH_2$ groups stretching frequencies. The sharp peaks at 2926 cm^{-1} and 2856 cm^{-1} [28] were attributed to asymmetric and symmetric C—H stretching vibration of $—CH_2$ groups respectively. Bending vibration of $—NH_2$ group found at 1633 cm^{-1} and C═O stretching vibration in —CONH group was ascribed at 1036 cm^{-1} and the peak of —CH bending vibrations in —CHOH group was observed at 1317 cm^{-1}.

The spectrum of MMT assigned vibrations of the hydrated —OH bond bands for bending at 1641 cm^{-1} and stretching at 3452 cm^{-1}