

Removal of nitrate and phosphate by starch and lanthanum modified montmorillonite

Su K.^{*}, Wang Q., Deng S., Li L., and Rong Cao R.

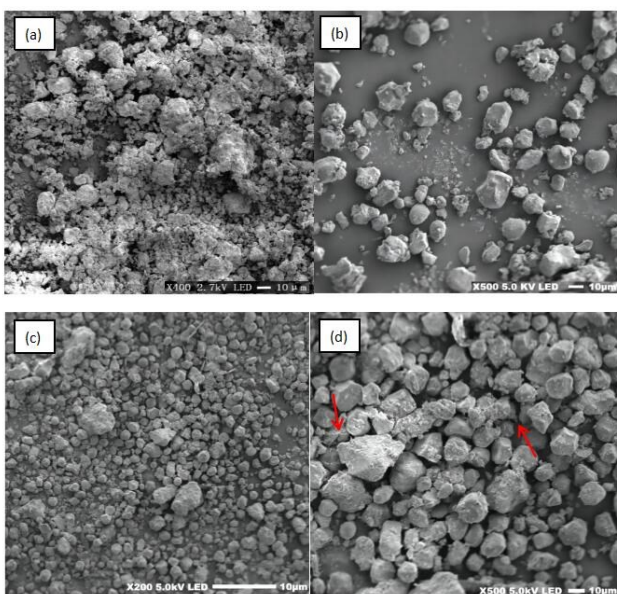
Faculty of Geosciences and Environmental Engineering, Southwest Jiaotong University, Chengdu 611756, China

Received: 15/07/2022, Accepted: 27/09/2022, Available online: 28/09/2022

*to whom all correspondence should be addressed: e-mail: ksu@swjtu.edu.cn

<https://doi.org/10.30955/gnj.004405>

Graphical abstract



Abstract

Unqualified treatment of the discharge of wastewater contains a large number of nitrogen and phosphorus and other nutrients, such wastewater into the water environment is easy to lead to eutrophication of water bodies, and cause harm to human health. In order to prepare a cost-effective, efficient and environmentally friendly adsorbent material for nitrogen and phosphorus removal, lanthanum modified montmorillonite (La₄-Mt), starch modified montmorillonite (St₆-Mt) and starch and lanthanum modified montmorillonite (St₆-La₄-Mt) were used in this paper to investigate the removal effect and adsorption mechanism of the three modified materials on nitrogen and phosphorus. The mechanism of modification and the properties of the modified montmorillonite were characterised by zeta potential and scanning electron microscopy (SEM) analysis. The test results show that : After the introduction of starch and lanthanum, the adsorption of both nitrogen and phosphorus by the modified montmorillonite was significantly enhanced. The mechanism of PO₄³⁻ removal by La₄-Mt and St₆-La₄-Mt, materials prepared from La-loaded montmorillonite, is due

to the binding of La³⁺ to OH⁻ in solution to produce La(OH)₃, which in turn removes the oxygenate PO₄³⁻ and NO₃⁻ from solution by electrostatic gravitation. The mechanism of removal of oxygenates by St-loaded montmorillonite St₆-Mt and St₆-La₄-Mt is that St itself is an electropositive natural polymeric organic substance, and by reducing the electronegativity of the system, St reduces the electrostatic repulsion between the system and the oxygenates and improves the effect of oxygenate removal, thus achieving the purpose of nitrogen removal and phosphorus removal.

Key words: Lanthanum, starch, montmorillonite, nitrogen and phosphorus removal, modification

1. Introduction

Due to the current social industry's and agriculture's rapid development, human production and life have produced increasing amounts of nitrogen, phosphorus, and other eutrophic substances (Lürling and van Oosterhout, 2013), which once introduced into the water environment can easily result in the eutrophication of water bodies and harm to human health (Xu *et al.*, 2021). Mitigating the prevalence of nitrogen and phosphorus pollution in the water environment through technical means to protect the ecological environment as well as human health has become one of the hot spots of current research concerns (Elser and Bennett, 2011; Xu and Xu, 2021; Sun, 2013).

Current methods for nitrogen and phosphorus removal from wastewater mainly include biological methods (Fanta Abaynesh *et al.*, 2021), chemicalprecipitation (Wang *et al.*, 2010), adsorption (Yu *et al.*, 2019) and crystallization (Wang *et al.*, 2006), etc. Biological nitrogen and phosphorus removal is less costly, produces less sludge, and has a wide range of phosphorus removal. However, microbial growth requires high environmental conditions, and the process of nitrogen and phosphorus removal is affected by a variety of factors, resulting in unstable effluent quality, which requires deep treatment to meet the nitrogen and phosphorus discharge standards (Oehmen *et al.*, 2007). The chemical precipitation method is fast, simple and effective in treating high nitrogen and phosphorus wastewater, but it is costly, susceptible to environmental conditions such as pH, prone to secondary pollution and the different phosphate precipitates produced can have an

impact on subsequent recycling (Crutchik *et al.*, 2013). The crystallization method can effectively remove phosphorus from wastewater with high recovery of pollutants, and the by-products formed, such as ammonium magnesium phosphate, can be used as agricultural fertilizer, but it is influenced by various factors in practice, such as the type and particle size of the crystalline species, the type of reactor, and the mixing method (Liat *et al.*, 2015; Che *et al.*, 2022; Xing *et al.*, 2022), so it is not widely used. The adsorption method is a simple process, easy to highly efficient and low consumption, stable performance of the adsorbent and easy to regenerate, and can also remove phosphorus in a wider pH range and at lower levels, while recovering phosphate (Cui *et al.*, 2020; Longjiang *et al.*, 2020). Although the current application of adsorption methods in nitrogen and phosphorus removal is more mature, many adsorbents have a small adsorption capacity for nitrate ions in complex water bodies in practical applications. Therefore, the development of an artificially modified adsorbent material that can remove nitrogen and phosphorus simultaneously, efficiently and at low cost remains an important research direction (Zuo *et al.*, 2021).

As a natural clay mineral material, montmorillonite is widely distributed in China, with large reserves and low mining costs, and has good structural stability and high temperature resistance. Also montmorillonite, as a 2:1 type layered clay mineral, has interlayer domains that provide sites for chemical reactions that improve its adsorption efficiency, and the presence of H⁺ on its surface further enhances its adsorption capacity (Xie *et al.*, 2022; Du *et al.*, 2021). Chen *et al.* (Chen *et al.*, 2019) prepared hollow layered mesoporous spheres of montmorillonite (MMTNS@CS-HMPHS) and showed that the material formed mesoporous pore channels and increased its specific surface area, while the active centres of MMT and chitosan on the material greatly improved its performance in terms of adsorption and catalyst carriers. Liang Chen *et al.* (Chen *et al.*, 2017) prepared a montmorillonite-biochar composite with a maximum adsorption capacity of 105.28 mg/g for PO₄³⁻. Zou Y *et al.* (Zou *et al.*, 2020) prepared a composite modified material (Zr-CaMs) from zirconium modified montmorillonite with a maximum phosphate adsorption capacity of 22.37 mg/g. In summary, montmorillonite has the advantages of large two-dimensional specific surface area, low cost, high chemical stability, low toxicity, and good environmental compatibility. (Li *et al.*, 2017) Therefore, montmorillonite is a good loading material through modification can improve its adsorption of nitrogen and phosphorus, and is an adsorbent material with research significance.

Lanthanum is widely available and less toxic, and lanthanum-based adsorbents are a promising phosphate adsorbent (Yimin *et al.*, 2022). The use of light rare earth elements such as lanthanum as a modifier is an important direction in the development of phosphorus removal adsorbents. For example, Mu *et al.* (Mu *et al.*, 2022) showed that polymeric aluminium chloride-lanthanum modified bentonite (PLMB) can efficiently adsorb phosphorus from water, and its adsorption capacity can

reach 57.629 mg/g. The lanthanum-loaded zeolite chitosan composite adsorbent (La-MZ/CTS) was prepared and synthesized by Zhang *et al.* (Zhang *et al.*, 2021) It was found that the lanthanum loading resulted in a uniform distribution of La(OH)₃ on the surface of the material, exhibiting a large pore size and specific surface area, and the adsorption capacity of the material for phosphate was increased by up to 10 times compared with the original material, reaching 27.9 mg·g⁻¹. W Luo *et al.* (Luo *et al.*, 2020) used La³⁺ loaded montmorillonite to remove phosphate from water with a material adsorption capacity of 0.39 mmol/g.

As a natural polymeric organic substance, starch is widely available in nature, simple to obtain, inexpensive and naturally exhibits electropositive properties, making it a good modifier. Both starch and lanthanum are excellent modifiers, but there are few studies on the use of lanthanum and starch as modifiers for montmorillonite at the same time. Therefore, this paper will prepare starch-modified, lanthanum-modified and starch-lanthanum-modified montmorillonite to investigate the effect and mechanism of the three modified materials on the adsorption and removal of nitrogen and phosphorus, so as to provide new ideas and directions for the preparation of an efficient, green and widely used adsorbent material for the removal of nitrogen and phosphorus.

2. Experiment

2.1. Materials

Montmorillonite (>97% purity) from Shijiazhuang, Hebei Province, whose main physical phase is calcium-based montmorillonite. Lanthanum nitrate hexahydrate ([La(NO₃)₃·6H₂O), acetic acid, corn starch, sodium hydroxide, sodium chloride, potassium dichromate, all purchased from Shanghai Aladdin Biochemical Technology Company. Concentrated sulphuric acid and concentrated nitric acid, both purchased from Shanghai Standard Technology Company. All the above reagents are analytically pure except for montmorillonite. The test water was deionised water.

Electronic balance (Shanghai Shangping Instruments Company, FA1004), pH meter (FE28-Standard), constant temperature incubator (HH-420), magnetic stirrer (85-2A), UV spectrophotometer (721/722N) were purchased from Shanghai Essence Instruments Technology Company. Benchtop low-speed centrifuge (Thermo Fisher Scientific, TDZ5-WS.)

2.2. Adsorbents preparation

To prepare sodium-based montmorillonite (Na-Mont), 10 g of 97% high purity montmorillonite [Montmorillonite (hereafter referred to as Mont)] was weighed into a 250 mL volumetric flask, added to a 1 mol/L NaCl solution, stirred in a magnetic stirrer for 24 hours, and then centrifuged. Then separate the supernatant from the coarse sediment at the bottom of the centrifuge tube, remove the montmorillonite adhering to the inner wall of the centrifuge tube and place it in a 250 mL beaker. The Na-based montmorillonite (Na-Mont) was obtained by

washing the beaker with 0.005 mol/L NaCl solution and repeating the washing procedure three times, filtering and drying in an electric blast oven at 65 °C for 24 h, and grinding to 200 mesh.

4 g of lanthanum nitrate hexahydrate $[\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}]$ and 10 g of the prepared Na-Mt were weighed into a 250 ml volumetric flask, fixed with deionised water and stirred on a magnetic stirrer for 8 hours. Remove the coarse residue at the bottom, then centrifuge at 4000 r/min, extract and dry in an electric blast oven at 65 °C for 24 h. Lanthanum-modified montmorillonite (La₄-Mt) was obtained by grinding to 200 mesh.

Weigh 6 g of the experimental corn starch into a 250 mL volumetric flask, add 50 ml of 5% acetic acid solution and stir to completely dissolve the corn starch in the acetic acid solution. Then add 10 g of the prepared Na-Mt to the volumetric flask, set the volume to 250 mL with deionised water, stir for 8 h on a magnetic stirrer, remove the coarse sediment at the bottom, load into a 50 mL centrifuge tube in batches, centrifuge at 4000 r/min, extract and dry for 24 h in an electric blast oven at 65 °C, grind to 200 mesh to produce St₆-Mt.

Weigh 6 g of the experimental corn starch into a 250 mL volumetric flask, add 50 ml of 5% acetic acid solution, stir to completely dissolve the corn starch in the acetic acid solution, then add 10 g of the prepared La₄-Mt to the volumetric flask and set the volume to 250 mL with deionised water, place on a magnetic stirrer for 8 h, remove the coarse sediment at the bottom, load into a 50 mL centrifuge tube in batches and centrifuge at 4000 r/min. The product was centrifuged at 4000 r/min, filtered and dried in an electric blast oven at 65 °C for 24 h. The product was ground to 200 mesh to co-modified montmorillonite (St₆-La₄-Mt) with starch and lanthanum nitrate hexahydrate.

2.3. Methods of analysis

The solution phosphorus concentration was determined by ammonium molybdate spectrophotometry (GB11893-89) with a test wavelength of 700 nm (721/722N, Shanghai Essence). Measurement of nitrate concentration by spectrophotometry.

The equations for the removal of PO_4^{3-} and NO_3^- from modified montmorillonite and the amount of adsorption are shown in equations (1) and (2).

$$\eta = \left(\frac{C_0 - C_e}{C_0} \right) \quad (1)$$

$$q_e = \frac{(C_0 - C_e) \times V}{W} \quad (2)$$

η --Removal rate of PO_4^{3-} and NO_3^- ; C_0 --the initial concentration of PO_4^{3-} and NO_3^- in the solution before adsorption, mg/L; C_e --the concentration of PO_4^{3-} and NO_3^- in the solution after adsorption equilibrium, mg/L; V --the volume of the solution, L; W --the amount of adsorbent; q_e - the amount of adsorption, mg/g.

The surface morphology of the modified montmorillonite was observed by field emission scanning electron

microscopy (SEM, Oxford X-max 80). High sensitivity Zeta potential and particle size analyzer (nano ZS) to characterize the Zeta potential and analyze the charge on the surface of montmorillonite before and after modification.

2.4. Adsorption experiment

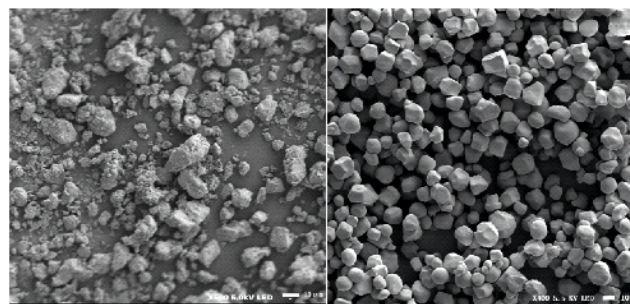
10 g of St, La, Na-Mt, La₄-Mt, St₆-Mt and St₆-La₄-Mt were dissolved in 250 mL of 10, 20 and 30 mg/L PO_4^{3-} contaminated solution, respectively, and shaken for 8 h at 30 °C in a water bath with a constant temperature of 200 r/min. After centrifugation and filtration through a 45 μm filter head, the phosphorus concentration in the filtrate was determined. Three sets of parallel samples were set up and the average values were taken.

10 g of St, La, Na-Mt, La₄-Mt, St₆-Mt and St₆-La₄-Mt were dissolved in 250 mL of 2.5, 5 and 10 mg/L NO_3^- contaminated solution, respectively, and shaken for 8 h at 200 r/min in a water bath thermostat at 30 °C. The filtrate was centrifuged and filtered through a 45 μm filter head to determine the NO_3^- concentration. Three sets of parallel samples were set up and the average values were taken.

3. Results and discussion

3.1. SEM analyses

Investigation of the changes in the surface structure of samples by scanning electron microscopy (SEM) to investigate the mechanism of adsorption of PO_4^{3-} and NO_3^- by the ternary system of lanthanum, starch and montmorillonite. It can be seen that the surface structure of Na-Mt is sparser after sodium purification, with an overall more uniform distribution of size particles and the appearance of some small lamellar structures. As can be seen from Figure 1(b), corn starch has a regular size and shape, with smooth surfaces and inter-clustered spherical, square and polygonal structures.



(a) Na-Mt; (b) St

Figure 1. SEM characterisation of Na-Mt and St.

The SEM characterisation of La₄-Mt in Figure 2(a) shows that the surface structure of montmorillonite has changed considerably after the La modification, and La is mainly loaded on the outer surface of Na-Mt by longitudinal or transverse synaptic-like structures, which makes the surface of La₄-Mt present a rough and loose pore structure. As displayed in Figure 2(b), After modification by starch, the small particle structure on the surface of Na-Mt is reduced, the surface becomes smoother and flatter, and St occupies an increasingly prominent position in the overall structure, so that the St particles attached to St₆-Mt have

the same opportunity to react with the external environment, forming small grooves and gap-like areas, and small amounts of St are more densely distributed. As shown in Figure 2(c), the granules attached to the surface of St₆-La₄-Mt after successive modification with lanthanum and starch are denser and the pore structure is more uniform, increasing the contact area of the material with phosphorus and nitrogen containing wastewater. Compared to the surface structure of La₄-Mt, the starch modified particles are smoother and shapelier, and there are almost no obvious gaps in the same layer. Figure 2(d) shows a plot of St₆-La₄-Mt at 500x, where the arrows point to the appearance of a La-loaded synaptic structure on the lower surface of the St-encapsulated outer layer, suggesting a possible 'encapsulation effect' during the St modification process, whereby starch adheres to the outer surface of the lanthanum-modified particles. A comparison of the SEM characterisation of the samples revealed that the surface pore structure of unmodified Na-Mt is less and the removal rate of nitrogen and phosphorus is lower, while the surface pores of all three materials modified by lanthanum and starch have increased and the surface attached particulate matter is more dense, which enhances the absorption and removal efficiency of the original materials for nitrogen and phosphorus.

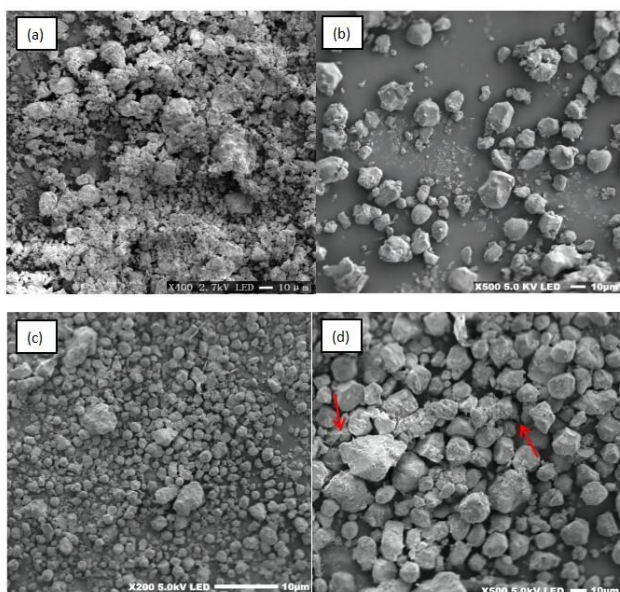


Figure 2. SEM characterisation of montmorillonite modified with different substances. (a) La₄-Mt; (b) St₆-Mt; (c and d) SEM characterization of St₆-La₄-Mt at different resolutions.

3.2. Zeta potential characterisation

To determine the changes in the overall electrical properties of starch, lanthanum and the composite modified montmorillonite before and after the Na-Mt modification process, the zeta potentials of samples were characterised respectively. The positive or negative value of the Zeta potential represents the positive or negative colloidal potential of the material in aqueous solution, and its absolute value represents the amount of charge carried by the material (Du *et al.*, 2022). As can be seen from Figure 3, the zeta potential of all four materials, Na-Mt, La₄-Mt,

St₆-Mt and St₆-La₄-Mt, are negative at -21.2 mV, -12.72 mV, -9.63 mV and -1.2 mV, respectively. In terms of zeta potential values, unmodified montmorillonite has the highest electronegativity, and montmorillonite modified with starch, lanthanum and starch and lanthanum together shows a decrease in electronegativity, and montmorillonite modified with starch and lanthanum together has the lowest electronegativity. It can be concluded that both starch and lanthanum can reduce the electronegativity of natural montmorillonite, and the joint modification of starch and lanthanum is more effective in reducing the electronegativity. The original montmorillonite basically does not have the ability to remove oxygenate by adsorption due to the coulombic repulsion between ions, while the electronegativity of montmorillonite modified by starch and lanthanum and modified by starch and lanthanum together are reduced, so the coulombic repulsion between the two is reduced when adsorbing oxygenate, thus achieving the purpose of removing PO₄³⁻ and NO₃⁻ oxygenate.

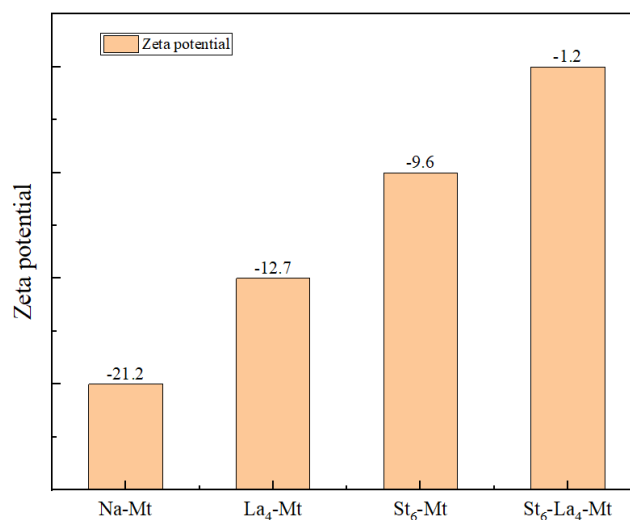


Figure 3. Zeta potentials of adsorbents.

3.3. Adsorption of contaminants on the adsorbents

3.3.1. Adsorption of PO₄³⁻

As illustrated in Table 1, the starch-, lanthanum- and co-modified montmorillonite all showed a significant improvement in the removal of PO₄³⁻ from the water. Among the three modified materials, the adsorption of PO₄³⁻ by lanthanum-modified montmorillonite increased with increasing PO₄³⁻ solution concentration, and the adsorption of starch-modified and starch-lanthanum-modified montmorillonite was highest at 20 mg/L PO₄³⁻ solution concentration.

As can be seen from Figure 4, the adsorption rates of Na-Mt on PO₄³⁻ at three concentration gradients of 10, 20 and 30 mg/L were 6.6%, 4.9% and 7.2%, respectively, indicating that Na-Mt basically did not have the ability to adsorb PO₄³⁻, which is also confirmed by the zeta potential, as Na-Mt exhibits high negativity and the Coulomb repulsion between it and PO₄³⁻, resulting in its poor adsorption capacity. In contrast, the modified materials both reduced the negative electrical properties and the Coulomb repulsion, so that the adsorption capacity of both

lanthanum and starch modified materials was increased. At the same time, it can be seen from the figure that the adsorption and removal efficiency of lanthanum on PO_4^{3-} is good. Na-Mt modified by lanthanum alone has significantly improved the adsorption of PO_4^{3-} by $\text{La}_4\text{-Mt}$, and is basically the same as the adsorption efficiency of La, which is the highest adsorption efficiency among the three modified materials, indicating that La possesses a better affinity for PO_4^{3-} . A study by Jin Suwan *et al.* (Jin *et al.*, 2021) pointed out that phosphorus removal by adsorption of loaded LaOH is mainly achieved by electrostatic interaction, ion exchange and Lewis acid-base interaction. Some studies have also indicated that La produces $\text{La}(\text{OH})_3$ in solution, which in turn produces LaPO_4 precipitate, both of which have a certain adsorption effect on PO_4^{3-} . However, Lu Yan *et al.*^[31] investigated the reaction between La_2O_3 and potassium dihydrogen phosphate in aqueous solution by IR spectroscopy and XRD spectroscopy, and concluded that the reaction product was still $\text{La}(\text{OH})_3$ and no LaPO_4 was

Table 1. Adsorption of phosphate by various adsorbents

PO_4^{3-} solution concentration	Adsorption of PO_4^{3-} (mg/g)					
	St	La	Na-Mt	$\text{La}_4\text{-Mt}$	$\text{St}_6\text{-Mt}$	$\text{St}_6\text{-La}_4\text{-Mt}$
10 mg/L	3.35	9.82	3.35	9.76	3.35	5.53
20 mg/L	6.2	19.14	0.98	17.26	6.64	8.68
30 mg/L	5.34	26.76	2.16	22.53	3.9	8.1

Table 2. Adsorption of St, La, Na-Mt, $\text{La}_4\text{-Mt}$, $\text{St}_6\text{-Mt}$ and $\text{St}_6\text{-La}_4\text{-Mt}$ on NO_3^-

NO_3^- solution concentration	Adsorption of NO_3^- (mg/g)					
	St	La	Na-Mt	$\text{La}_4\text{-Mt}$	$\text{St}_6\text{-Mt}$	$\text{St}_6\text{-La}_4\text{-Mt}$
2.5 mg/L	1.152	0.352	0.058	0.514	1.243	1.363
5 mg/L	2.016	0.559	0.230	0.936	1.948	2.309
10 mg/L	3.597	0.979	0.407	1.507	3.507	3.625

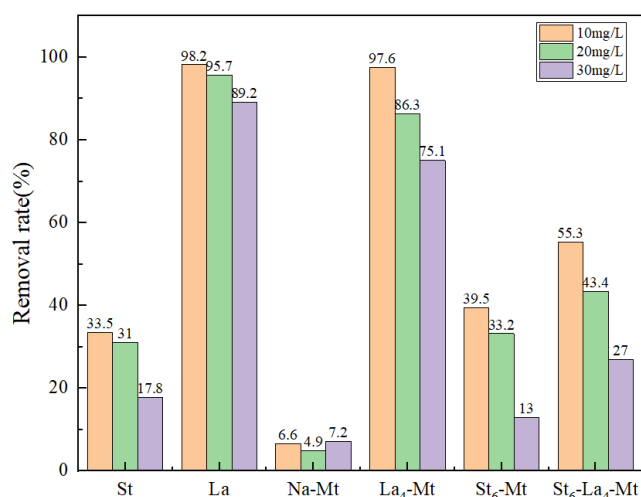


Figure 4. Phosphorus removal by various adsorbents. at different PO_4^{3-} concentrations.

3.3.2. Adsorption of NO_3^-

The results of denitrification of adsorbents at 2.5 mg/L, 5 mg/L and 10 mg/L NO_3^- solution concentrations were obtained after the tests. As can be seen from Table 2, lanthanum, starch and montmorillonite were less effective in the adsorption of NO_3^- . The removal of phosphate can rely on electrostatic adsorption between systems and complexation by ligand exchange, but most studies have

produced, arguing that the adsorption of La^{3+} on PO_4^{3-} was a chemical reaction to produce $\text{La}(\text{OH})_3$, and $\text{La}(\text{OH})_3$ removed PO_4^{3-} by electrostatic adsorption. The reduction in the electronegativity of $\text{La}_4\text{-Mt}$, as characterised by its zeta potential, also confirms that the removal of phosphorus by adsorption of $\text{La}_4\text{-Mt}$ is partly due to the reduced electrostatic repulsion between the two, which makes it easier for adsorption and thus removal of phosphorus to occur. Starch is a natural polymeric organic substance which is inherently electropositive. $\text{St}_6\text{-Mt}$ modified with St alone reduces the electronegativity of the original montmorillonite and enhances the removal of PO_4^{3-} but not as effectively as the lanthanum modification. The adsorption of PO_4^{3-} on montmorillonite $\text{St}_6\text{-La}_4\text{-Mt}$ after modification with La is higher than that of $\text{St}_6\text{-Mt}$ but lower than that of $\text{La}_4\text{-Mt}$, indicating that the "wrapping effect" during the St modification process has a limiting effect on the adsorption of PO_4^{3-} on $\text{La}_4\text{-Mt}$ surface particles.

shown that the removal of NO_3^- relies on redox reactions. For example, Su Kai *et al.* (Su *et al.*, 2022) found that structural ferrous iron on the surface of modified montmorillonite removes NO_3^- from water by a redox reaction with nitrate. In the system studied in this paper, only lanthanum has the ability to redox, and Na is slightly more metallic than La, La does not have the ability to replace Na^+ from the $\text{Na}^+\text{-NO}_3^-$ system, so there are no conditions for redox reactions, so the adsorption process of NO_3^- by the materials prepared in this paper mainly relies on the electrostatic gravitational force provided by La^{3+} and St for the system.

As shown in Figure 5, Na-Mt basically does not have the ability to adsorb NO_3^- , but the denitrification of NO_3^- solution concentrations of 2.5 mg/L, 5 mg/L and 10 mg/L is enhanced by starch, lanthanum and the montmorillonite modified by both together. As can be seen from the figure, the removal of NO_3^- by the lanthanum-modified montmorillonite $\text{La}_4\text{-Mt}$ is better than the removal of NO_3^- by La. From the above analysis, it can be seen that the adsorption process of NO_3^- by the modified materials in this paper mainly relies on the electrostatic gravitational force provided by La^{3+} and St for the system, while La is weaker in metallicity than Na. During the adsorption process of NO_3^- by $\text{La}_4\text{-Mt}$, Na^+ will inhibit the La^{3+} attached to the surface of montmorillonite from binding to OH^- in solution,

thus weakening the electrostatic adsorption effect, resulting in the denitrification effect of La₄-Mt being inferior to the other two modified materials. Starch-modified montmorillonite St₆-Mt was also more effective than St in removing NO₃⁻ and the removal of NO₃⁻ by St₆-Mt was significantly better than that by La₄-Mt. From the SEM characterisation results, the modified St was more uniformly distributed on the surface of montmorillonite and some of the surface particles of St₆-Mt aggregated and formed pores, which provided reaction sites for the adsorption and removal of NO₃⁻. The zeta potential also indicated that the electronegativity of St₆-Mt was reduced, thus reducing the Coulomb repulsion with NO₃⁻ and enhancing the removal of NO₃⁻. Among the modified materials, St₆-La₄-Mt has the best effect on NO₃⁻ removal. The SEM characterisation shows that St₆-La₄-Mt has the most homogeneous and dense pore surface, providing a large specific surface area for NO₃⁻ adsorption, and the "wrapping effect" of St inhibits the negative effect of La on NO₃⁻ adsorption, thus making St₆-La₄-Mt the best for NO₃⁻ adsorption.

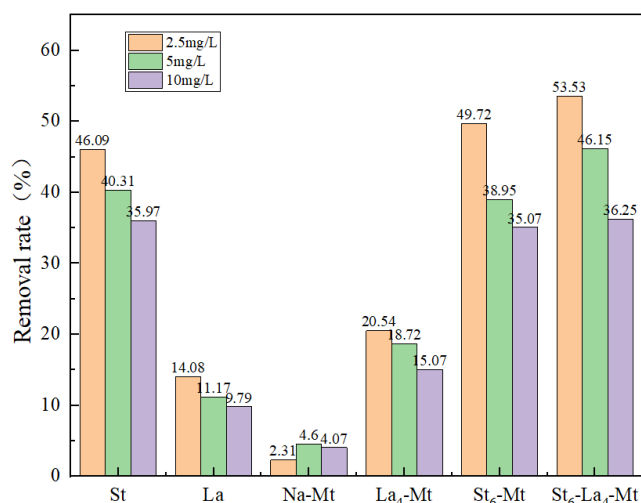


Figure 5. Nitrogen removal rates for various adsorbents at different NO₃⁻ concentrations.

4. Conclusion

In summary, we prepared and characterised lanthanum-modified montmorillonite (La₄-Mt), starch-modified montmorillonite (St₆-Mt) and montmorillonite co-modified with starch and lanthanum (St₆-La₄-Mt) by combining the advantages of starch and montmorillonite. It was found experimentally that sodium-based montmorillonite (Na-Mt) is essentially incapable of adsorption of nitrogen and phosphorus. After the introduction of starch and lanthanum, the adsorption of both nitrogen and phosphorus by the modified montmorillonite was significantly enhanced. Among the modified materials, La₄-Mt has the highest removal rate of 97.6% for nitrogen and St₆-La₄-Mt has the highest removal rate of 53.53% for phosphorus.

La₄-Mt and St₆-La₄-Mt is due to the fact that La³⁺ binds to OH⁻ in solution thus generating La(OH)₃, which can be electrostatically attracted to PO₄³⁻ in solution. There is also an exchange of ligands between O-H and PO₄³⁻ during the

adsorption process. The adsorption of NO₃⁻ occurs electrostatically due to the ability of La³⁺ to bind OH⁻ in water to form La(OH)₃. Meanwhile, the St modification has a certain "wrapping effect", i.e. the starch is uniformly wrapped around the surface of the modified material. St is loaded on the surface of St₆-Mt and St₆-La₄-Mt and reacts directly with PO₄³⁻ and NO₃⁻, but can also enter the interior of the montmorillonite and reduce its layer spacing, so that in the removal of NO₃⁻ by St₆-La₄-Mt, the St wrapped around the exterior of the material can reduce the negative effect of the interaction between La³⁺ and Na⁺ on electrostatic gravity.

The mechanism of St loading montmorillonite St₆-Mt and St₆-La₄-Mt to remove oxygenates is that St itself is an electropositive natural polymeric organic substance and St reduces the electrostatic repulsion between the system and oxygenates by reducing the electronegativity of the system to improve the effect on nitrogen and phosphorus.

The starch, lanthanum and montmorillonite used in this paper are all substances that exist widely in nature, and are inexpensive and environmentally friendly. This paper combines these three elements to prepare a new adsorbent to improve the adsorption and removal rate of nitrogen and phosphorus in water by montmorillonite, and discusses the mechanism of nitrogen and phosphorus removal of adsorbent, which provides a new idea for the preparation of adsorbent for nitrogen and phosphorus removal in water, and expects to find a better ratio to achieve efficient nitrogen and phosphorus removal in future research.

Acknowledgement

This study is supported by Sichuan Science and Technology Program (2021YFS0284, 2022NSFSC1162, 2022YFS0503, 2021YFS0289).

Conflicts of Interest

The authors declare that they have no conflicts of interest to report regarding the present study.

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