Research on the removal of pollutants from water environment by lanthanum modified montmorillonite

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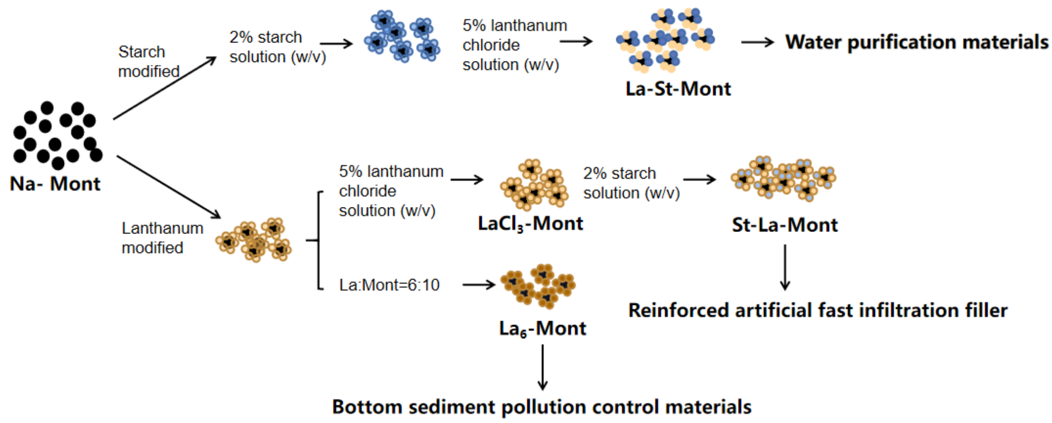
GRAPHICAL ABSTRACT



Abstract:

The management of water pollution has been one of the main problems as people pay more and more attention in the current society to the preservation and repair of the natural environment. In this paper, natural montmorillonite was modified with starch as well as lanthanum chloride. The removal efficiency of various modified montmorillonites on pollutants was examined by simulating the water quality conditions of heavily polluted lake reservoirs in order to provide new eco-friendly and effective materials for the treatment of heavily polluted lakes and reservoirs. The experimental results showed that: The nitrogen removal rates of Na-Mont, St-Mont,

La-Mont, St-La-Mont and La-St-Mont for 2 mg/L TN solution were 28.48%, 5.18%, 59.55%, 98.39%, 64.73%, respectively, and total phosphorus removal rates for 10 mg/L TP contaminated solution were 6.24%, 4.16%, 87.41%, 93.66%, 91.58% and for 100 mg/L COD solution the removal rates were 32.37%, 41.46%, 51.68%, 86.89%, 77.8%, respectively. By exploring the effect of La_6-Mont adsorption for Cr^{6+} removal at different temperatures as well as reaction times, the results showed that the Cr^{6+} removal at saturation of La_6-Mont adsorption was 76%, 80.5%, and 82.5% at the reaction temperatures of 15℃, 25℃, and 35℃, respectively. Among them, the removal rates of St-La-Mont reached more than 85%, 50% and 70% for COD, TN and for TP, respectively, and can be applied as fillers for enhanced artificial fast infiltration systems. The light rare earth composites La-St-Mont and $LaCl_3$-Mont have achieved removal rates of 35%, 50% and more than 90% for COD, TN and for TP, respectively, and can be used as effective purification materials for treating water quality of heavily polluted lakes and reservoirs. Meanwhile, La_6-Mont can effectively fix heavy metal ions and avoid the release of endogenous pollution in the bottom mud, which can be used as a material for the treatment of bottom mud in lake reservoirs. This shown that lanthanum, a light rare earth element, modified montmorillonite can not only remove a range of pollutants from water bodies but also has excellent removal rates. Additionally Besides, starch, lanthanum and montmorillonite are widely available materials with high economic benefits. Therefore, further studies on St-La-Mont, La-St-Mont, $LaCl_3$-Mont and La_6-Mont can provide new materials for the treatment of pollution in heavily polluted lakes and reservoirs.

Key words: Lanthanum; Starch; Montmorillonite; Nitrogen and phosphorus removal; COD removal; Modification;

1 Introduction

Water is both the source of vitality and the foundation of human life and social development[1]. It has a significant role in the construction of both plant and animal tissues[2]. In nature, total water resources are finite and unequally distributed[3].. During the early stage of high-speed economic development, insufficient attention was paid to the protection and restoration of the local ecological environment. The natural environment has also been severely harmed and polluted by numerous instances of incidents like the random disposal and dumping of domestic waste and the direct discharge of domestic sewage without standard treatment. Most surface and groundwater resources have been contaminated to varying degrees[4], and slow-flowing bodies of water such as lakes and reservoirs are particularly susceptible to pollution accumulation[5]. Strengthening various technical methods to eliminate water contaminants is required to maintain both the water environment and human survival and development[6-7]. The preparation of low-cost and efficient adsorbent materials for the treatment of COD, TP, TN, and heavy metal pollution in lakes and reservoirs has become one of the current research hotspots[8-10].

At present, the main methods for removing Chemical oxygen demand (COD) from water include adsorption[11], chemical-biological coagulation[12], electrochemical treatment[13], ozone-biological oxidation[14], biological oxidation[15], and microelectrolysis[16]. Common methods for treating nitrogen, phosphorus, and heavy metal pollution include ion exchange[17], biological method[18], chemical precipitation[19], adsorption[20], and crystallization[21]. The coagulant method for removing COD directly adds chemical coagulants to wastewater and uses physical effects such as bridge building and compression of double-conductor electronic coatings and chemical nets to transform chemical colloids and other chemical suspensions in water into chemical flocs[22]. Although photocatalytic wastewater oxidation technology has been widely used in the field of wastewater treatment, its processing cost is high and is easily affected in practical applications[23]. Although microbial treatment for eliminating water pollutants is inexpensive, it is challenging to manage the circumstances in which microorganisms grow and are easily influenced by outside variables, leading to unpredictable effluent water quality[24]. The ion exchange method is less affected by pH and temperature, and the removal rate can generally reach more than 90%. However, a large amount of high-salt liquid wastewater is produced, and the effluent is a highly corrosive liquid. The subsequent wastewater treatment process will take longer time[25]. Adsorption has many advantages, such as wide raw material sources, strong economic feasibility, significant pollution removal effect, and no secondary pollution. Many materials have been applied in the practice of using adsorption to treat water pollution[26-27]. Therefore, the development of green-efficient, low-cost, and multi-pollutant removal artificial modified materials through adsorption is an important research direction[28-29].

Natural materials with low pollution and effective adsorption properties include clay minerals, which are affordable and abundantly available[30]. One of the hottest issues in the field of adsorption study right now is selective research on clay minerals and modified clay minerals[31-32]. From a crystal configuration perspective, montmorillonite has an upper and lower layer of Si-O tetrahedron and a layer of Al-O octahedron sandwiched between the two layers of Si-O tetrahedron. This is the main structural unit of montmorillonite and belongs to the 2:1 type clay mineral[33]. The upper and lower layers of Si-O tetrahedron and the layer of Al-O octahedron in the middle are negatively charged, and they can be modified by cation exchange, intercalation, and surface modification to improve the adsorption performance of clay minerals[34]. Kumararaja et al.[35] used Keggin ions to synthesize aluminum column-supported montmorillonite Al-OH-Mt. The results showed that the maximum monolayer adsorption of Al-OH-Mt for Zn^{2+}, Cu^{2+} and Ni^{2+} reached 61.4 mg/g, 32.3 mg/g and 50.3 mg/g. Ghorbanzadeh et al.[36] studied the removal of arsenate and arsenite from rivers by adsorption of montmorillonite, and the results showed that the adsorption of arsenate by montmorillonite was 99.5% and 68.2% for arsenite.

Lanthanum is a metallic rare earth element with active chemical properties, which is mostly used in the preparation of various chemical materials. In addition, lanthanum is employed in agricultural photoconversion films and as a catalyst in the synthesis of numerous organic compounds. Due to its active nature, lanthanum can be used to modify materials for water pollution control[37-38]. Wang et al.[39] developed and synthesized a low-cost P-type zeolite by a modified hydrothermal method using thermal power plant solid waste fly ash as the main raw material. The results revealed that at a modified lanthanum ion concentration of 0.5%, a pH value of 4-8, and a dosing rate of 10 g/L, the modified synthetic zeolite was able to remove ammonia nitrogen and phosphorus at rates of 90% and 95%, respectively Activated carbon fiber loaded with lanthanum-doped titanium dioxide photocatalyst (La-TiO_2 /ACF) was studied by Xie et al.[40] for its ability to decolorize, remove COD, and enhance the biochemistry of wastewater used in printing and dyeing. According to the findings, after 50 minutes of treatment, the decolorization rate could approach 90%, the COD removal rate could reach 69.2%, and the biochemical performance could be greatly enhanced.

As a kind of natural polymer organic material, starch shows electropositivity, and is widely present in nature, simple and easy to obtain, low price, is a good modified material. Ben-Hong[41] prepared a composite of starch with montmorillonite. Starch, lanthanum and montmorillonite, are widely available and inexpensive, and the materials are simple to prepare and operate, which can efficiently remove a variety of pollutants from water bodies. In this paper, lanthanum modified montmorillonite and starch and lanthanum modified montmorillonite were prepared to explore the effect and mechanism of different modified materials on the adsorption and removal of COD, nitrogen and phosphorus and heavy metals in water. It is expected to provide new fillers for artificial rapid infiltration system and provide new light rare earth composite materials for water purification of heavily polluted lakes and reservoirs.

2 Experiment

2.1 Materials

The main phase of montmorillonite was composed of calcium-based montmorillonite with a small amount of quartz impurities, and the chemical composition was mainly Si, O, Al, Ca, etc. Lanthanum chloride, lanthanum nitrate hexahydrate, acetic acid, test corn starch, sodium hydroxide, sodium chloride, potassium dichromate, potassium hydrogen phthalate and potassium persulfate were purchased from Shanghai Aladdin Biochemical Technology Company. Concentrated sulfuric acid, concentrated nitric acid and concentrated hydrochloric acid were purchased from Shanghai Standard Technology Company. The above reagents, except montmorillonite, were all analytically pure. The test water was deionized water.

2.2 Adsorbents preparation

Weigh 20 g of montmorillonite in a 250 mL conical flask, then add 1 mol /L NaCl solution, put it into a shaker and shake for 12 h. After the material has finished shaking, centrifuge it at 4000 rpm for 15 minutes to remove the bottom precipitate. Then, transfer the material to a 250 ml beaker, wash it with a solution of 0.005 mol/L sodium chloride, and repeat the process two more times. The sodium-based montmorillonite solution was obtained. The resulting solution was filtered with deionized water and dried in a high-temperature drying oven at 65 °C for 24 h. The resulting particles were crushed with a universal crusher, and finally sodium-based montmorillonite (Na-Mont) was produced. 2.0 g of Na-Mont was mixed with 5% lanthanum chloride solution(w/v), the solution was stirred continuously at room temperature for 6 h. The resulting solution was extracted with deionized water, dried in a high temperature drying oven at 65 °C for 24 h after extraction, crushed and ground to produce Lanthanum modified montmorillonite ($LaCl_3$-Mont). Mix 2.0 g Na-Mont with 2% starch solution (w/v), stirring constantly for 6 hours at room temperature. Following the reaction, the precipitate was separated, filtered, and dried for 24 h at 65 °C. By crushing and grinding, starch-modified montmorillonite (St-Mont) was created. $LaCl_3$-Mont was reacted with 2% starch solution (w/v) and St-Mont with 5% lanthanum chloride solution (w/v) in a shaker for about 12 h. After the reaction time, the precipitates were separated by filtration, dried for 24 h, crushed and ground to obtain St-La-Mont and La-St-Mont. Weigh 10 g of Na-Mont and 6 g of lanthanum nitrate were dissolved in a 250 mL conical flask, shaken in a constant temperature water bath at 25°C for 8 h at 200 r/min, washed with deionized water and then filtered by extraction, then dried for 24 h, crushed and ground to produce La_6-Mont.

2.3 Methods of analysis

The phosphorus concentration in the solution was determined by ammonium molybdate spectrophotometry (GB11893-89). The concentration of TN was measured by alkaline potassium persulfate UV spectrophotometry, the concentration of COD was determined by using rapid dissipative luminescence photometry, and the concentration of chromium ions in the samples was measured by flame atomic spectrophotometer.

The formula for calculating the removal rate of pollutants by modified montmorillonite is shown in Equation (1).

$$\eta = \left(\frac{Co-Ce}{Co}\right) \quad (1)$$

η--Removal rate of pollutants; C_o--the initial concentration of pollutants in the solution before adsorption, mg/L; C_e--the concentration of pollutants in the solution after adsorption equilibrium, mg/L.

2.4 Adsorption experiment

Weighed 0.5 g of Na-Mont, $LaCl_3$-Mont, St-Mont, St-La-Mont and La-St-Mont in conical flasks and added 100 mL of 10 mg/L PO_4^{3-}contaminated solution, respectively, and shaken for 6 h at 30 ℃ in a water bath thermostat shaker at 200 r/min. Then weigh 1 g of Na-Mont, $LaCl_3$-Mont, St-Mont, St-La-Mont and La-St-Mont in 10 conical flasks, add 100 mL of 100 mg/L COD contamination solution and 100 mL of 2 mg/L TN contamination solution, shake at 30 ℃ for 6 h in a water bath thermostatic shaker at 200 r/min, after the reaction is completed, centrifuge and filter, remove the supernatant, and determine the concentrations of PO_4^{3-}, TN and COD in the supernatant. 40 mL of hexavalent chromium ion solution with a concentration of c0=100 mg/L and 5 g of La6-Mont mixed solution were adsorbed at 15° C, 25° C and 35 ℃, respectively, and the Cr^{6+} concentration in the solution was measured by sampling at 0 min, 15 min, 30 min, 45 min, 60 min, 75 min, 90 min, 105 min and 120 min, respectively.

3 Results and discussion

The adsorption amounts and phosphorus removal rates of Na-Mont, $LaCl_3$-Mont, St-Mont, St-La-Mont, and La-St-Mont for 10 mg/L PO_4^{3-} solution are shown in Figure 1 below.The phosphorus removal rates of St-La-Mont, La-St-Mont, $LaCl_3$-Mont, St-Mont, Na-Mont for total phosphorus removal rates were 93.66%, 91.58%, 87.41%, 4.16%, and 6.24%, respectively. This demonstrated that Na-Mont has little to no phosphorus removal effect, whereas the modified montmorillonite made with lanthanum and starch significantly increases this effect. This is due to the fact that starch is a natural macromolecule that presents electropositivity, which can improve the attraction to PO_4^{3-}, and the La^{3+} loaded on the montmorillonite also provides electrostatic attraction for the phosphorus removal by the modified montmorillonite.

The nitrogen removal rates of Na-Mont, St-Mont, $LaCl_3$-Mont, St-La-Mont, and La-St-Mont at 2 mg/L TN solution were 28.48%, 5.18%, 59.55%, 98.39%, and 64.73%, respectively, where the highest efficiency of nitrogen removal was achieved by St-La-Mont. The results demonstrated that the modification of montmorillonite with lanthanum chloride can significantly improve its ability to remove nitrogen, while the modification of montmorillonite with lanthanum and starch may be due to the ternary system's overall electronegativity decreasing, which has a better adsorption effect on nitrate ions and other ions in the polluted solution.

The removal rates of Na-Mont, St-Mont, $LaCl_3$-Mont, St-La-Mont, and La-St-Mont for 100 mg/L COD solution were 32.37%, 41.46%, 51.68%, 86.89%, and 77.8%, respectively. The effect of COD removal by Na-Mont, $LaCl_3$-Mont, St-Mont, St-La-Mont and La-St-Mont showed that montmorillonite modified by lanthanum chloride can effectively remove COD from solution. Moreover, the COD removal efficiency of montmorillonite modified only by starch and lanthanum alone did not improve very much, while the montmorillonite modified by both at the same time could effectively remove COD pollution from water bodies under certain conditions.

Among them, the removal rates of St-La-Mont for total phosphorus, total nitrogen and COD reached 93.66%, 98.39% and 86.89%, respectively, which can be effectively used to strengthen the artificial fast infiltration system; the removal rates of La-St-Mont and $LaCl_3$-Mont for total phosphorus, total nitrogen and COD were 93.66%, 64.73%, 77.8% and 91.58%, 59.55%, and 51.65%, respectively. These two light rare earth modified materials can be effectively used in the preparation of water purification materials for heavily polluted lake reservoirs for their efficient removal of pollutants in water bodies.

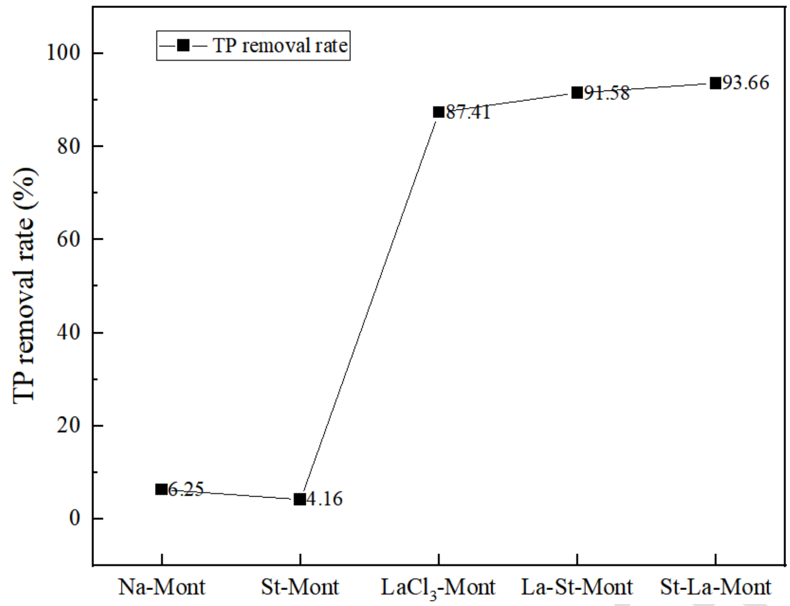


Figure 1 Removal efficiency of TP by five modified montmorillonites

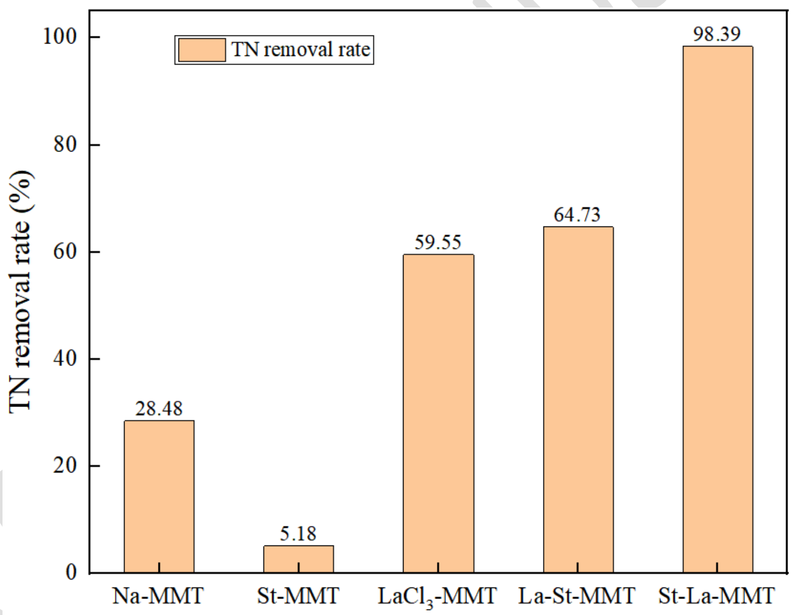


Figure 2 Removal efficiency of TN by five modified montmorillonites

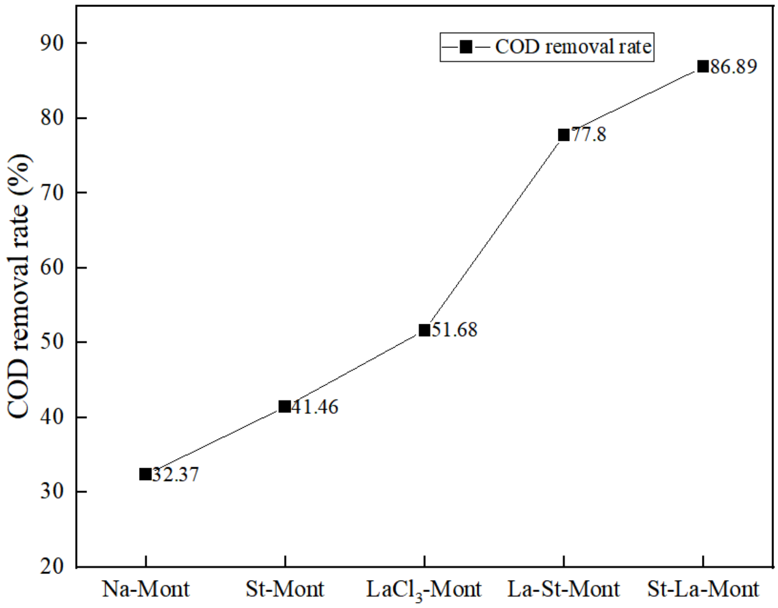


Figure 3 Removal efficiency of COD by five modified montmorillonites

By simulating the release of heavy metals in the substrate in the water column, lanthanum modified montmorillonite with light rare earth elements has a high removal efficiency of Cr^{6+} and has a good application prospect as a substrate treatment material. When the adsorption reached saturation, the adsorption rate at 35 ℃ was 82.5% slightly greater than 80.5% at 25 ℃and more than 76% at 15 ℃, which indicated that the higher temperature was favorable for the adsorption reaction in a certain temperature range. Table 1 showed the variation of Cr^{6+} concentration values at different temperatures and times. Figure 4 showed the time variation curves of Cr^{6+} adsorption by La_6-Mont at 15℃, 25℃, and 35℃. The overall curve indicated an upward trend, and the adsorption rate gradually increased as the response time increased. At the same time, it was obvious that the adsorption rate increased with the increase of temperature. This fully illustrated the fact that the reaction of Cr^{6+} adsorption by La_6-Mont was a heat absorption reaction. Additionally, the three curves might be seen as roughly parallel and having the same slope between 30 and 105 min.

Similarly, with the increase of the oscillation time, the slope of all three curved slowly decreased, which was due to the continuous adsorption process and the decreasing concentration of Cr^{6+}, resulting in smaller kinetics and lower reaction rates. When the reaction reached 120 min, the slopes of the curves were all close to 0 and the adsorption amount reached saturation, which also showed that the different temperatures did not affect the reaction proceeding time, but affected the maximum adsorption rate.

Table 1 Concentration of Cr^{6+} at different times and temperatures

Time（min）		0	15	30	45	60	75	90	105	120
Concentration of Cr^{6+}（mg/L）	15℃	20	16.1	15.2	13.1	11.6	9.8	7.6	5.1	4.8
	25℃	20	14.1	12.9	11.2	10	8.3	6.1	4.2	3.9
	35℃	20	13.0	11.7	10.5	9.2	7.3	5	3.7	3.5

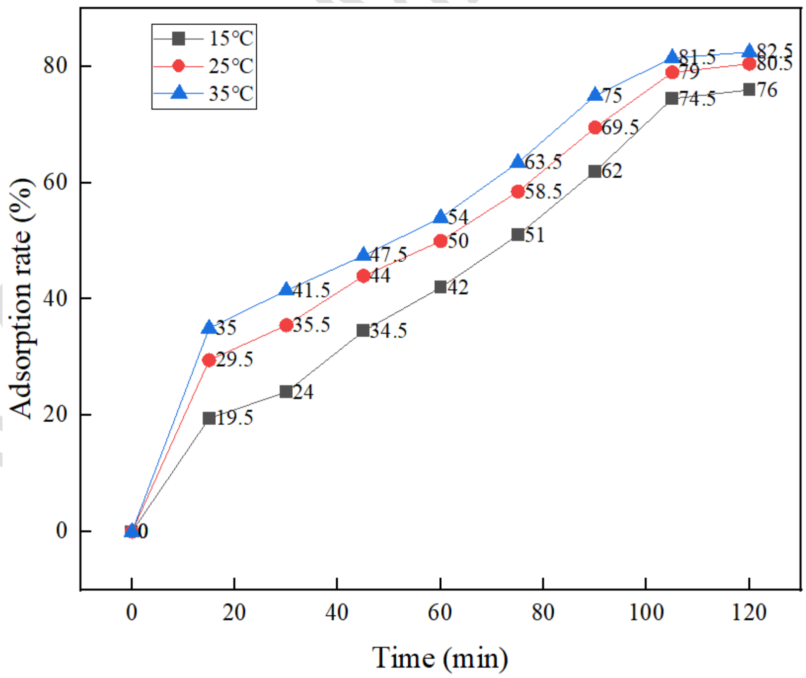


Figure 4 Removal rate of Cr^{6+} by La_6-Mont at different temperatures

St-La-Mont, La-St-Mont, $LaCl_3$-Mont and La_6-Mont, the modifiers of the four materials, starch, lanthanum and montmorillonite, are widely available and inexpensive, and the materials are simple to prepare and operate, which can efficiently remove a variety of pollutants from water bodies. The existing economic effect has reached 10 million, and when these new materials are prepared and put into use, the expected benefit can reach 20 million.

4 Conclusion

In the adsorption TP removal experiments, Na-Mont basically had no phosphorus removal effect, and the phosphorus removal effect of montmorillonite was effectively enhanced by starch and lanthanum modification. The best total phosphorus removal effect was achieved by $LaCl_3$-Mont with 93%, while the phosphorus removal rates of St-La-Mont and La-St-Mont also reached over 90%. The nitrogen removal rates of Na-Mont, St-Mont, $LaCl_3$-Mont, St-La-Mont and La-St-Mont for 2 mg/L TN solution were 28.48%, 5.18%, 59.55%, 98.39% and 64.73%, respectively. The removal rates of Na-Mont, St-Mont, $LaCl_3$-Mont, St-La-Mont, and La-St-Mont for 100 mg/L COD solution were 32.37%, 41.46%, 51.68%, 86.89%, and 77.8%, respectively. By exploring the effect of La_6-Mont adsorption for Cr^{6+} removal at different temperatures as well as reaction times, the results showed that the Cr^{6+} removal rates at the saturation of La_6-Mont adsorption were 76%, 80.5% and 82.5% at the reaction temperatures of 15 ℃, 25 ℃ and 35 ℃, respectively, and the experiments showed that the best adsorption efficiency of La6-Mont was achieved at 35 ℃.

By simulating polluted lake water bodies, the effect of various materials on the removal of pollutants from water bodies is investigated in this paper. It can be concluded that St-La-Mont can effectively remove 85% of COD, 50% of TN, and more than 70% of TP, which can be used to strengthen the artificial fast infiltration system. La-St-Mont and $LaCl_3$-Mont achieved a removal rate of 35% for COD, 50% for TN and more than 90% for TP. These two light rare earth modified materials can be effectively used in the preparation of water purification materials for heavily polluted lake reservoirs for their efficient removal of pollutants in water bodies. Meanwhile, La_6-Mont can remove 82.5% of Cr^{6+} in water under certain conditions, which had a good application prospect as a substrate treatment material. This showed that lanthanum-modified montmorillonite has a high removal rate, which can offer a new approach to treating water pollution. It can also remove a variety of pollutants from water bodies. Future research is anticipated to offer a novel class of very effective adsorbents for bottom sediment treatment and water purification in highly contaminated lakes and reservoirs.

At the same time, the method of preparing adsorbent in the text is simple, easy to operate and inexpensive to produce. The prepared material is friendly to the environment and not easy to produce pollution. In future research, the mechanism of pollutant removal by the composite material can be further explored so that the preparation of the material can be optimized and it can be more widely used in different practical scenarios.

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

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