

Removal of Nitrate and Phosphate by Starch and

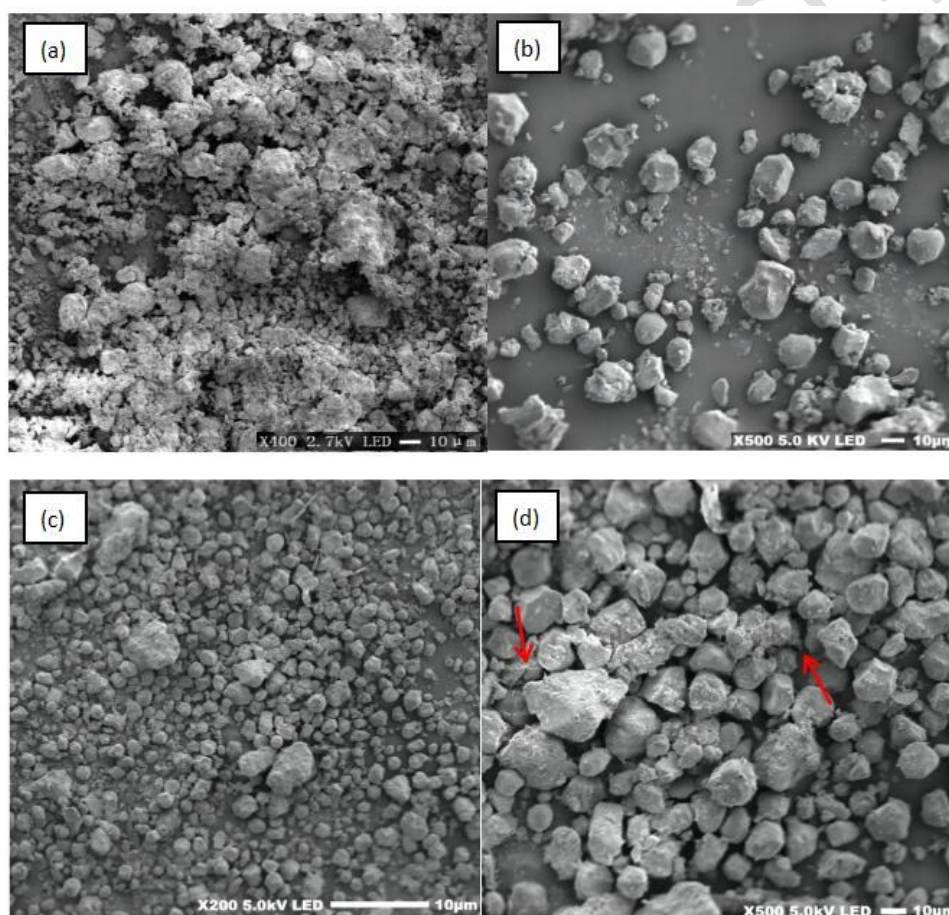
Lanthanum Modified Montmorillonite

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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

16 friendly adsorbent material for nitrogen and phosphorus removal, lanthanum modified
17 montmorillonite(La₄-Mt), starch modified montmorillonite(St₆-Mt) and starch and
18 lanthanum modified montmorillonite(St₆-La₄-Mt) were used in this paper to
19 investigate the removal effect and adsorption mechanism of the three modified
20 materials on nitrogen and phosphorus. The mechanism of modification and the
21 properties of the modified montmorillonite were characterised by zeta potential and
22 scanning electron microscopy (SEM) analysis. The test results show that: After the
23 introduction of starch and lanthanum, the adsorption of both nitrogen and phosphorus
24 by the modified montmorillonite was significantly enhanced. The mechanism of PO₄³⁻
25 removal by La₄-Mt and St₆-La₄-Mt, materials prepared from La-loaded
26 montmorillonite, is due to the binding of La³⁺ to OH⁻ in solution to produce La(OH)₃,
27 which in turn removes the oxygenate PO₄³⁻ and NO₃⁻ from solution by electrostatic
28 gravitation. The mechanism of removal of oxygenates by St-loaded montmorillonite
29 St₆-Mt and St₆-La₄-Mt is that St itself is an electropositive natural polymeric organic
30 substance, and by reducing the electronegativity of the system, St reduces the
31 electrostatic repulsion between the system and the oxygenates and improves the effect
32 of oxygenate removal, thus achieving the purpose of nitrogen removal and
33 phosphorus removal.

34

35 **Key words:** Lanthanum; Starch; Montmorillonite; Nitrogen and phosphorus removal;
36 Modification

37 **1 Introduction**

38 Due to the current social industry's and agriculture's rapid development, human
39 production and life have produced increasing amounts of nitrogen, phosphorus, and
40 other eutrophic substances^[1], which once introduced into the water environment can
41 easily result in the eutrophication of water bodies and harm to human health^[2].
42 Mitigating the prevalence of nitrogen and phosphorus pollution in the water
43 environment through technical means to protect the ecological environment as well as

44 human health has become one of the hot spots of current research concerns^[3-5].

45 Current methods for nitrogen and phosphorus removal from wastewater mainly
46 include biological methods^[6], chemical precipitation^[7], adsorption^[8] and
47 crystallization^[9], etc. Biological nitrogen and phosphorus removal is less costly,
48 produces less sludge, and has a wide range of phosphorus removal. However,
49 microbial growth requires high environmental conditions, and the process of nitrogen
50 and phosphorus removal is affected by a variety of factors, resulting in unstable
51 effluent quality, which requires deep treatment to meet the nitrogen and phosphorus
52 discharge standards^[10]. The chemical precipitation method is fast, simple and effective
53 in treating high nitrogen and phosphorus wastewater, but it is costly, susceptible to
54 environmental conditions such as pH, prone to secondary pollution and the different
55 phosphate precipitates produced can have an impact on subsequent recycling^[12]. The
56 crystallization method can effectively remove phosphorus from wastewater with high
57 recovery of pollutants, and the by-products formed, such as ammonium magnesium
58 phosphate, can be used as agricultural fertilizer, but it is influenced by various factors
59 in practice, such as the type and particle size of the crystalline species, the type of
60 reactor, and the mixing method^[13-15], so it is not widely used. The adsorption method
61 is a simple process, easy to highly efficient and low consumption, stable performance
62 of the adsorbent and easy to regenerate, and can also remove phosphorus in a wider
63 pH range and at lower levels, while recovering phosphate^[16-17]. Although the current
64 application of adsorption methods in nitrogen and phosphorus removal is more mature,
65 many adsorbents have a small adsorption capacity for nitrate ions in complex water
66 bodies in practical applications. Therefore, the development of an artificially modified
67 adsorbent material that can remove nitrogen and phosphorus simultaneously,
68 efficiently and at low cost remains an important research direction^[18].

69 As a natural clay mineral material, montmorillonite is widely distributed in
70 China, with large reserves and low mining costs, and has good structural stability and
71 high temperature resistance. Also montmorillonite, as a 2:1 type layered clay mineral,
72 has interlayer domains that provide sites for chemical reactions that improve its
73 adsorption efficiency, and the presence of H⁺ on its surface further enhances its

74 adsorption capacity^[19-20]. Chen et al.^[21] prepared hollow layered mesoporous spheres
75 of montmorillonite (MMTNS@CS-HMPHS) and showed that the material formed
76 mesoporous pore channels and increased its specific surface area, while the active
77 centres of MMT and chitosan on the material greatly improved its performance in
78 terms of adsorption and catalyst carriers. Liang Chen et al.^[22] prepared a
79 montmorillonite-biochar composite with a maximum adsorption capacity of 105.28
80 mg/g for PO_4^{3-} . Zou Y et al.^[23] prepared a composite modified material (Zr-CaMs)
81 from zirconium modified montmorillonite with a maximum phosphate adsorption
82 capacity of 22.37 mg/g. In summary, montmorillonite has the advantages of large
83 two-dimensional specific surface area, low cost, high chemical stability, low toxicity,
84 and good environmental compatibility.^[24] Therefore, montmorillonite is a good
85 loading material through modification can improve its adsorption of nitrogen and
86 phosphorus, and is an adsorbent material with research significance.

87 Lanthanum is widely available and less toxic, and lanthanum-based adsorbents
88 are a promising phosphate adsorbent^[25]. The use of light rare earth elements such as
89 lanthanum as a modifier is an important direction in the development of phosphorus
90 removal adsorbents. For example, Mu et al.^[26] showed that polymeric aluminium
91 chloride-lanthanum modified bentonite (PLMB) can efficiently adsorb phosphorus
92 from water, and its adsorption capacity can reach 57.629 mg/g. The lanthanum-loaded
93 zeolite chitosan composite adsorbent (La-MZ/CTS) was prepared and synthesized by
94 Zhang et al.^[27] It was found that the lanthanum loading resulted in a uniform
95 distribution of $\text{La}(\text{OH})_3$ on the surface of the material, exhibiting a large pore size and
96 specific surface area, and the adsorption capacity of the material for phosphate was
97 increased by up to 10 times compared with the original material, reaching $27.9 \text{ mg}\cdot\text{g}^{-1}$.
98 W Luo et al.^[28] used La^{3+} loaded montmorillonite to remove phosphate from water
99 with a material adsorption capacity of 0.39 mmol/g.

100 As a natural polymeric organic substance, starch is widely available in nature,
101 simple to obtain, inexpensive and naturally exhibits electropositive properties, making
102 it a good modifier. Both starch and lanthanum are excellent modifiers, but there are
103 few studies on the use of lanthanum and starch as modifiers for montmorillonite at the

104 same time. Therefore, this paper will prepare starch-modified, lanthanum-modified
105 and starch-lanthanum-modified montmorillonite to investigate the effect and
106 mechanism of the three modified materials on the adsorption and removal of nitrogen
107 and phosphorus, so as to provide new ideas and directions for the preparation of an
108 efficient, green and widely used adsorbent material for the removal of nitrogen and
109 phosphorus.

110 **2 Experiment**

111 **2.1 Materials**

112 Montmorillonite (>97% purity) from Shijiazhuang, Hebei Province, whose main
113 physical phase is calcium-based montmorillonite. Lanthanum nitrate
114 hexahydrate($[\text{La}(\text{NO}_3)_3] \cdot 6\text{H}_2\text{O}$), acetic acid, corn starch, sodium hydroxide, sodium
115 chloride, potassium dichromate, all purchased from Shanghai Aladdin Biochemical
116 Technology Company. Concentrated sulphuric acid and concentrated nitric acid, both
117 purchased from Shanghai Standard Technology Company. All the above reagents are
118 analytically pure except for montmorillonite. The test water was deionised water.

119 Electronic balance (Shanghai Shangping Instruments Company, FA1004), pH
120 meter (FE28-Standard), constant temperature incubator (HH-420), magnetic stirrer
121 (85-2A), UV spectrophotometer (721/722N) were purchased from Shanghai Essence
122 Instruments Technology Company. Benchtop low-speed centrifuge (Thermo Fisher
123 Scientific, TDZ5-WS.)

124 **2.2 Adsorbents preparation**

125 To prepare sodium-based montmorillonite (Na-Mont), 10 g of 97% high purity
126 montmorillonite [Montmorillonite (hereafter referred to as Mont)] was weighed into a
127 250 ml volumetric flask, added to a 1 mol/L NaCl solution, stirred in a magnetic
128 stirrer for 24 hours, and then centrifuged. Then separate the supernatant from the
129 coarse sediment at the bottom of the centrifuge tube, remove the montmorillonite

130 adhering to the inner wall of the centrifuge tube and place it in a 250 mL beaker. The
131 Na-based montmorillonite (Na-Mont) was obtained by washing the beaker with 0.005
132 mol/L NaCl solution and repeating the washing procedure three times, filtering and
133 drying in an electric blast oven at 65 °C for 24 h, and grinding to 200 mesh.

134 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
135 Na-Mt were weighed into a 250 ml volumetric flask, fixed with deionised water and
136 stirred on a magnetic stirrer for 8 hours. Remove the coarse residue at the bottom,
137 then centrifuge at 4000 r/min, extract and dry in an electric blast oven at 65 °C for 24
138 h. Lanthanum-modified montmorillonite (La₄-Mt) was obtained by grinding to 200
139 mesh.

140 Weigh 6 g of the experimental corn starch into a 250 mL volumetric flask, add
141 50 ml of 5% acetic acid solution and stir to completely dissolve the corn starch in the
142 acetic acid solution. Then add 10 g of the prepared Na-Mt to the volumetric flask, set
143 the volume to 250 mL with deionised water, stir for 8 h on a magnetic stirrer, remove
144 the coarse sediment at the bottom, load into a 50 mL centrifuge tube in batches,
145 centrifuge at 4000 r/min, extract and dry for 24 h in an electric blast oven at 65 °C,
146 grind to 200 mesh to produce St₆-Mt.

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

156 **2.3 Methods of analysis**

157 The solution phosphorus concentration was determined by ammonium
158 molybdate spectrophotometry (GB11893-89) with a test wavelength of 700 nm
159 (721/722N, Shanghai Essence). Measurement of nitrate concentration by
160 spectrophotometry.

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

$$163 \quad \eta = \left(\frac{C_0 - C_e}{C_0} \right) \quad (1)$$

$$164 \quad q_e = \frac{(C_0 - C_e) \times V}{W} \quad (2)$$

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

169 The surface morphology of the modified montmorillonite was observed by field
170 emission scanning electron microscopy (SEM, Oxford X-max 80). High sensitivity
171 Zeta potential and particle size analyzer (nano ZS) to characterize the Zeta potential
172 and analyze the charge on the surface of montmorillonite before and after
173 modification.

174 **2.4 Adsorption experiment**

175 10 g of St, La, Na-Mt, La₄-Mt, St₆-Mt and St₆-La₄-Mt were dissolved in 250 mL
176 of 10, 20 and 30 mg/L PO_4^{3-} contaminated solution, respectively, and shaken for 8 h at
177 30 °C in a water bath with a constant temperature of 200 r/min. After centrifugation
178 and filtration through a 45 μm filter head, the phosphorus concentration in the filtrate
179 was determined. Three sets of parallel samples were set up and the average values
180 were taken.

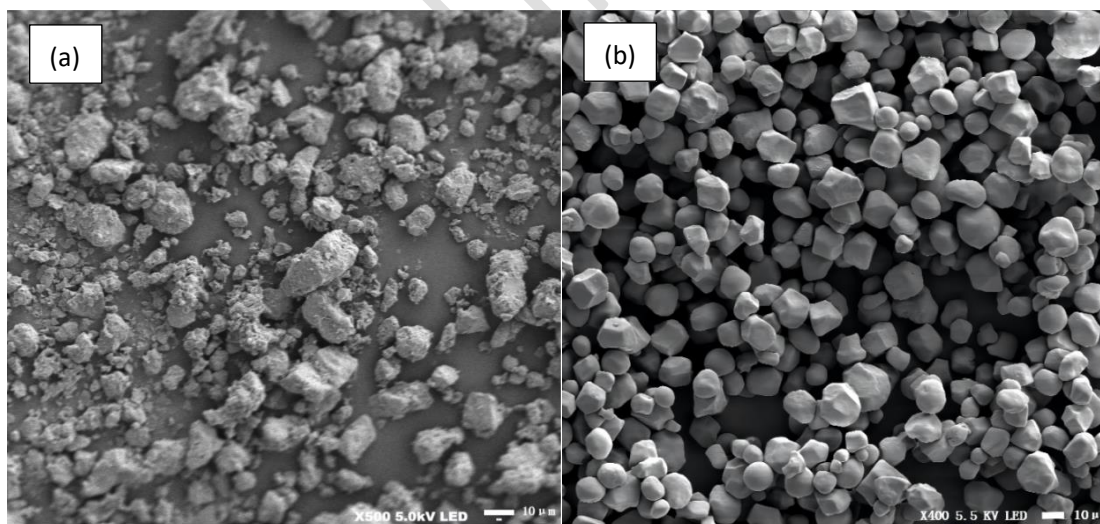
181 10 g of St, La, Na-Mt, La₄-Mt, St₆-Mt and St₆-La₄-Mt were dissolved in 250 mL
182 of 2.5, 5 and 10 mg/L NO_3^- contaminated solution, respectively, and shaken for 8 h at

183 200 r/min in a water bath thermostat at 30 °C. The filtrate was centrifuged and filtered
184 through a 45 µm filter head to determine the NO₃⁻ concentration. Three sets of parallel
185 samples were set up and the average values were taken.

186 3 Results and discussion

187 3.1 SEM analyses

188 Investigation of the changes in the surface structure of samples by scanning
189 electron microscopy (SEM) to investigate the mechanism of adsorption of PO₄³⁻ and
190 NO₃⁻ by the ternary system of lanthanum, starch and montmorillonite. It can be seen
191 that the surface structure of Na-Mt is more sparse after sodium purification, with an
192 overall more uniform distribution of size particles and the appearance of some small
193 lamellar structures. As can be seen from Figure 1(b), corn starch has a regular size and
194 shape, with smooth surfaces and inter-clustered spherical, square and polygonal
195 structures.



196
197 (a) Na-Mt; (b) St

198 **Figure 1 SEM characterisation of Na-Mt and St**

199 The SEM characterisation of La₄-Mt in Figure 2(a) shows that the surface
200 structure of montmorillonite has changed considerably after the La modification, and
201 La is mainly loaded on the outer surface of Na-Mt by longitudinal or transverse
202 synaptic-like structures, which makes the surface of La₄-Mt present a rough and loose

203 pore structure. As displayed in Figure 2(b), After modification by starch, the small
204 particle structure on the surface of Na-Mt is reduced, the surface becomes smoother
205 and flatter, and St occupies an increasingly prominent position in the overall structure,
206 so that the St particles attached to St₆-Mt have the same opportunity to react with the
207 external environment, forming small grooves and gap-like areas, and small amounts
208 of St are more densely distributed. As shown in Figure 2(c), the granules attached to
209 the surface of St₆-La₄-Mt after successive modification with lanthanum and starch are
210 more dense and the pore structure is more uniform, increasing the contact area of the
211 material with phosphorus and nitrogen containing wastewater. Compared to the
212 surface structure of La₄-Mt, the starch modified particles are smoother and more
213 shapely, and there are almost no obvious gaps in the same layer. Figure 2(d) shows a
214 plot of St₆-La₄-Mt at 500x, where the arrows point to the appearance of a La-loaded
215 synaptic structure on the lower surface of the St-encapsulated outer layer, suggesting a
216 possible 'encapsulation effect' during the St modification process, whereby starch
217 adheres to the outer surface of the lanthanum-modified particles. A comparison of the
218 SEM characterisation of the samples revealed that the surface pore structure of
219 unmodified Na-Mt is less and the removal rate of nitrogen and phosphorus is lower,
220 while the surface pores of all three materials modified by lanthanum and starch have
221 increased and the surface attached particulate matter is more dense, which enhances
222 the absorption and removal efficiency of the original materials for nitrogen and
223 phosphorus.

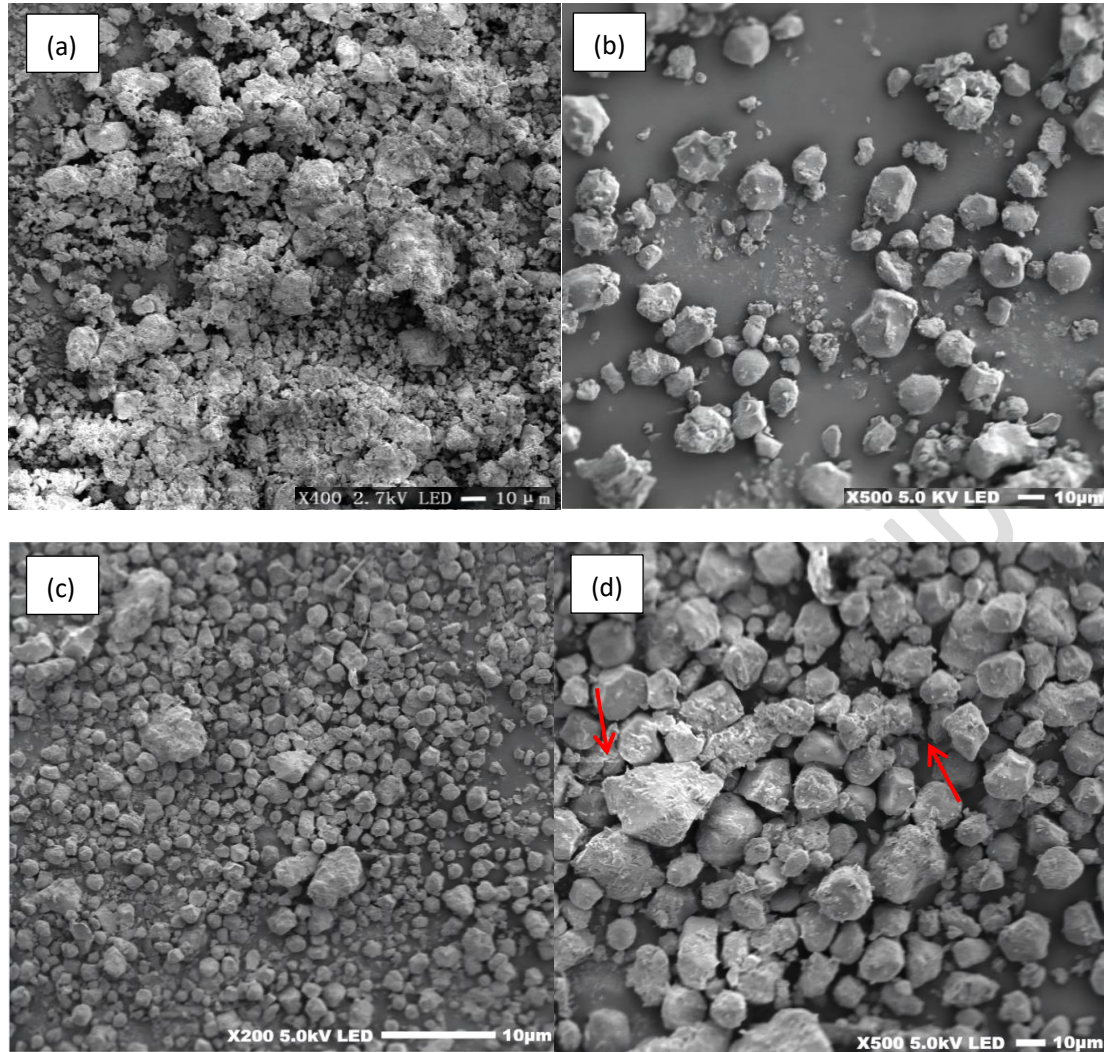
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(a) La₄-Mt; (b) St₆-Mt;

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(c) 、 (d) SEM characterization of St₆-La₄-Mt at different resolutions

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Figure 2 SEM characterisation of montmorillonite modified with different substances

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3.2 Zeta potential characterisation

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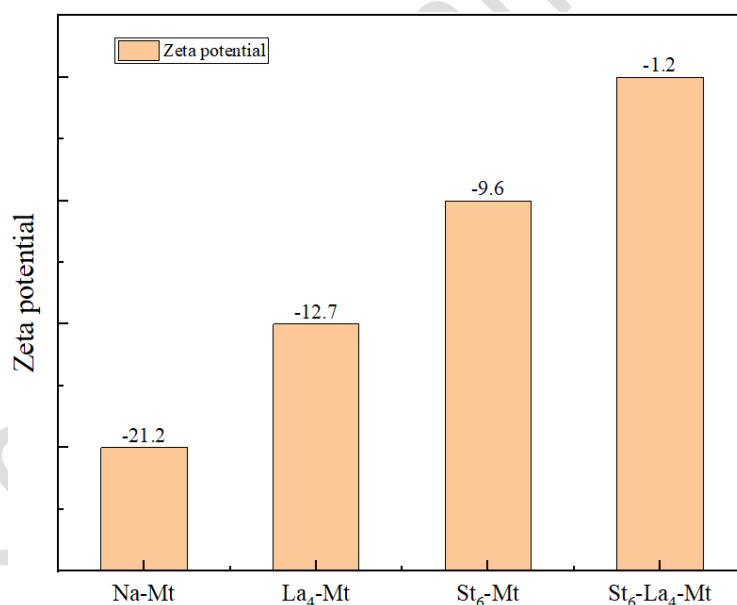
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To determine the changes in the overall electrical properties of starch, lanthanum and the composite modified montmorillonite before and after the Na-Mt modification process, the zeta potentials of samples were characterised respectively. The positive 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^[29]. 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

242 -21.2 mV, -12.72 mV, -9.63 mV and -1.2 mV, respectively. In terms of zeta potential
243 values, unmodified montmorillonite has the highest electronegativity, and
244 montmorillonite modified with starch, lanthanum and starch and lanthanum together
245 shows a decrease in electronegativity, and montmorillonite modified with starch and
246 lanthanum together has the lowest electronegativity. It can be concluded that both
247 starch and lanthanum can reduce the electronegativity of natural montmorillonite, and
248 the joint modification of starch and lanthanum is more effective in reducing the
249 electronegativity. The original montmorillonite basically does not have the ability to
250 remove oxygenate by adsorption due to the coulombic repulsion between ions, while
251 the electronegativity of montmorillonite modified by starch and lanthanum and
252 modified by starch and lanthanum together are reduced, so the coulombic repulsion
253 between the two is reduced when adsorbing oxygenate, thus achieving the purpose of
254 removing PO_4^{3-} and NO_3^- oxygenate.



255
256 **Figure 3 Zeta potentials of adsorbents**

257 **3.3 Adsorption of contaminants on the adsorbents**

258 **3.3.1 Adsorption of PO_4^{3-}**

259 As illustrated in Table1, the starch-, lanthanum- and co-modified

260 montmorillonite all showed a significant improvement in the removal of PO_4^{3-} from
261 the water. Among the three modified materials, the adsorption of PO_4^{3-} by
262 lanthanum-modified montmorillonite increased with increasing PO_4^{3-} solution
263 concentration, and the adsorption of starch-modified and starch-lanthanum-modified
264 montmorillonite was highest at 20 mg/L PO_4^{3-} solution concentration.

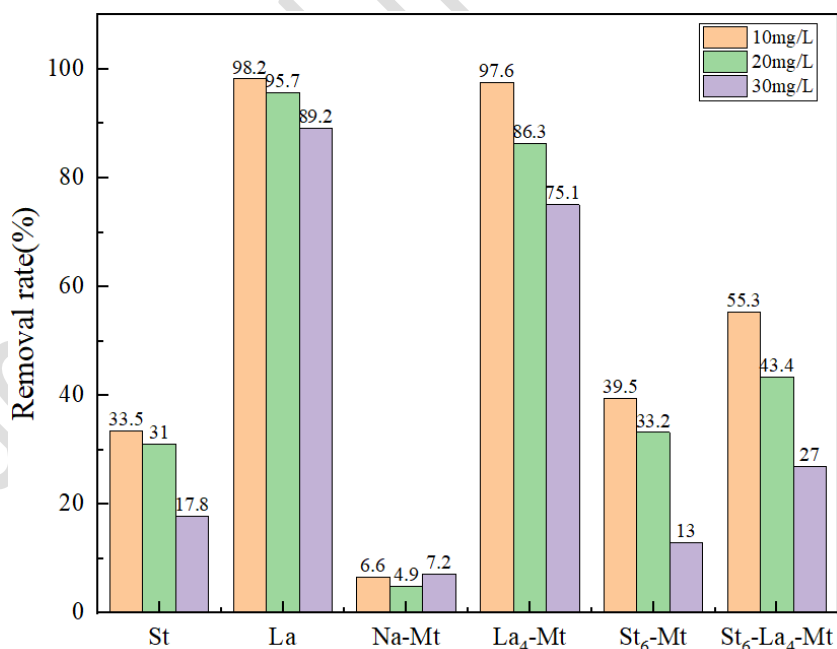
265 As can be seen from Figure 4, the adsorption rates of Na-Mt on PO_4^{3-} at three
266 concentration gradients of 10, 20 and 30 mg/L were 6.6%, 4.9% and 7.2%,
267 respectively, indicating that Na-Mt basically did not have the ability to adsorb PO_4^{3-} ,
268 which is also confirmed by the zeta potential, as Na-Mt exhibits high negativity and
269 the Coulomb repulsion between it and PO_4^{3-} , resulting in its poor adsorption capacity.

270 In contrast, the modified materials both reduced the negative electrical properties and
271 the Coulomb repulsion, so that the adsorption capacity of both lanthanum and starch
272 modified materials was increased. At the same time, it can be seen from the figure that
273 the adsorption and removal efficiency of lanthanum on PO_4^{3-} is good. Na-Mt modified
274 by lanthanum alone has significantly improved the adsorption of PO_4^{3-} by La₄-Mt, and
275 is basically the same as the adsorption efficiency of La, which is the highest
276 adsorption efficiency among the three modified materials, indicating that La possesses
277 a better affinity for PO_4^{3-} . A study by Jin Suwan et al.^[30] pointed out that phosphorus
278 removal by adsorption of loaded LaOH is mainly achieved by electrostatic interaction,
279 ion exchange and Lewis acid-base interaction. Some studies have also indicated that
280 La produces $\text{La}(\text{OH})_3$ in solution, which in turn produces LaPO_4 precipitate, both of
281 which have a certain adsorption effect on PO_4^{3-} . However, Lu Yan et al.^[31]
282 investigated the reaction between La_2O_3 and potassium dihydrogen phosphate in
283 aqueous solution by IR spectroscopy and XRD spectroscopy, and concluded that the
284 reaction product was still $\text{La}(\text{OH})_3$ and no LaPO_4 was produced, arguing that the
285 adsorption of La^{3+} on PO_4^{3-} was a chemical reaction to produce $\text{La}(\text{OH})_3$, and
286 $\text{La}(\text{OH})_3$ removed PO_4^{3-} by electrostatic adsorption. The reduction in the
287 electronegativity of La₄-Mt, as characterised by its zeta potential, also confirms that
288 the removal of phosphorus by adsorption of La₄-Mt is partly due to the reduced
289 electrostatic repulsion between the two, which makes it easier for adsorption and thus

290 removal of phosphorus to occur. Starch is a natural polymeric organic substance
 291 which is inherently electropositive. St₆-Mt modified with St alone reduces the
 292 electronegativity of the original montmorillonite and enhances the removal of PO₄³⁻
 293 but not as effectively as the lanthanum modification. The adsorption of PO₄³⁻ on
 294 montmorillonite St₆-La₄-Mt after modification with La is higher than that of St₆-Mt
 295 but lower than that of La₄-Mt, indicating that the "wrapping effect" during the St
 296 modification process has a limiting effect on the adsorption of PO₄³⁻ on La₄-Mt
 297 surface particles.

Adsorption of PO ₄ ³⁻ (mg/g)						
PO ₄ ³⁻ solution concentration	St	La	Na-Mt	La ₄ -Mt	St ₆ -Mt	St ₆ -La ₄ -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

298 **Table 1 Adsorption of phosphate by various adsorbents.**
 299



300 **Figure 4 Phosphorus removal by various adsorbents.**
 301 **at different PO₄³⁻ concentrations**
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 303

304 **3.3.2 Adsorption of NO₃⁻**

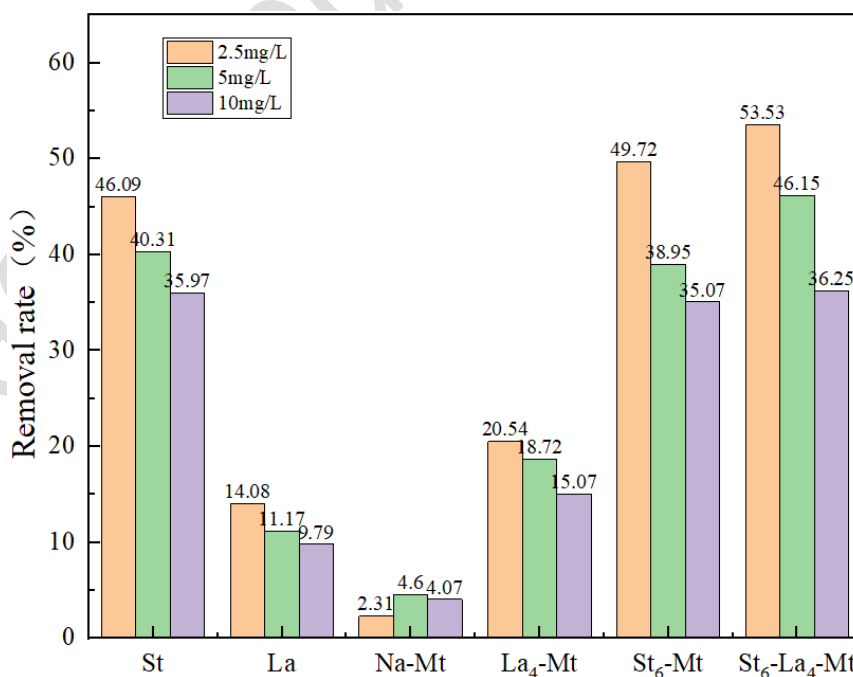
305 The results of denitrification of adsorbents at 2.5 mg/L, 5 mg/L and 10 mg/L
306 NO₃⁻ solution concentrations were obtained after the tests. As can be seen from Table
307 2, lanthanum, starch and montmorillonite were less effective in the adsorption of NO₃⁻.
308 The removal of phosphate can rely on electrostatic adsorption between systems and
309 complexation by ligand exchange, but most studies have shown that the removal of
310 NO₃⁻ relies on redox reactions. For example, Su Kai et al.^[32] found that structural
311 ferrous iron on the surface of modified montmorillonite removes NO₃⁻ from water by
312 a redox reaction with nitrate. In the system studied in this paper, only lanthanum has
313 the ability to redox, and Na is slightly more metallic than La, La does not have the
314 ability to replace Na⁺ from the Na⁺-NO₃⁻ system, so there are no conditions for redox
315 reactions, so the adsorption process of NO₃⁻ by the materials prepared in this paper
316 mainly relies on the electrostatic gravitational force provided by La³⁺ and St for the
317 system.

318 As shown in Figure 5, Na-Mt basically does not have the ability to adsorb NO₃⁻,
319 but the denitrification of NO₃⁻ solution concentrations of 2.5 mg/L, 5 mg/L and 10
320 mg/L is enhanced by starch, lanthanum and the montmorillonite modified by both
321 together. As can be seen from the figure, the removal of NO₃⁻ by the
322 lanthanum-modified montmorillonite La₄-Mt is better than the removal of NO₃⁻ by La.
323 From the above analysis, it can be seen that the adsorption process of NO₃⁻ by the
324 modified materials in this paper mainly relies on the electrostatic gravitational force
325 provided by La³⁺ and St for the system, while La is weaker in metallicity than Na.
326 During the adsorption process of NO₃⁻ by La₄-Mt, Na⁺ will inhibit the La³⁺ attached to
327 the surface of montmorillonite from binding to OH⁻ in solution, thus weakening the
328 electrostatic adsorption effect, resulting in the denitrification effect of La₄-Mt being
329 inferior to the other two modified materials. Starch-modified montmorillonite St₆-Mt
330 was also more effective than St in removing NO₃⁻ and the removal of NO₃⁻ by St₆-Mt
331 was significantly better than that by La₄-Mt. From the SEM characterisation results,
332 the modified St was more uniformly distributed on the surface of montmorillonite and

333 some of the surface particles of St₆-Mt aggregated and formed pores, which provided
 334 reaction sites for the adsorption and removal of NO₃⁻. The zeta potential also indicated
 335 that the electronegativity of St₆-Mt was reduced, thus reducing the Coulomb repulsion
 336 with NO₃⁻ and enhancing the removal of NO₃⁻. Among the modified materials,
 337 St₆-La₄-Mt has the best effect on NO₃⁻ removal. The SEM characterisation shows that
 338 St₆-La₄-Mt has the most homogeneous and dense pore surface, providing a large
 339 specific surface area for NO₃⁻ adsorption, and the "wrapping effect" of St inhibits the
 340 negative effect of La on NO₃⁻ adsorption, thus making St₆-La₄-Mt the best for NO₃⁻
 341 adsorption

Adsorption of NO ₃ ⁻ (mg/g)						
NO ₃ ⁻ solution concentration	St	La	Na-Mt	La ₄ -Mt	St ₆ -Mt	St ₆ -La ₄ -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

342 **Table 2 Adsorption of St, La, Na-Mt, La₄-Mt, St₆-Mt and St₆-La₄-Mt on NO₃⁻**



344
345 **Figure 5 Nitrogen removal rates for various adsorbents at different NO₃⁻ concentrations**

346 **4 Conclusion**

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

356 La₄-Mt and St₆-La₄-Mt is due to the fact that La³⁺ binds to OH⁻ in solution thus
357 generating La(OH)₃, which can be electrostatically attracted to PO₄³⁻ in solution.
358 There is also an exchange of ligands between O-H and PO₄³⁻ during the adsorption
359 process. The adsorption of NO₃⁻ occurs electrostatically due to the ability of La³⁺ to
360 bind OH⁻ in water to form La(OH)₃. Meanwhile, the St modification has a certain
361 "wrapping effect", i.e. the starch is uniformly wrapped around the surface of the
362 modified material. St is loaded on the surface of St₆-Mt and St₆-La₄-Mt and reacts
363 directly with PO₄³⁻ and NO₃⁻, but can also enter the interior of the montmorillonite
364 and reduce its layer spacing, so that in the removal of NO₃⁻ by St₆-La₄-Mt, the St
365 wrapped around the exterior of the material can reduce the negative effect of the
366 interaction between La³⁺ and Na⁺ on electrostatic gravity.

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

372 The starch, lanthanum and montmorillonite used in this paper are all substances
373 that exist widely in nature, and are inexpensive and environmentally friendly. This
374 paper combines these three elements to prepare a new adsorbent to improve the

375 adsorption and removal rate of nitrogen and phosphorus in water by montmorillonite,
376 and discusses the mechanism of nitrogen and phosphorus removal of adsorbent, which
377 provides a new idea for the preparation of adsorbent for nitrogen and phosphorus
378 removal in water, and expects to find a better ratio to achieve efficient nitrogen and
379 phosphorus removal in future research.

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381

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386

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