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1 **Secondary particle size determining sedimentation and**
2 **adsorption kinetics of titanate-based materials for ammonia**
3 **nitrogen and methylene blue removal**

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13 **Abstract**

14 The effect of the main size distribution of particles on the adsorption process for
15 adsorbent materials has been well-recognized; however, the impact of secondary
16 particles size (agglomerated, aggregated or hydrated ones) on adsorbent properties and
17 performance was rarely reported so far. In this study, a series of sodium titanates (STs)
18 and peroxide modified sodium titanates (PSTs) with different primary particle sizes,
19 and secondary sizes are synthesized by controlling synthesis conditions and

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20 subsequently applied to batch adsorption experiment. By employing scanning electron
21 microscopes and Laser particle size analyzers, the particle size of STs and PSTs are
22 found to be closely correlated with synthesis conditions. The surface morphology and
23 specific surface area of titanates are size-dependent, while the components of all the
24 samples maintained constant. The sedimentation experiment and CFD simulation
25 demonstrated that particles with larger secondary sizes tended to settle more quickly
26 than those with a bigger sizes. PSTs or STs particles with smaller secondary sizes could
27 reach equilibrium more rapidly than those with the bigger size. The fitting results from
28 Elovich and Weber-Morris models demonstrated that the particles size affect kinetics
29 mainly through the liquid film diffusion process within the initial stages.

30 **Keywords:** Titanate; Secondary size; Sedimentation; Adsorption; Water treatment

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44 **1. Introduction**

45 Recently, there has been considerable concerns about emerging threats from the
46 total nitrogen (TN) and chemical oxygen demand (COD) in water and other ecosystems
47 [1, 2]. The removal of ammonia nitrogen (NH_4^+) or methylene blue (MB) from
48 wastewater has drawn much attention in water purification due to their great
49 contribution to TN or COD pollution, respectively [3, 4]. Adsorption, one of the
50 practical and popular physicochemical techniques used in water treatment, has been
51 frequently employed for removing NH_4^+ and MB because of its high efficiency, cost-
52 effective and easy operation [5, 6]. Numerous studies have been carried out to
53 understand the adsorption process [7]. It has been widely demonstrated that solution
54 pH, environment temperature or contact time, and the properties of an adsorbent such
55 as surface charge, functional groups, or pore structure can significantly impact the
56 adsorption performance[8-12]. However, the particle size effect on the adsorbent
57 properties and adsorption process is less still unclear, even though most adsorbent
58 materials for NH_4^+ or MB are powders or particles in nature [13, 14]. It has been shown
59 that many fundamental properties of powder materials like mechanical and electrical
60 performance are size-dependent when the diameter of particles are nanoscale [15].
61 Indeed, particle size change could impact the movement of particles in solution
62 according to the Brownian motion. In addition, the particle size of materials could also

63 affect the value of surface free energy and then might have effects on the adsorption
64 interaction [16].

65 It has been found that the adsorption of MB onto diatomite is size-dependent when
66 the size scale is larger than 250 μm , and the maximum uptake capacity decreases with
67 the reduction of size. The same phenomenon was found in the adsorption of bisphenol
68 A onto montmorillonite [16, 17]. However, the particle size value discussed in most
69 reports was determined directly from SEM image or sieve action, which could not show
70 the actual scale of particles in solution because of aggregation [18]. The size of solid
71 materials in an aqueous environment could be described through two different
72 approaches: the primary size for individual particles and the secondary size for
73 agglomerated, aggregated or hydrated particles [19]. Therefore, the secondary size
74 value is closer to the actual conditions and appropriate for the size-dependent discussion.

75 Titanate, one of the common inorganic ion-exchange adsorbents or photocatalysts
76 [20, 21], was chosen as the main adsorbent for size dependence experiment according
77 to the following two merits: 1) amorphous sodium titanate (ST) and peroxide modified
78 sodium titanate (PST) particles can be facily synthesized through only mild
79 hydrolysis method. The secondary particle size can be easily controlled for ST and PST
80 by changing synthesis conditions such as the ratio and concentration of reagents. 2)
81 Titanate based materials exhibit excellent adsorption efficiency for cationic
82 contaminants due to their ion-exchange ability demonstrated by literature [22-25].

83 In this study, NH_4^+ and MB were chosen as the targeted contaminants not only
84 because of their contribution to TN and COD but also due to their large difference in

85 molecular weight and size, which might help uncover the relation between particle size
86 dependence and adsorbate molecular properties. Several challenges in secondary
87 particle size-dependent sedimentation and adsorption kinetics of titanate-based
88 materials for ammonia nitrogen and methylene blue removal have been systematically
89 studied: 1) a series of titanates named sodium titanates (STs) and peroxide modified
90 sodium titanates (PSTs) with different particle sizes were facilely synthesized by
91 changing synthesis conditions. 2) The effect of titanates particle secondary size on
92 adsorbent properties and adsorption performance in removal of NH_4^+ or MB were
93 conducted and discussed. 3) The potential mechanisms of the effect of particle size were
94 also revealed.

95 **2. Experimental procedures**

96 **2.1. Materials**

97 TIPT (titanium isopropoxide, $\text{Ti}(\text{OC}_3\text{H}_7)_4$), H_2O_2 (hydrogen peroxide, 30 wt%),
98 NaOH (sodium hydroxide), HCl (hydrochloric acid), anhydrous ethanol(99.7%), HDA
99 (hexadecylamine, 90 wt%) and isopropanol were of analytical reagent grades and used
100 without any further purification. The simulated wastewater used in this study were
101 obtained by dissolving ammonium chloride (NH_4Cl , GR) or methylene blue (MB, BS,
102 Fig. S1) (both from Sinopharm Chemical Reagent Co. Ltd, China) into deionized water.
103 The deionized water used for all the experiments was prepared by an EPED-40TF Super
104 pure Water System, China.

105 **2.2. Synthesis of titanate samples**

106 A series of sodium titanates (STs) with different particle sizes were prepared based
107 on our previous study [22]. The particle size of STs powders was adjusted by controlling
108 the hydrolysis rate of TIPT, where the volume of H₂O was changed according to the
109 molar ratio of TIPT: H₂O (1:1, 1:10, 1:20). HDA was served as a structure-directing
110 agent [26]. In a typical synthesis procedure, 0.8 g of NaOH and 2 g of HDA were
111 dissolved in a mixed solution of 200 mL ethanol and a certain amount of H₂O (0.61,
112 6.10 and 12.2 mL) with agitation at ambient temperature. 10 mL of TIPT was added
113 dropwise into the above solution under stirring. After 24 h, the white suspension was
114 recovered by centrifugation. The solid sample was washed with ethanol five times and
115 dried at 60 °C for 12 h [27]. The as-prepared white samples were labelled as ST (1:1),
116 ST(1:10) and ST(1:20) according to the TIPT: H₂O molar ratio. All the samples were
117 further purified by the sieve with 200 mesh.

118 A series of peroxide modified sodium titanate (PSTs) with different particle sizes
119 were synthesized as follows: a mixture of TIPT (10 mL) and isopropanol with the
120 volume ratio of 5:2 was added into 200 mL NaOH solution (0.1 mol·L⁻¹) with magnetic
121 stirring at 60 °C [28]. Afterwards, an appropriate amount of H₂O₂ (5 mL, 10 mL and 20
122 mL respectively) was dropwise added into the white suspension in 1 h, accompanied
123 by stirring. The solution gradually became transparent and bright yellow, and then the
124 yellow suspension was stirred for another 30 min at ambient temperature. The yellow
125 solid was filtered out and subsequently washed with deionized water until the filtrate
126 pH reached approximately 7.0, then dried at 60 °C for 12 h. The as-prepared PST
127 samples were denoted as PST-5, PST-10 and PST-20 according to the volume of H₂O₂

128 used in the synthesis process, respectively. All the samples were sieved by the sieve
129 with 200 mesh.

130 **2.3. Analysis and characterization methods**

131 The morphology of samples was investigated by scanning electron microscopy
132 (SEM, MAIA3 LMH, US). The imaging and elemental mapping were performed using
133 acceleration voltages of 15 kV. The element's contents of powder samples were
134 measured by X-ray Fluorescence (XRF, Bruker S8 Tiger, Germany) without any
135 pretreatment. The sample's secondary size in solution was determined by a laser particle
136 size analyzer (LS-909, China). The actual density of samples was tested by a Gas
137 Displacement Pycnometer (AccuPyc II 1340, US). The surface functional groups of
138 adsorbents were identified by a Fourier transform infrared spectrometer (FTIR, Bruker,
139 Germany) with the KBr pellet method at the wavenumber ranging from 400 to 4000
140 cm^{-1} . The Brunauer-Emmett-Teller specific surface area (S_{BET}) and pore structure
141 characteristics of samples were determined by the Builder SSA-4300 (Beijing, China)
142 at 77 K using the Barrett-Joyner-Halenda (BJH) method. The zeta potentials of the
143 samples were measured with Brookhaven 90plus Zeta, samples of which (1.0 mg) were
144 added into 10 ml NaCl solution ($10^{-3} \text{ mol}\cdot\text{L}^{-1}$) at different pH values (adjusted by 0.5
145 $\text{mol}\cdot\text{L}^{-1}$ HCl and NaOH solution).

146 The control experiment was conducted to evaluate the property of as-prepared
147 materials in solution as follows: 0.5 g of powders were added into a measuring cylinder
148 with 25 mL deionized water and dispersed under ultrasound sonication for 30 min.

149 Afterwards, the cylinder with PSTs or STs solution was put on the surface of a flat desk,
150 respectively. The photos were taken at different time intervals.

151 **2.4. Numerical simulations**

152 In the present study, Computational Fluid Dynamics (CFD) was also conducted to
153 reveal the relationship between settlement property and particles size. Considering the
154 symmetry of the test tube, a 2D axisymmetric domain with a height of 200 mm and a
155 width of 20 mm was employed. Structured grids were firstly generated for the
156 computational domain through software ICEM. Then, based on the finite volume
157 method, numerical simulation was carried out using the software ANSYS-Fluent to
158 analyze unsteady flow behavior. The Eulerian multiphase model was utilized to model
159 granular flow, allowing two phases to share a single pressure and momentum, and
160 continuity equations are solved for each phase [29]. The phase coupled SIMPLE
161 algorithm was used for the pressure-velocity coupling scheme. The velocities were
162 calculated coupled by phases in a segregated method, and the pressure correction
163 equations were established based on total continuity. According to ANSYS-Fluent
164 theory guide, the k - ε dispersed turbulence model was applicable when there is one
165 primary continuous phase, and the rest are dispersed dilute secondary phases. Thus, the
166 k - ε dispersed turbulence model with standard wall function was adopted to close the
167 turbulence terms in the simulation. Moreover, the gravitational acceleration was
168 specified as 9.81 m/s^2 to consider the gravity, and the Gidaspow method [30] was
169 implemented for the drag law. The thickness of the initial particle layer was set as 5 mm

170 with a volume fraction of 0.2. The models with different particle diameters and densities
171 were constructed to study their effect on the setting ability.

172 **2.5. Adsorption experiments**

173 Unless otherwise stated, NH_4^+ and MB removal experiments were performed at
174 25°C in a temperature-controlled shaker with a 200 rpm stirring rate. The initial
175 concentration of NH_4^+ and MB were 45 and $275\text{ mg}\cdot\text{L}^{-1}$, respectively. The suspensions
176 after adsorption were filtered in syringes equipped with $0.45\ \mu\text{m}$ cellulose acetate
177 membrane filters.

178 To investigate the effect of the solution pH on the adsorption of pollutants, 0.4 g
179 of as-prepared STs or PSTs separately mixed with 20 mL individual NH_4^+ or MB
180 solution at different pH values ranging from 2.0-12.0 (adjusted by either HCl or NaOH)
181 in 50 mL centrifugal tube. The above solution was shaken for 120 min.

182 Adsorption kinetic experiments were carried out in a conical flask by adding 0.2
183 g of adsorbent into a 100 mL solution containing NH_4^+ or MB with initial pH of 7.0. At
184 various time intervals, 1.5 mL suspension was withdrawn and filtered for determination.

185 Adsorption isotherms experiments were performed as follows: 0.04 g of each
186 adsorbent (PSTs and STs) was added into a 50 mL centrifuge tube containing 20 mL
187 solution with different initial concentrations varying from 10 to $160\text{ mg}\cdot\text{L}^{-1}$ for NH_4^+ ,
188 $50\text{-}300\text{ mg}\cdot\text{L}^{-1}$ for MB at $\text{pH}=7.0$. The mixture was shaken at ambient temperature for
189 120 min.

190 The NH_4^+ concentration remaining in the solution was determined by the
191 conventional salicylate spectrophotometric method. The MB concentration in solution
192 was determined by a direct UV-Vis spectrophotometry method at a wavelength of 665

193 nm. The amounts of adsorbates adsorbed on the as-prepared STs or PSTs at a certain
 194 time Q_t ($\text{mg}\cdot\text{g}^{-1}$) and equilibrium Q_e ($\text{mg}\cdot\text{g}^{-1}$) were calculated by Eqs. (1)-(2). The
 195 adsorption efficiency R (%) was calculated by Eq. (3). Where C_0 ($\text{mg}\cdot\text{L}^{-1}$) is the initial
 196 concentration of adsorbates, C_t ($\text{mg}\cdot\text{L}^{-1}$) and C_e ($\text{mg}\cdot\text{L}^{-1}$) are the residual adsorbate
 197 concentration at time t (min) and equilibrium; m (g) is the mass of adsorbent and V (L)
 198 is the solution volume. As shown in Eqs. (S1)-(S6), four kinetic models (pseudo-first
 199 order, pseudo-second order, elovich and web-morris models) and two isotherms models
 200 (Langmuir and Freundlich models) were used to analyze the adsorption data [31-33].

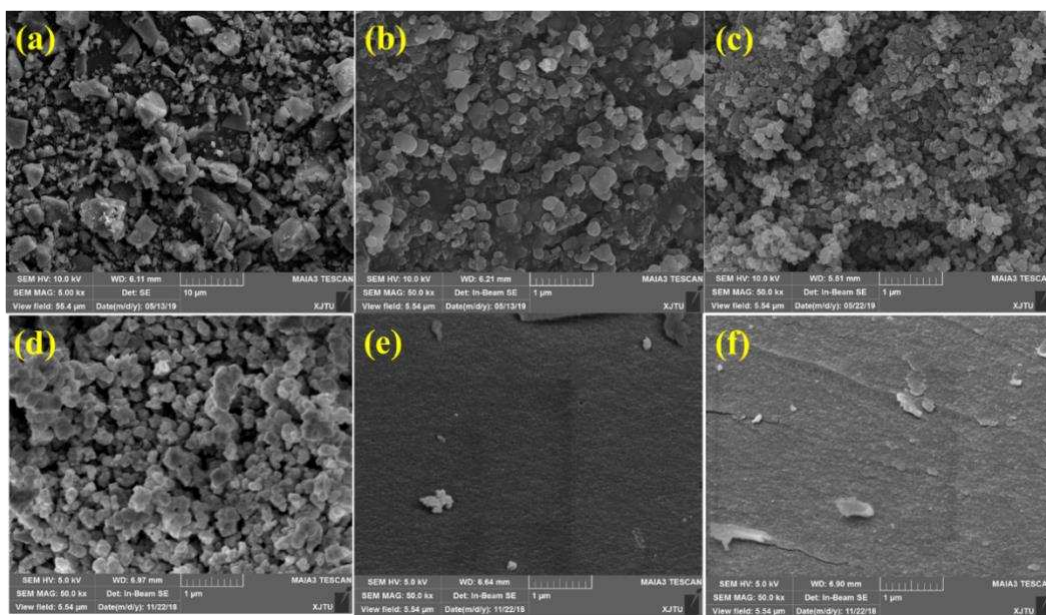
$$201 \quad Q_t = \frac{C_0 - C_t}{m} \times V \quad (1)$$

$$202 \quad Q_e = \frac{C_0 - C_e}{m} \times V \quad (2)$$

$$203 \quad R = \frac{C_0 - C_t}{C_0} \times 100 \quad (3)$$

204 3. Results and discussion

205 3.1. Structure and morphology analyses



206

207 Figure 1. SEM images of ST (1:1) (a), ST (1:10) (b), ST (1:20) (c), PST-5 (d), PST-10
208 (e) and PST-20 (f).

209 The morphology of the primary size samples was analyzed by SEM, as shown in
210 Fig. 1. It is observable that the diameter of granules in STs (Fig. 1 a-c) decrease with the
211 increase of H₂O volume in the synthesis procedure. The reduction of the Ti/H₂O molar
212 ratio increased the hydrolysis rate of Ti precursor and cut down the production of large
213 particles [34]. The average primary size of ST(1:1), ST(1:10) and ST(1:20) is about 500
214 nm, 300 nm and 150 nm, respectively. Agglomeration occurs primarily on the surface
215 of ST(1:20) because the size of nano-particles is small [35]. The change of particles
216 size and morphology in STs might affect the sample properties like surface area and the
217 adsorption behavior in the aqueous phase [16]. The effect of synthesis condition on the
218 morphology of PSTs is more significant than that of STs, as shown in Fig. 1 d-f. The
219 complexation reaction between H₂O₂ and Ti⁴⁺ can be affected by increasing H₂O₂
220 content during synthesis and result in different morphology and particles size [36]. It
221 can be seen that the images that PST-5 (prepared with 5 mL H₂O₂) still maintains a
222 rough surface consisting of particles like STs. However, PST-10 and PST-20 exhibit a
223 well-organized morphology with tiny drapes and fewer particles, which might have a
224 negative effect on the pore volume and specific surface area of samples. All the above
225 results suggest that the modification process succeeded in changing the primary size of
226 samples, favouring the modulation of secondary size in the aqueous phase.

227 Though the primary size is influential on the property of the sample, the secondary
228 size of powder samples is possibly more significant when served as adsorbents in the
229 aqueous phase [19]. The actual particles size (secondary size) of STs and PSTs owing

230 to agglomeration or hydration in agitating solution was measured by a Laser particle
 231 size analyzer and shown in Table 1. It is illustrated that the secondary size of samples
 232 is greatly different from the primary size of SEM images. The results also indicate that
 233 secondary particle size of STs and PSTs are in the order of ST(1:1)> ST(1:10)> ST(1:20)
 234 and PST-20> PST-10> PST-5, respectively. Controlling the hydrolysis rate (for STs)
 235 and complexation degree (for PSTs) successfully caused the difference in secondary
 236 particle size. It is also indicated from Table 1 and Fig. S2 that the surface area and pore
 237 volume of STs vary with the particle size value. The reduction of particle diameter
 238 resulted in an order of specific surface area as ST(1:20)> ST(1:10)> ST(1:1) and PST-
 239 5> PST-10> PST-20. However, the surface area value of PSTs is relatively low because
 240 the addition of H₂O₂ could effectively break the morphology of samples and reduce the
 241 number of pores. In addition, the XRF result (Table 1) demonstrated that the distribution
 242 of the element of STs or PSTs was hardly affected by the synthesis procedure.

243 Table 1. Physical-chemical properties of STs and PSTs by BET, XRF and Laser particle
 244 size analyzer.

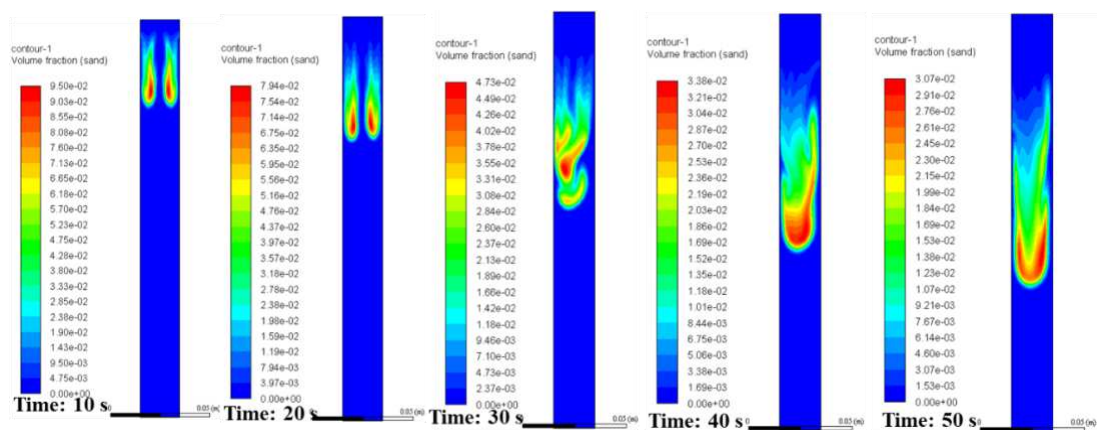
Samples	ST(1:1)	ST(1:10)	ST(1:20)	PST-5	PST-10	PST-20
$D_{50}/\mu\text{m}$	89.13	72.78	53.56	62.81	76.59	92.40
$D_{90}/\mu\text{m}$	200.21	166.92	131.99	149.99	174.27	211.18
$\rho/\text{g}\cdot\text{cm}^{-3}$	2.48	2.77	2.60	3.05	2.98	3.06
$S_{BET}/\text{m}^2\cdot\text{g}^{-1}$	55.2	73.56	139.2	6.9	1.36	0.85
$V/\text{cm}^3\cdot\text{g}^{-1}$	0.30	0.22	0.52	0.06	0.03	0.03
$R_{\text{pore}}/\text{nm}$	10.7	5.9	7.5	16.7	40.7	72.5
Ti/wt%	64.6	63.9	63.2	66.3	64.5	63.6
O/wt%	26.3	28.7	29.7	27.7	28.8	30.2
Na/wt%	7.1	7.4	7.1	6.0	6.7	6.2

245 It is evident from FTIR spectra of STs (Fig. S3a) and PSTs (Fig. S3b) that the
246 typical peak responding to Ti-O-Na⁺ (Ti-OH destroyed in the alkaline environment [37])
247 in 1340 cm⁻¹ remains unchanged in these samples. Meanwhile, the peak responding to
248 the Ti-O bond at about 900 cm⁻¹ appears in PSTs and becomes stronger in the PST-10
249 and PST-20, which accounts for the coordination between the Ti-O framework and Na⁺
250 instead of bridge connection[38]. During the PSTs synthesis, Na⁺ might enter into the
251 interior structure and made the sample's surface more negative in solution [36], which
252 is meaningful for the adsorption of positive pollutants like cationic dyes. In addition, it
253 is observed that Ti-O-O bonds (responding to 680 cm⁻¹ peak [39]) appears in PSTs after
254 the modification by H₂O₂, which might increase the acidity of the surface and promote
255 attracting cations. In addition, the zeta potential results (Fig. S4a-b) show that the p*H*_{iep}
256 (pH at isoelectric point) of ST(1:1), ST(1:10), ST(1:20), PST-20, PST-10 and PST-5 are
257 1.58, 2.01, 2.23, 1.15, 1.52 and 2.33, all of which are in low pH range. It is acceptable
258 that the change of synthesis conditions only brought about a slight difference in the
259 surface charge distribution. Therefore, the surface of STs and PSTs samples in solution
260 would be negatively charged in a wide range of pH, which is beneficial for the cationic
261 contaminants adsorption behavior [40].

262 **3.2. Sedimentation property/adsorbent separation**

263 The sedimentation property of adsorbent powders can reflect their separation
264 tendency or affinity from the water after the adsorption process [41]. It is well known
265 that some theoretical formulas are describing the sedimentation velocity of a spherical
266 particle in a static solution, like the Stokes equation for the laminar region and Newton

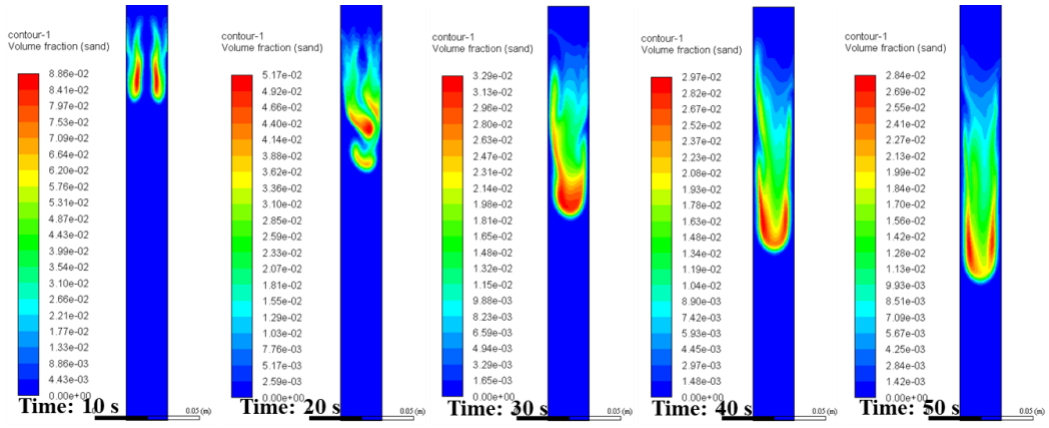
267 equation for the turbulent region [42]. A meaningful conclusion can be made from these
 268 equations that the diameter and density of sphere particles could affect the
 269 sedimentation process. However, these ideal or empirical equations sometimes can't
 270 perfectly predict the sedimentation of powders because the actual environment is
 271 complicated. Therefore, the sedimentation experiment and CFD simulation are
 272 necessary for analyzing the role of particle size in sedimentation. The density and
 273 secondary size of as-prepared ST and PST samples have been changed through
 274 controlling the synthesis conditions and are showed in Table 1. It is evident that the
 275 density of PST samples is different from STs though the density value among PSTs or
 276 STs is similar. The setting experiment evaluated all the samples' setting properties, and
 277 the resulting photos are shown in Fig. S5. It can be seen that the settling velocity of
 278 PSTs or STs particles changes significantly with the change of synthesis conditions.
 279 The setting ability of these samples are in the order of ST(1:1)> ST(1:10)> ST(1:20)
 280 and PST-20> PST-10> PST-5, which is consistent with the order of secondary size.



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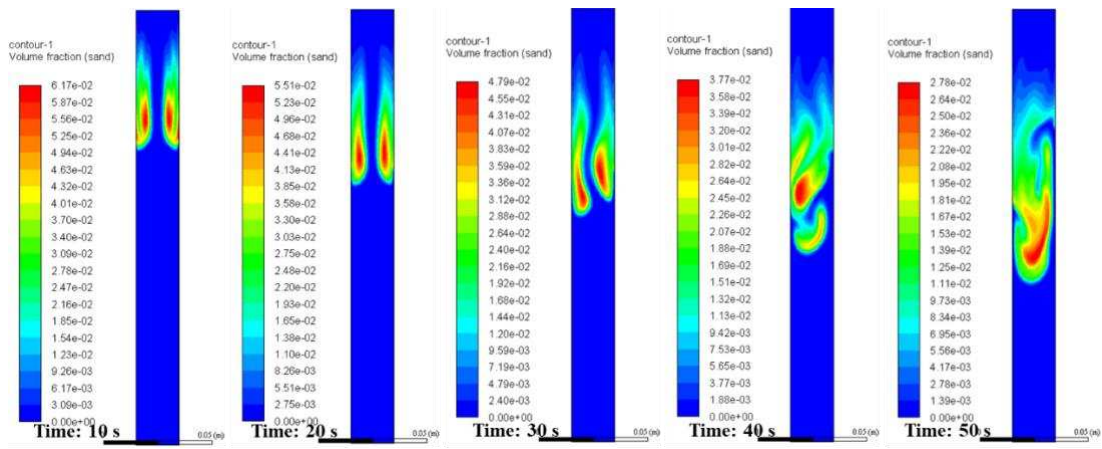
(a) ST(1:1)



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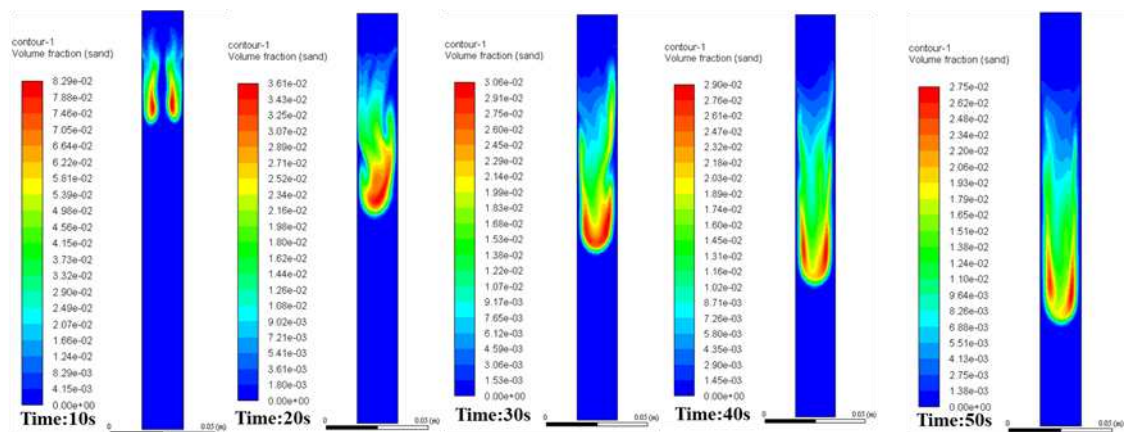
(b) ST(1:10)



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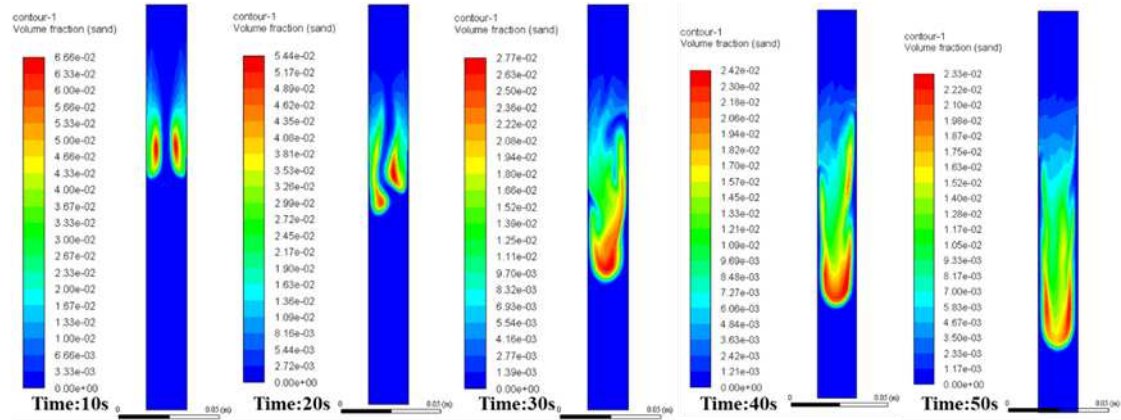
(c) ST(1:20)



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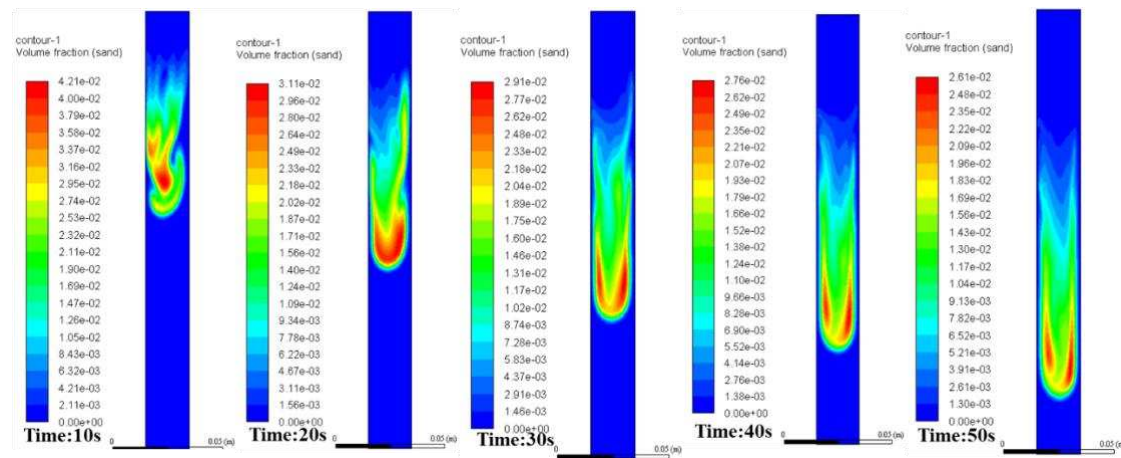
(d) PST-5



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(e) PST-10



291

292

(f) PST-20

293 Figure 2. The simulation results of the setting process of STs and PSTs samples by
 294 Ansys-Fluent.

295 The simulation by CFD was also conducted to figure out the effect of secondary
 296 size and density on the setting ability of adsorbent particles. The numerical method is
 297 showed in section 2.4, and the parameters of particles were set according to the results
 298 in Table 1. For convenience, diameter D_{50} and average true density ρ were used to
 299 represent the chaotic state of actual particles in solution. On this basis, the simulation
 300 of the settlement process of these samples is showed in Fig. 2. The simulated settling
 301 conditions of STs or PSTs are consistent with the actual state, as shown in Fig. S5,
 302 which demonstrates the rationality of the numerical and simplification method. In

303 addition, we found that smaller particles tend to interact with others in a longer time
304 than the larger ones in the initial phase of the settling process. The phenomenon can be
305 attributed to the fact that the diffusion movement of particles with smaller sizes is
306 stronger than particles with larger sizes due to the Brownian movement [43]. From
307 Table 1 and Fig. 2, sample particles with larger density (PSTs) settle more easily and
308 quickly than the small ones (STs). However, for the same kind of samples whose
309 synthesis procedures are identical, the true density value of particles are similar. Thus,
310 the main factor that affects the settling process is only secondary particle size. Therefore,
311 controlling the diameter of particles through finitely changing synthesis conditions can
312 effectively enhance or reduce the settlement ability of samples, which is meaningful for
313 regulating the separation ability of saturated adsorbent materials.

314 **3.3. Adsorption results**

315 **3.3.1. Effect of pH**

316 Usually, the initial solution pH in adsorption experiments is one of the remarkable
317 influence factors since the surface property of adsorbents and the form of adsorbate
318 are pH-dependent [44, 45]. It is illustrated that the adsorption capacity of NH_4^+ onto
319 STs or PSTs reached the maximum when the initial solution pH is 3~4 (Fig. S6a-b).
320 The adsorption capacity of MB onto these adsorbents increased along with the increase
321 of initial solution pH (Fig. S6c-d). The above results can be explained with the
322 following two reasons: firstly, MB is cationic in all the tested pH ranges, and ammonia
323 nitrogen is mainly cationic in the solution $\text{pH} < 7$ (NH_4^+); secondly, the STs and PSTs
324 samples could be negatively charged at a large pH range according to the zeta potential

325 results [46]. In addition, considering the conclusion from the above characterization,
326 the only particle size of samples is highly affected by synthesis conditions, but the
327 particles' size has little effect on the adsorption capacity of NH_4^+ and MB by STs or
328 PSTs. The adsorbent samples with smaller particle sizes possess a slight better
329 adsorption performance at the same pH value. However, it is also indicated that the
330 optimal pH value for the adsorption behavior of STs or PSTs is kept constant among
331 different samples, which means that the particle size of the adsorbent sample is
332 irrelative to the pH adaption.

333 **3.3.2. Adsorption isotherms**

334 The adsorption isotherm experiments of NH_4^+ and MB onto samples were
335 conducted to find the effect of particle size on adsorption behavior with a series of initial
336 solution concentrations. It is observable that the difference in particle size has a more
337 powerful impact on MB adsorption than NH_4^+ for the same adsorbent material (please
338 see Fig. S7). In addition, the difference in adsorption capacity for the same contaminant
339 among the three PST samples is higher than that among the STs. The above results
340 demonstrate that the effect degree of particle size on adsorption performance is relative
341 to the property of both adsorbent and adsorbate. The diagram also indicates that smaller
342 particle size is favorable for adsorption when other conditions remain constant. For
343 instance, the adsorption of MB on STs is in order of $\text{ST}(1:20) > \text{ST}(1:10) > \text{ST}(1:1)$. The
344 increasing specific surface area and more intensive diffusion movement for smaller size
345 samples might provide more active adsorption sites and contacts.

346 Two typical isotherm models (Langmuir and Freundlich model) were employed to
 347 fit the experimental data to understand the effect of particle size on the adsorption
 348 process and evaluate the adsorption performance. The nonlinear fitting curves were
 349 plotted in Fig. S7a-d, and a list of corresponding parameters was showed in Table 2.
 350 The correlation coefficients (R^2) value reveals that the Langmuir model is more
 351 reasonable than the Freundlich model in describing the process, which also indicates
 352 that the change of particle size doesn't bring effects on the monolayer adsorption nature
 353 of MB or NH_4^+ onto STs and PSTs [47, 48].

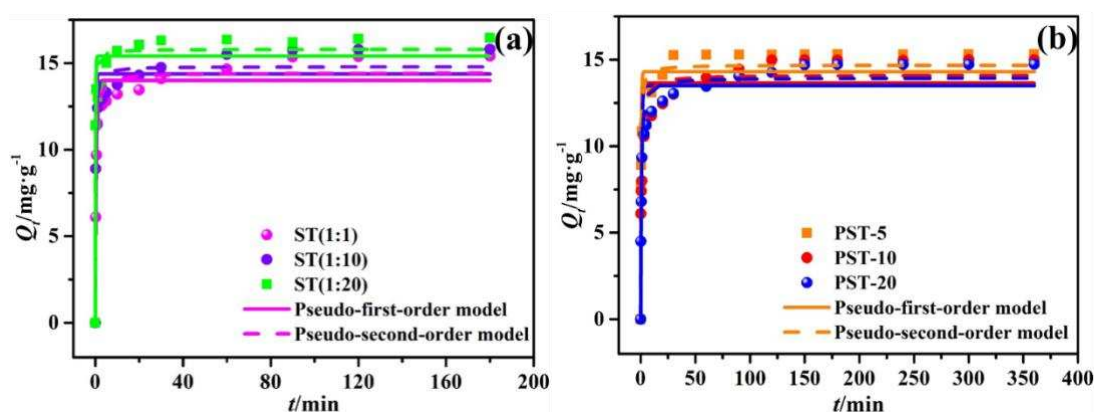
354 Table 2. Isotherm parameters of NH_4^+ or MB adsorption onto STs and PSTs.

Adsorbates	Samples	Langmuir model			Freundlich model		
		$Q_{max}/\text{mg}\cdot\text{g}^{-1}$	$K_L/\text{L}\cdot\text{mg}^{-1}$	R^2	$K_F/(\text{mg}^{(n-1)}\cdot\text{L})^{1/n}\cdot\text{g}^{-1}$	$1/n$	R^2
MB	ST(1:1)	52.81	0.012	0.9978	3.30	0.46	0.9526
	ST(1:10)	51.76	0.017	0.9875	4.48	0.42	0.9963
	ST(1:20)	58.94	0.013	0.9780	3.76	0.47	0.9750
	PST-5	98.52	0.010	0.9904	3.59	0.56	0.9474
	PST-10	94.47	0.007	0.9943	2.61	0.59	0.9743
	PST-20	98.23	0.007	0.9942	2.13	0.62	0.9602
NH_4^+	ST(1:1)	44.82	0.029	0.9921	3.61	0.50	0.9806
	ST(1:10)	44.48	0.031	0.9888	3.90	0.48	0.9725
	ST(1:20)	45.97	0.032	0.9926	3.93	0.49	0.9776
	PST-5	45.26	0.034	0.9886	4.22	0.48	0.9713
	PST-10	46.18	0.027	0.9916	3.40	0.51	0.9773
	PST-20	42.91	0.028	0.9942	3.26	0.51	0.9747

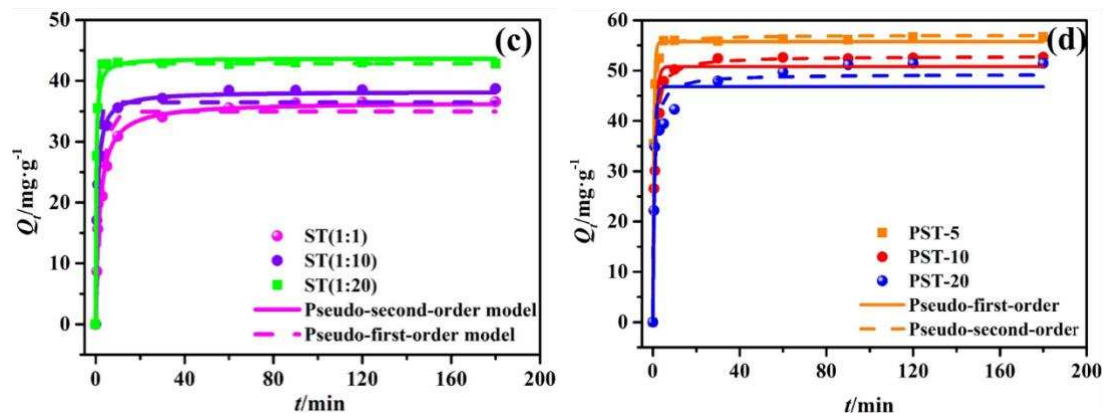
355 3.3.3. Adsorption kinetics

356 The kinetic experiment was conducted to find the relationship between particle
 357 size and adsorption kinetics, and the results of the experiments are shown in Fig. 3. It
 358 is illustrated that samples with smaller particle sizes can reach the adsorption
 359 equilibrium of either NH_4^+ or MB more quickly than those with a bigger size. For

360 example, the adsorption of MB onto ST(1:20) ($D_{50}= 53.56 \mu\text{m}$) can be finished within
 361 10 min, which is shorter than the 60 min of ST(1:10) ($D_{50}= 72.78 \mu\text{m}$) and 90 min of
 362 ST(1:1) ($D_{50}= 89.13 \mu\text{m}$) at the same conditions. Thus, the effect of particle size on the
 363 equilibrium time was independent of the adsorbate species. In addition, two typical
 364 kinetic models (pseudo-first-order and pseudo-second-order models) were used to fit
 365 the experimental data to find the effect of particle size on the kinetic nature of the
 366 adsorption process. The fitting curves are shown in Fig. 3, and the related parameters
 367 are listed in Table S1. The value of kinetic constants (K_1 and K_2) of the two models
 368 indicate the order of adsorption rate values as ST(1:20)> ST(1:10)> ST(1:1) and PST-
 369 5> PST-10> PST-20. The value of correlation coefficient R^2 indicates that the pseudo-
 370 second-order model is more suitable for describing the kinetic adsorption process of
 371 both NH_4^+ and MB onto the as-prepared samples, which further demonstrates that the
 372 difference in particle size doesn't have a pronounced effect on the chemisorption nature
 373 of the kinetic process.



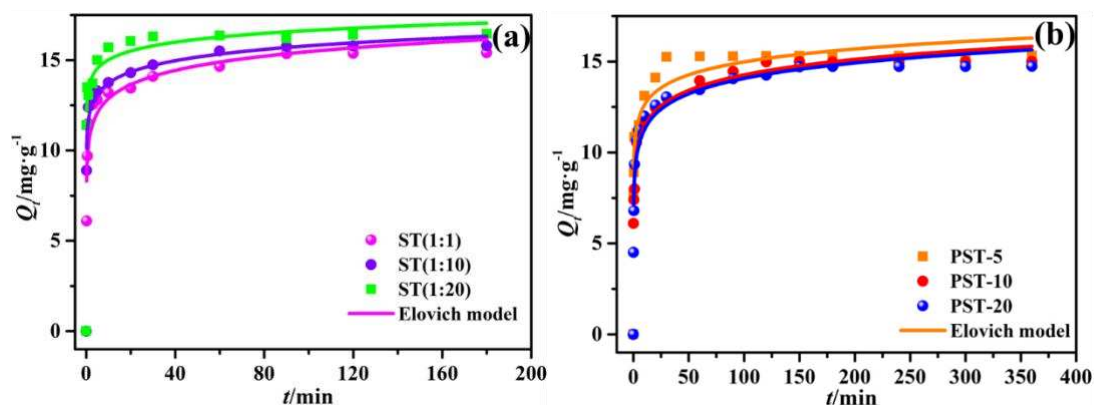
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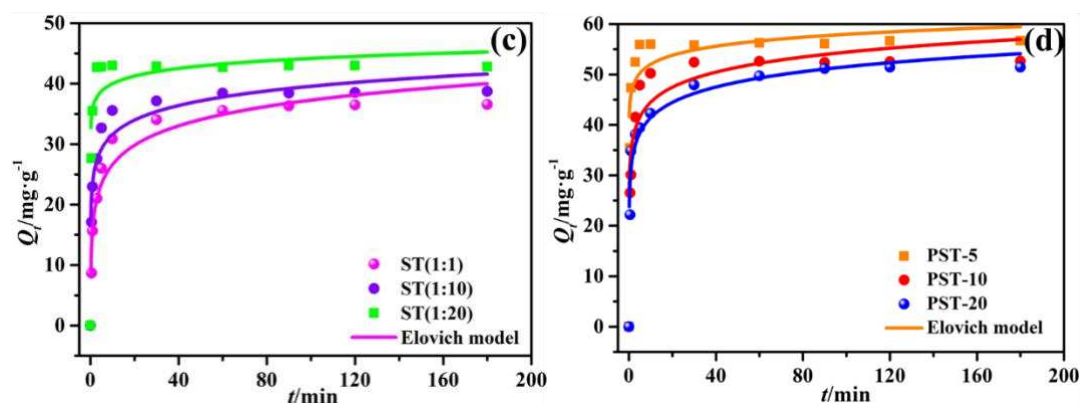
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376 Figure 3. Adsorption kinetics of NH_4^+ onto STs (a), PSTs (b) and MB onto STs (c),
 377 PST(d). (Experimental conditions: $C_0= 45 \text{ mg}\cdot\text{L}^{-1}$ for NH_4^+ and $275 \text{ mg}\cdot\text{L}^{-1}$ for MB;
 378 initial solution $\text{pH}=7$)

379 It is also illustrated from the experimental data that samples with smaller sizes
 380 could adsorb pollutants more quickly than those with bigger sizes at the beginning short
 381 time, which reveals that the size value of particles can significantly affect the adsorption
 382 rate at the primary stage. Therefore, the Elovich model was also employed to fit the
 383 experimental data, as shown in Fig. 4 and Table S2. It is evident that the value of α
 384 (initial adsorption rate) of STs and PSTs in adsorption of MB and NH_4^+ are all in the
 385 order of $\text{PST-5} > \text{PST-10} > \text{PST-20}$ and $\text{ST(1:20)} > \text{ST(1:10)} > \text{ST(1:1)}$, which is opposite
 386 to the order of secondary particle size. The above results demonstrate that the effect of
 387 particle size on the difference of adsorption rate mainly occurs at the very early time
 388 when samples just in contact with the solution.



389



390

391 Figure 4. The fitting results of adsorption of NH_4^+ onto STs (a), PSTs (b) and adsorption
 392 of MB onto STs (c), PSTs (d) by Elovich model.

393 The entire aqueous adsorption process usually contains three stages: liquid film
 394 diffusion, intraparticle diffusion and internal adsorption reaction [32]. In the early time
 395 of the adsorption process, adsorbate molecules can move to the surface of sample
 396 particles and enter into the internal framework through liquid film diffusion. The
 397 decrease of particle size would make adsorbent powders diffuse more easily and quickly
 398 in the solution and reduce the liquid film thickness, which successfully accelerated the
 399 initial adsorption stage [49]. To make sure that the liquid film diffusion process is one
 400 of the rate-limiting steps in the adsorption of NH_4^+ or MB onto STs and PSTs, the
 401 Weber-Morris model was used to fit the experimental data as shown in Fig. 5 and Table
 402 S3. The fitting curves don't cross the origin, and the value of C are all bigger than zero,
 403 which indicates that intraparticle diffusion is not the only rate-limiting step. The whole
 404 adsorption rate is controlled by multiple diffusion modes [50]. Therefore, the effect of
 405 particle size on the liquid film diffusion process can affect the adsorption rate to some
 406 extent, especially at the early contact time.

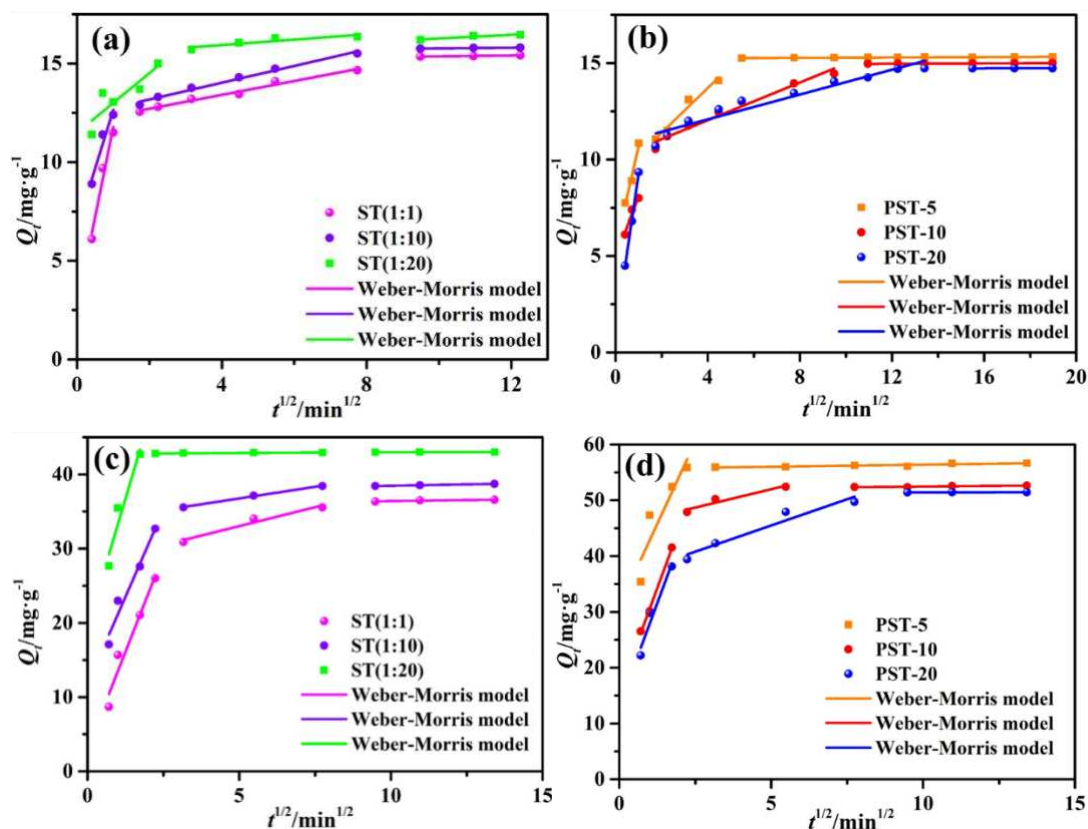


Figure 5. Adsorption kinetics of NH_4^+ (a, b) and MB (c, d) onto samples with the fitting of the Weber-Morris model.

Therefore, the regulation of secondary size value can be carried out to improve the separation ability and adsorption kinetics for the powder-shape adsorbent. The enhancement of sedimentation ability can increase the separation efficiency and reduce the relative cost for recovering the exhausted adsorbents. However, the larger secondary size would mean more prolonged adsorption kinetics and finally reduce the adsorption efficiency. A balance or a key point should be found between these two opposite results. Therefore, an entire cost calculation is suggested to help determine the secondary size value when designing adsorbent materials in the actual application. The investigation of this issue will be focused on in future studies.

4. Conclusions

In this study, a series of sodium titanates (STs) and peroxide modified sodium

422 titanates (PSTs) particles with different sizes were synthesized through the control of
423 hydrolysis and complexation by changing the ratio of reagents. The as-prepared
424 samples were applied in the adsorption of NH_4^+ and MB from an aqueous solution to
425 figure out the effect of particle size on the adsorbent properties and adsorption
426 performance. The sedimentation experiment and CFD simulation indicated that the
427 change of secondary size (particles size after agglomeration, aggregation or hydration
428 in solution) could effectively affect the settling ability of adsorbent powders, which is
429 meaningful for regulating the separation ability of adsorbent materials. In addition, the
430 effect of secondary size on adsorption kinetics is also non-negligible. The PSTs or STs
431 particles with smaller secondary sizes can reach adsorption equilibrium for NH_4^+ and
432 MB more quickly than those with a bigger size. The fitting results from Elovich and
433 Weber-Morris models demonstrate that the particles size affect kinetics mainly in the
434 liquid film diffusion process at the early contact time. Therefore, the secondary size
435 significantly affects the sedimentation ability and adsorption kinetics of titanate-based
436 adsorbents in the opposite results, which is helpful for adsorbent design and mechanism
437 analysis.

438

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442 **Appendix A. Supplementary data**

443 Eqs. (S1)- (S2): Langmuir and Freundlich models

444 Eqs. (S3)- (S4): Pseudo-first order and Pseudo-second models.

445 Eqs. (S5)- (S6): Elovich model and Web-morris model

446

447 Table S1. Parameters of the kinetics models for the adsorption of NH_4^+ and MB onto STs and PSTs.
448 Table S2. Parameters of the Elovich model for the adsorption of NH_4^+ and MB onto STs and PSTs.
449 Table S3. Parameters of the Weber-Morris model for the adsorption of NH_4^+ and MB onto STs and
450 PSTs.

451

452 Figure S1. The molecular structures of methylene blue.

453 Figure S2. N_2 gas adsorption-desorption isotherm of STs and PSTs. The inset is the corresponding
454 pore size distribution.

455 Figure S3. FTIR spectra of (a) STs and (b) PSTs.

456 Figure S4. Zeta potential of (a) STs and (b) PSTs at different solution pH.

457 Figure S5. The setting state of PSTs at (a) 0s, (b) 60s, (c) 10 min, (d) 30 min and STs at (e) 0s, (f)
458 60s, (g) 10 min, (h) 30 min.

459 Figure S6. Effect of initial solution pH on the adsorption capacity of NH_4^+ onto STs (a), PSTs (b)
460 and adsorption capacity of MB onto STs (c), PSTs (d).

461 Figure S7. Adsorption isotherm results of NH_4^+ onto STs (a), PSTs (b) and MB onto STs (c), PSTs
462 (d).

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