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# Rapid and Facile Detection of PBTC Antiscalant Using Functionalized Polystyrene Nanoparticles and Latex Agglutination

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## Abstract

Organophosphate-based compounds, particularly 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC), have played a crucial role in circulating cooling systems and wastewater treatments as corrosion inhibitors preventing scale deposits in industrial facilities. Employing the reagent within its optimum concentration range is essential for effective performance, minimizing costs and environmental impacts. However, measuring PBTC separately can be challenging due to its functional groups' similarity to other common molecules found in natural water, necessitating complex procedures. In this study, amine-functionalized polystyrene (PS) latex nanoparticles were synthesized through emulsifier-free emulsion polymerization and utilized as nanosorbents for PBTC detection via a straightforward latex agglutination method. This phenomenon is facilitated by electrostatic and hydrogen bonding interactions between the positively charged layers on the particle's surface and the negatively charged PBTC molecules. The pH and concentration of the PBTC solution are key factors influencing the adsorption behaviour and capacity of the functionalized latex particles. A graphical representation of aggregation domains, dependent on both PBTC concentration and pH, was created. This map serves as an effective tool for detecting PBTC concentration. The resulting particles show great promise for monitoring

29 the concentration range of phosphate additives in water, offering a simple, rapid detection  
30 process with low costs and reduced chemical and equipment requirements.

31

32 **Keywords:** PBTC, Latex agglutination, Cationic particles, Polystyrene, Phosphate detection

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### 34 Graphical abstract

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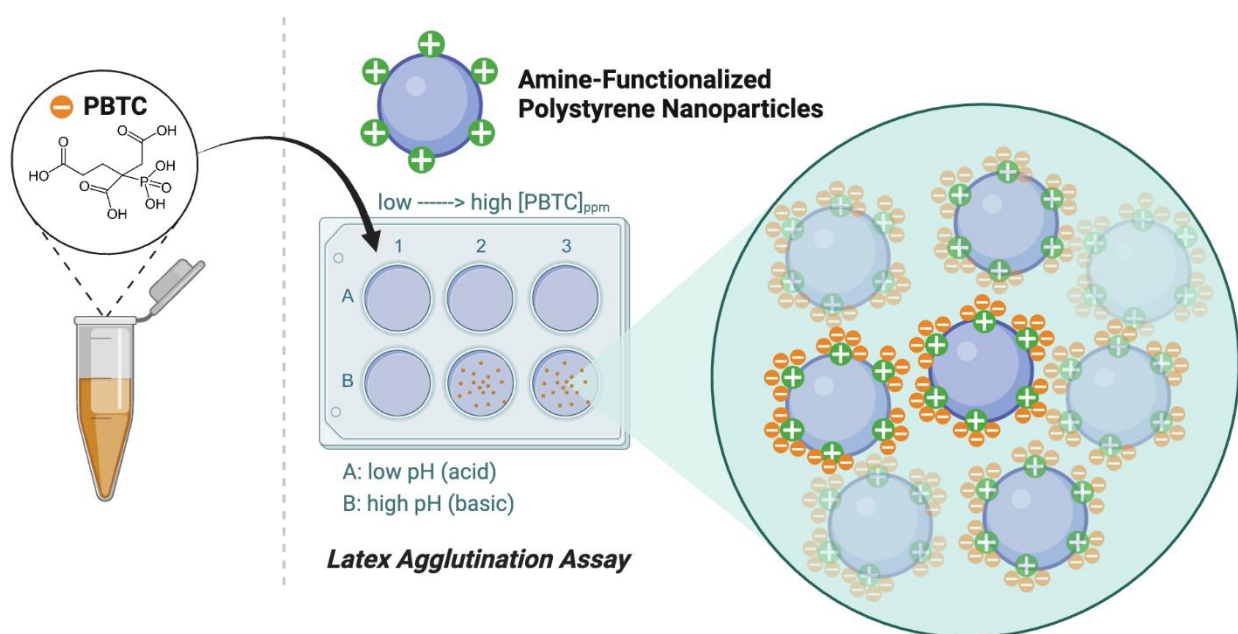
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## 55 **1. Introduction**

56           Scale formation poses a significant challenge in industrial processes. To address this  
57 issue, antiscalant agents are employed to inhibit scale formation. Among these, 2-  
58 phosphonobutane-1,2,4-tricarboxylic acid (PBTC) is a crucial organophosphate reagent widely  
59 used in industrial processes, particularly in circulating cooling water systems. This compound  
60 effectively prevents mineral scale formation and corrosion [1-4]. PBTC contains carboxylic and  
61 phosphonic acid groups, providing high solubility and strong binding capabilities with various  
62 metal ions [5-7]. The fast and accurate monitoring of PBTC concentration during operations and  
63 corresponding wastewater treatment processes is essential [8, 9]. In cooling water applications,  
64 continuous addition of PBTC is necessary to maintain its optimal concentration and prevent scale  
65 formation and corrosion in pipelines and manufacturing equipment [10]. Inadequate  
66 organophosphate content in the cooling system can lead to corrosion and scale accumulation  
67 during operations. Conversely, an excessive phosphate presence results in higher operating costs  
68 and challenges in wastewater treatment. Improper treatments before discharging can degrade  
69 water quality and contribute to eutrophication in water resources [11-13]. In aquatic ecosystems,  
70 elevated levels of dissolved nutrients can lead to the accelerated growth of water plants or algae  
71 blooms, directly affecting surface water conditions and reducing dissolved oxygen levels in  
72 water bodies [14, 15].

73           Detecting the presence of phosphate in a water-cooling system is challenging using  
74 conventional spectrophotometric methods because phosphate lacks both fluorescence groups and  
75 chromophores. Consequently, it becomes necessary to convert phosphate into free phosphorus,  
76 which can then be quantified through optical emission microscopy or a colorimetric method with  
77 a reasonable degree of accuracy [16-18]. However, this approach is time-consuming, expensive,  
78 and involves intricate processes, the use of toxic chemicals, and costly instruments [19, 20].  
79 Therefore, there is a growing interest in developing novel materials and eco-friendly methods  
80 that offer swift responses, enabling time-efficient, accurate monitoring of phosphate in industrial  
81 settings at a lower cost.

82           Adsorption is a promising technology for phosphate removal, demonstrating favourable  
83 performance across a wide range of pH values. It offers ease of operation, rapid capture  
84 capabilities, cost-effectiveness, a high removal rate for highly toxic pollutants, and generates low  
85 levels of harmful secondary products [21-25]. The interaction between compounds and

86 adsorbents varies depending on environmental factors, including the nature of the adsorbent  
87 surface, the pH of the medium, surface charge density, incubation time and temperature, solvent  
88 polarity, and the presence of competing molecules [26-28]. Numerous natural silica-based  
89 adsorbents, such as zeolites, diatomite, clays, and porous silica materials, have proven effective  
90 for phosphate removal. However, raw silica materials lack functional groups or adsorption sites  
91 for phosphate adsorption [29]. Modified adsorbents with functional groups have enhanced  
92 adsorptive removal efficiency, typically measured in terms of selectivity for specific compounds,  
93 adsorption capacity, renewability, and durability. A range of surface functionalization techniques  
94 can be employed to improve various surface properties, including hydrophilicity, electrostatic  
95 interaction, surface energy, roughness, and biocompatibility [30, 31]. Recently, we developed  
96 carboxylated magnetic polymeric nanoparticles (MPNPs) as nanosorbents for the removal of  
97 calcium ions ( $\text{Ca}^{2+}$ ) [32]. The formulated MPNPs exhibited a 92% efficiency in  $\text{Ca}^{2+}$  removal  
98 and can be effectively reused for up to four cycles. This efficiency is achieved through  
99 electrostatic interactions between the negatively charged polymer containing carboxylate groups  
100 and the hydrated  $\text{Ca}^{2+}$ , resulting in precipitation that prevents calcium carbonate scale formation.

101         Developing a rapid and user-friendly technique for detecting target compounds in  
102 practical environments remains a challenge. Polystyrene (PS) is considered a highly promising  
103 material due to its cost-effectiveness, versatility, and minimal negative environmental impact. PS  
104 is frequently used to create latex nanoparticles and is applied in various applications due to its  
105 substantial surface area, low density, and stability [33, 34]. The latex agglutination test quantifies  
106 a measurable aggregation phenomenon that can be easily observed with the naked eye. The  
107 particle supports are functionalized with active sites. When specific targets bind to these sites,  
108 particle clumping occurs, serving as an indicator of the presence of the target components or  
109 molecules. The extent of aggregation can be assessed visually by examining the area of the  
110 aggregate formations. Latex agglutination, using synthetic PS particles, has been extensively  
111 applied in various fields, including in vitro biomedical diagnosis, ecological risk assessment, and  
112 food contamination monitoring [35-38] thanks to its advantages, ease of use, cost-effectiveness,  
113 and high reliability. Furthermore, the reaction is visible, eliminating the need for specialized  
114 equipment or complex detection systems [39-41].

115         This research aims to develop functionalized polystyrene nanoparticles suitable for the  
116 rapid detection of the commonly used organophosphate, PBTC, in industrial water-cooling

117 systems and wastewater treatment processes using a latex agglutination assay. The research  
118 findings will be used to construct a map of aggregation domains as a function of PBTC  
119 concentration and pH, offering an effective approach for detecting PBTC concentration in  
120 unknown samples.

121

## 122 **2. Materials and Methods**

### 123 **2.1 Materials**

124 Styrene monomer (Janssen Chimica), 2,2'-azobis(2-amidinopropane) dihydrochloride  
125 (V50; >97%, Wako Chemical), 2-amino ethyl methacrylate hydrochloride (AEMH; Kodak  
126 chemicals), 2-phosphonobutane-1,2,4,-tricarboxylic acid (PBTC; >47% solution, Carl Roth),  
127 potassium antimony (III) oxide tartrate trihydrate (Carl Roth), ascorbic acid (Carl Roth),  
128 ammonium molybdate tetrahydrate (>99%, Sigma-Aldrich), sodium hydroxide (98%, Thermo  
129 Scientific), sulfuric acid (95%, VWR chemical BDH) were used as received. Deionized (DI)  
130 water was used throughout the study.

131

### 132 **2.2 Methods**

#### 133 **2.2.1 Preparation of cationic polystyrene latex particles**

134 PS latexes bearing cationic amine groups were prepared following the procedure described  
135 elsewhere [42, 43]. Briefly, 20 g of styrene monomer and  $2.5 \times 10^{-3}$  g of AEMH functional  
136 monomer were added to a thermostat glass reactor containing 200 g deoxygenated water (DI  
137 water boiled under a nitrogen atmosphere). The mixture was continuously stirred at 300 rpm  
138 under a controlled temperature of 70 °C. After that, a small amount of initiator solution (V50,  
139 0.32 g) was added to the mixture, and the polymerization was conducted for 20 h.

140

#### 141 **2.2.2 Characterization of cationic PS latex particles**

142 The specimen was positioned inside a vacuum chamber with an accelerated voltage of 120  
143 kV. The hydrodynamic size and size distribution of the prepared PS latex particles were  
144 measured using dynamic light scattering (DLS) with a ZetaSizer (nano series 3000MS, Malvern  
145 Instruments). The obtained polymer particles were diluted in 1 mM NaCl at a given pH. The  
146 reported size value was the average of three measurements. The morphology of the prepared

147 particles was examined using a scanning electron microscope (SEM, COXEM EM-30Plus). A  
148 droplet of the diluted latex particles was evaporated at room temperature, and the dried solid  
149 sample was gold-coated before analysis. Additionally, the synthesized particles were  
150 characterized using a transmission electron microscope (TEM, JEOL 1400 FLASH – Source  
151 LaB6). A droplet of diluted latex particles was deposited onto a formvar/carbon-coated copper  
152 200-mesh grid. The specimen was positioned inside a vacuum chamber with an accelerated  
153 voltage of 120 kV.

154

### 155 **2.2.3 Electrokinetic study of cationic PS latex particles**

156 Electrophoretic mobility analysis was conducted on a ZetaSizer (nano series 3000HS,  
157 Malvern instrument). The measurements were operated using highly diluted dispersed latexes in  
158 1 mM NaCl solution. The zeta potential deduced from the electrophoretic mobility of the PS  
159 latex particles was measured as a function of pH. The effect of PBTC concentrations (10-2,000  
160 ppm) under different pH conditions (pH 3-11) on the electrokinetic behaviour was investigated.  
161 All measurements were conducted at 25 °C and interpreted as a direct study of the effective total  
162 surface charge density.

163

### 164 **2.2.4 Adsorption of PBTC on cationic PS particles**

165 A titration using a standard molybdate solution was employed to determine the amount of  
166 the adsorbed PBTC on the cationic PS particles. Molybdate reagent was prepared by combining;  
167 the following components: 100 mL of 2.5 M sulfuric acid solution, 10 mL of potassium  
168 antimony tartrate solution (dissolution of 0.28 g in 80 mL of distilled water and diluted to 100  
169 mL), 30 mL of ammonium molybdate solution (prepared at 4% w/v), and 60 mL of ascorbic acid  
170 solution (1.76 g in 100 mL of DI water). After mixing, a light-yellow solution was obtained.

#### 171 *Adsorption kinetic of PBTC on PS latex particles*

172 The synthesized PS latex particles (10 mg) were added to a series of centrifuge tubes,  
173 containing 10 mL of PBTC solution at an initial concentration of 1,000 ppm (with a fixed pH of  
174 5). The samples were mixed for 0 – 120 min. At specific intervals during this period, the  
175 mixtures were centrifuged to separate the remaining phosphate phase. The supernatant of each  
176 sample was collected and filtered using a nylon microfilter (0.20 µm pore size). The post-  
177 treatment solution (5 mL) was transferred into a clean cuvette, and 0.8 mL of molybdate reagent

178 was added to the mixture for colorimetric measurements. The solution changed to a blue colour  
179 between 15-20 min. Subsequently, the solution's absorbance was recorded at 880 nm using an  
180 ultra-fast UV/Vis spectrometer (FLUOstar Omega). The batch experiment and sampling method  
181 were applied to obtain the adsorption kinetic of PBTC on the cationic PS latexes, as illustrated in  
182 Fig 1.

#### 183 *Adsorption rate of PBTC on PS particles*

184 The adsorption isotherms were investigated in a similar manner to the kinetic  
185 experiments with 1 g/L of each solid-liquid latex. PBTC solutions at various concentrations  
186 ranging from 0 to 15,000 ppm were prepared at fixed pH values of 5, 6.5, and 11. The samples  
187 were gently mixed end-over-end at 35 rpm for 20 min. Subsequently, the mixtures were  
188 centrifuged at 7,500 rpm for 5 min, followed by filtration. The adsorption of the phosphate  
189 compound was examined using a colorimetric technique employing UV/Vis spectroscopy.

190

#### 191 **2.2.5 Latex agglutination assay for PBTC detection**

192 The detection of PBTC at varied concentrations, from 0 to 2,000 ppm at a pH range from  
193 3 to 11, was performed on a clean glass slide. Droplets of 10  $\mu$ L of the synthesized PS latexes  
194 (containing 1 mg of particles) were deposited on the glass slide, forming separate circular  
195 domains. Subsequently, 30  $\mu$ L of the prepared PBTC solutions at different concentrations were  
196 added and manually mixed for 15 seconds. The presence of agglutination phenomenon at each  
197 condition was observed by the naked eye, and photographs were taken.

198

### 199 **3. Results and Discussion**

#### 200 **3.1 Characterization of cationic PS latex particles**

201 The PS latex particles were successfully prepared with a high polymerization conversion  
202 (~98%) using cationic 2-amino ethyl methacrylate hydrochloride (AEMH) as a functional  
203 monomer and 2,2'-azobis(2-amidinopropane) dihydrochloride (V50) as an initiator. The  
204 morphology of the prepared particles was examined by SEM and TEM, as shown in Figs 2(A  
205 and B). Spherical polymeric particles with smooth surfaces were generated. The synthesized  
206 particles exhibited uniform shape and morphology, as evidenced by the particle diameter of  
207 approximately  $100 \pm 11$  nm. Similar results were also observed from TEM analyses, where the  
208 average size of the functionalized PS colloidal particles, calculated from the statistical



209 distribution was  $98\pm 35$  nm. A hydrodynamic particle size of  $107.8\pm 14$  nm was observed (Fig  
210 2C). It is important to note that the size determined from DLS is generally larger than that from  
211 TEM images [44], as the results from DLS represent the hydrodynamic diameter, which includes  
212 the hydrated layers on the colloidal surface. In contrast, TEM measures the diameter of the  
213 particles, under a dried state [45]. Nevertheless, high-quality size distribution curves of the  
214 colloidal dispersion were observed using the Contin analysis mode. This reflects the well-defined  
215 dispersion composed of homogeneous nano-spherical particles with a standard deviation of 27.92  
216 nm relatively narrow size distribution [46].

217

### 218 **3.2 Electrokinetic study**

219 The zeta potential deduced from the electrophoretic mobility of the prepared PS latex  
220 particles was measured as a function of pH (with 1 mM NaCl solution), as summarized in Fig  
221 3(A). The zeta potential exhibited positive values in the investigated pH range (3-12), indicating  
222 the cationic characteristic of the protonated amine groups on the particle's surfaces. The  
223 incorporated primary amine ( $-\text{NH}_2$ ) groups from the functional monomer copolymerized with  
224 styrene onto the PS particles, were protonated, resulting in a high positive zeta potential at a pH  
225 lower than 10 [47, 48]. The zeta potential of the PS latex particles exhibited a rapid decrease in a  
226 strong basic environment (pH 11-12). The decrease of the zeta potential at high basic  
227 environments can be attributed to the deprotonation of ammonium ions to amine since the pH is  
228 above the pKa value of the applied 2-amino ethyl methacrylate hydrochloride, which is between  
229 9 and 10. In addition, the decrease in the zeta potential at high pH can also be attributed to the  
230 possible condensation of hydroxyl groups on the particles' surface. However, the salinity  
231 variation is too low to induce the observed phenomenon. These results indicate that the  
232 synthesized products are suitable materials with high cationic properties, which should interact  
233 with the negatively charged compounds through favourable attractive electrostatic interactions  
234 [49, 50]. In addition, the electrophoretic mobility has been investigated as a function of  
235 electrolyte concentration, as presented in Fig 3(B). As expected, the electrophoretic mobility (in  
236 absolute value) decreases with increasing the salinity of the medium. This is in good agreement  
237 with the theory [51].

238 The surface charge density of the prepared particles was calculated using the following  
239 Helmholtz and Smoluchowski equation (Eq. 1):

240

$$241 \quad \mu_e \approx \frac{\sigma}{\eta K} \quad \text{Eq. 1}$$

242 where;  $\mu_e$  is the electrophoretic mobility ( $\mu\text{m}\cdot\text{cm}/\text{V}\cdot\text{s}$ );  $\sigma$  is the surface charge density  
243 ( $\mu\text{C}/\text{cm}^2$ );  $\eta$  is the dynamic viscosity of the continuous medium ( $\text{Pa}\cdot\text{s}$ ); and  $K$  (Greek kappa) is  
244 referred to as the inverse Debye length ( $\text{k}^{-1}$ ) which is called the double layer thickness.

245

246 Since the surface potential is replaced by zeta potential (which is also an approximation  
247 approach), the surface charge density is not far from the presented approximated equation. In  
248 fact, the results data in which the surface charge density is reported as a function of surface  
249 potential, the deduced zeta potential was found to be in the limit of the linearity domain.  
250 Therefore, the equation used in this study is just for estimating the surface charge density rather  
251 than its exact determination [43]. It is noted that the surface charge density was calculated by  
252 considering the electrophoretic mobility, *i.e.*, the zeta potential of +46 mV, at a plateau value.  
253 The deduced surface charge density was  $10 \mu\text{C}/\text{cm}^2$  (where the specific surface area is  $56 \text{ m}^2/\text{g}$ ).  
254 The value is comparable to those reported for PS latexes with amine or amidine groups prepared  
255 *via* the same polymerization process, which showed similar electrophoretic mobility tendencies  
256 [52].

257

### 258 **3.3 pH effect on particles as a function of PBTC concentrations**

259 The effect of adding the amine-functionalized colloidal latexes to PBTC stock solutions  
260 on the pH of the solutions was initially investigated, as shown in Fig 4. The addition of amine-  
261 functionalized PS latex particles did not affect the pH levels of the organophosphate solution,  
262 regardless of its concentrations. This confirms that the cationic characteristic of the polymer  
263 latex did not interfere with the controlled parameter in subsequent experiments. The zeta  
264 potential of amine-functionalized particles added to PBTC solutions was then examined as a  
265 function of pH, as summarized in Fig 5. As expected, the zeta potential was positive and  
266 slightly decreased due to the deprotonation of the primary amine and amidine groups from the  
267 AEMH copolymer and V50 initiator. Interestingly, the zeta potential remains positive until

268 reaching the vicinity of pH 10, which is close to the pKa of the primary amine [53]. Therefore,  
269 the zeta potential of latex particles was investigated as a function of both pH and PBTC  
270 concentration. The positive zeta potential of latex particles decreased with increasing PBTC  
271 concentrations, irrespective of their incubation pH. This decrease can be attributed to (i) the  
272 adsorption of negatively charged PBTC on the positively charged functionals (protonated amines  
273 and amidines) and (ii) the ionic strength effect of PBTC. Increasing the PBTC concentration  
274 increases the ionic strength of the incubation medium, leading to a reduction in the zeta potential.

275 PBTC has multiple acid functional groups (carboxylic acid), resulting in multiple pKa  
276 values ( $1.08 \pm 0.42$ ,  $3.99 \pm 0.21$ ,  $4.44 \pm 0.10$ ,  $4.99 \pm 0.14$ , and  $8.59 \pm 0.50$  for pKa 1-5, respectively)  
277 [6]. The pH is a significant factor that should be considered for controlling the number of  
278 negatively charged sites in the system. Furthermore, the zeta potential is highly influenced by the  
279 organophosphoric acid, which typically exhibits a positive charge in strongly acidic  
280 environments (pH 3-4), but immediately reduces in ionic strength with an increase in the PBTC  
281 dosage. The increase in the initial concentration results in more negative potential values,  
282 especially in basic conditions. The negative ion values likely originate from the three carboxylic  
283 groups and the orthophosphates, which are correlate with the amount of the reagent and the pKa  
284 of the solutions.

285

### 286 **3.4 Adsorption behavior of PBTC on amine-functionalized PS latex particles**

287 The adsorption efficiency of absorbents is commonly influenced by several factors,  
288 including electrostatic and other available interactions. For materials, the aggregation  
289 phenomenon typically occurs when the zeta potential reaches zero mV, which is defined as the  
290 isoelectric point and is often used as a reliable indicator of the pH range of instability [54, 55].  
291 The surface charge represents the effective net and counter ions on the contact layer and reflects  
292 the ability of the amino-functional group to interact with negative counter ions. The observed  
293 changes in this study are associated with the adsorption of negative ions from PBTC structures in  
294 the solutions. Even though the ionic strength is the key determining factor for aggregation-  
295 dispersion according to DLVO theory, in this study, the salinity in the PBTC solution to be  
296 analyzed the critical coagulation concentration (CCC) is low (below 1 mM NaCl, since pure  
297 water is generally used in cooling systems). Therefore, the PBTC concentration to be detected is  
298 below the CCC of the applied latex particles.

299 *Adsorption kinetics of PS latex particles*

300 The adsorption kinetics of PBTC on the functionalized PS latex particles was investigated  
301 by measuring the adsorption capacity as a function of incubation time, as shown in Fig 6. The  
302 sorption event rapidly occurred during the first 3 min of the experiment. As the ionic strength of  
303 the functionalized PS particles at the studied pH (pH 5) is positive and the target PBTC  
304 compound contains anionic species, it appears that the primary mechanism of this adsorption is  
305 induced by electrostatic attraction. However, after 10 min, however, there is no significant  
306 increase in the adsorption capacity, indicating an equilibrium state. The observed relatively short  
307 equilibrium time is consistent with prior studies, where the strong interaction from oppositely-  
308 charged molecules/groups on the particle surfaces led to a fast equilibrium within 10-20 min [56,  
309 57]. These results confirm the interactions between the protonated amine groups and the  
310 available active anions in the PBTC structures.

311 *Adsorption isotherms of PBTC as a function of pH and initial PBTC concentration*

312 The adsorption isotherms of the organophosphate reagent on the PS latex particles's surfaces at  
313 different pH conditions are compared in Fig 7. The equilibrium adsorption capacity of the  
314 particles as a function of residual PBTC concentration is compared at different pH conditions.  
315 The equilibrium adsorption capacity increased with the residual PBTC concentration from 0 to  
316 9000 ppm, due to higher contents of available negatively charged species in the system. The  
317 value reached a plateau value of around 0.011-0.012  $\mu\text{mol}/\text{cm}^2$ , reflecting the maximum  
318 adsorption capacity. This indicates that the essential factor affecting the adsorption capacity is  
319 the concentration of PBTC, as its -COOH and -PO<sub>3</sub>H<sub>2</sub> groups undergo ionization *via*  
320 deprotonation. The increase in the initial concentration of PBTC leads to higher adsorption  
321 capacity on the adsorbent surface, due to the electrostatic force between the protonated  
322 functionalized nanoparticles and negative PBTC in the media [58, 59]. Similar results were also  
323 observed at all pH conditions. Although the effect of pH on the adsorption capacity has not been  
324 widely studied, the results on PBTC adsorption as a function of pH on ZrFeZn adsorbent, which  
325 carries positive charges have been reported [60]. The authors reported a similar tendency, where  
326 the adsorption of PBTC occurred at pH range > 5 and did not significantly change with increased  
327 pH values. It is noted that upon closer examination of our results, the PBTC adsorption capacity  
328 was slightly reduced in the solution with high pH (> 10). This is likely because the charge on the  
329 PS adsorbent particles may shift in the negative direction with increasing solution pH due to a

330 lower degree of protonation. Even though the critical coagulation concentration (CCC) can be  
 331 estimated from the surface charge density and macroscopically examined for such latex particles,  
 332 also the CCC domain has been estimated from quick latex particle agglutination as a function of  
 333 NaCl and found to be in between  $5 \times 10^{-2}$  to  $10^{-1}$  M. In this work, the salinity of the PBTC  
 334 solution to be analyzed is very low (below 1mM NaCl, since pure water is generally used in  
 335 cooling systems). Thus, the PBTC concentration to be detected is below the CCC of the used  
 336 latex particles.

337 Considering that the surface charge density of latex particles is related to the number of  
 338 mobile charges carried per unit area, the adsorption experiments were performed under a  
 339 controlled number of particles that carry positive charges to investigate the adsorption  
 340 mechanism. The proton equivalents were calculated to reveal a suitable mechanism for the  
 341 adsorption features. The total surface charge was estimated by equation (Eq. 2);

342

$$343 \quad \sigma \approx \frac{e_p \phi_p}{6} \times n_{eq} \times N_A \times C_e^- \quad \text{----- (Eq. 2)}$$

344

345 where;  $\sigma$  is the surface charge density ( $\mu\text{C}/\text{cm}^2$ ) deduced from zeta potential as discussed above;  
 346  $e_p$  is the solid density ( $\text{g}/\text{cm}^3$ );  $\phi_p$  is particle diameter (nm);  $n_{eq}$  is the number of protons  
 347 equivalent ( $\mu\text{mole}/\text{cm}^2$ );  $N_A$  is the Avogadro's number ( $6.022 \times 10^{23} \text{ mol}^{-1}$ ); and  $C_e^-$  is the  
 348 electric charge ( $1.602 \times 10^{-19} \text{ C}$ , coulomb).

349

350 The  $n_{eq}$  value of the original PS latex particles, calculated from Eq. 2 was  $1.04 \times 10^{-4} \mu\text{mole}/\text{cm}^2$ .  
 351 From the adsorption experiments, the total adsorption amount of PBTC on the positively charged  
 352 particles is also expressed in  $\mu\text{mole}/\text{cm}^2$ . The calculated values as a function of pH are  
 353 summarized in Fig 8. The PBTC adsorption capacity is significantly higher than the available  
 354 positive sites for adsorption. This indicated that the available protonated amino groups on the  
 355 surface completely interact with an equimolar amount of negative PBTC ions through  
 356 electrostatic interaction. Additionally, the presence of a large excess of adsorbed PBTC is likely  
 357 due to hydrogen bonding between carboxylic acids and  $-\text{NH}_2$  acceptor [61].

358

### 359 **3.5 Latex aggregation assay**

360 From the adsorption results, the observed aggregation of the latex particles is likely  
361 correlated with the incubation pH and PBTC concentration at a given latex particle content.  
362 However, in this study, however, specific attention is dedicated to the rapid agglutination only to  
363 detect the PBTC concentration range of unknown aqueous samples, as shown in Fig 9. As  
364 evidenced from the experiments (agglutination *vs.* pH and PBTC concentrations), two  
365 macroscopic aggregation domains were well distinguished, *i.e.*, stable (no macroscopic  
366 aggregation) and unstable domain. Below 50 ppm of PBTC, only a stable domain was observed,  
367 irrespective of pH. This is due to the low PBTC adsorption amounts. In contrast, when the PBTC  
368 concentration was above 50 ppm, the presence of the aggregation domain was dependent on both  
369 PBTC concentration and pH. At 100 ppm PBTC, the aggregation appeared at pH 11, while at  
370 500 and 1000 to 2000 ppm PBTC, this occurred at  $\text{pH} > 6.5$ , and  $> 5$ , respectively. As discussed  
371 above, the amount of adsorbed PBTC increases with increasing PBTC initial concentration. In  
372 addition, increasing the incubation pH above the average pKa of PBTC also leads to an increase  
373 in adsorption capacity. The excess adsorption of PBTC, in turn, causes surface charge screening,  
374 leading to lower surface charge density and low colloidal stability of the dispersion. Therefore,  
375 aggregation of the latex particles is observed. This phenomenon can also be deduced from zeta  
376 potential measurement as a function of both pH and PBTC concentration. The results, as reported  
377 in Fig 10, quantitatively indicate the macroscopic phenomenon observed in Fig 9. At low PBTC  
378 concentration ( $< 500$  ppm) and acidic pH ( $< 5$ ), PBTC dissociation is low. Consequently, low  
379 PBTC adsorption occurred, and no zero-zeta potential domain was observed. By increasing the  
380 PBTC concentration and the incubation pH, the aggregation phenomenon occurred in the zero-  
381 zeta potential range. This is mainly governed by charge-charge electrostatic interactions. This  
382 phenomenon can be applied in rapidly detecting the PBTC concentration range of unknown  
383 aqueous solutions.

384 In the practical detection of PBTC concentration, an unknown solution is sampled, and its  
385 pH is measured. PBTC or PBTC derivatives are employed in a low concentration range. The  
386 major competitive compounds that possess similar functional groups may be other phosphate  
387 species. The experiments were conducted in a phosphate buffer solution, which accounts for a  
388 high concentration of possible competitors. Then, the agglutination test is performed by mixing  
389 the solution and the synthesized PS latexes at a given ratio. After 1 min, the aggregation domain  
390 state (stable/unstable) is evaluated. For example, if the unknown sample (measured at pH 7)

391 shows macroscopic aggregation after mixing, this means that the concentration range of PBTC is  
392 higher than 500 ppm. The sample's pH is then adjusted to a more acidic value until a stable  
393 domain (no macroscopic aggregation) is observed. The concentration of PBTC in the unknown  
394 solution is therefore identified. However, if there is still macroscopic aggregation after adjusting  
395 the pH to strong acidic conditions, dilution of the unknown sample is required, and the diluted  
396 solution is subjected to the same procedure. In contrast, if the macroscopic aggregation is not  
397 detected at the first test, the pH of the solution is adjusted to more basic conditions until  
398 aggregation occurs. However, if no macroscopic aggregation is observed after reaching very  
399 strong basic conditions, it may be due to an excessively low PBTC concentration, and the  
400 unknown solution needs to go through a concentrating process (e.g., by evaporation method).  
401 The developed latex agglutination assay is facile and does not require special skills or equipment  
402 for operation. The technique is applicable for monitoring a wide range of PBTC concentrations  
403 and has high potential for practical use in various fields, especially in industrial water-cooling  
404 systems, wastewater treatment processes, and toxic compound monitoring.

405

#### 406 **4. Conclusions**

407 A process for qualitative and quantitative detection of organophosphate (PBTC) has been  
408 successfully developed using a simple latex agglutination assay. Positively charged PS latex  
409 particles, prepared through emulsifier-free emulsion polymerization, serve as the adsorbent. The  
410 obtained amine-functionalized PS particles exhibit monodispersity with an average diameter of  
411  $100\pm 11$  nm. The incorporation of primary amine from the AEMH comonomer results in a high  
412 positive zeta potential value (+46 mV) at a pH below 10. In addition, the behaviour of the  
413 nanoparticles under different conditions (pH and PBTC concentration) was investigated. The  
414 zeta potential decreased with the rising pH and PBTC concentration, especially at high  
415 concentrations. This rapid modification of the surface charge is attributed to an overload of  
416 negative charge values in the system. Furthermore, increasing the PBTC dosage led to a decrease  
417 in the zeta potential of the particles, eventually reaching equilibrium under basic conditions,  
418 indicating that suitable positive sites were completely occupied. Adsorption kinetics and  
419 isotherms of PBTC on the material's surface were examined to determine the adsorption capacity  
420 and mechanism using a colorimetric method. The quantitative results indicated that increasing

421 PBTC content in the aqueous medium improves the particle's adsorption capacity. In addition,  
422 increasing the pH value generated more negative ions from the deprotonation of the acid groups,  
423 leading to increased adsorption capacity. The results suggest that the electrostatic interactions  
424 and hydrogen bonding between the positively charged layer on the particle's surface and  
425 negatively charged organophosphate molecules drive the latex aggregation mechanism. This  
426 mechanism can be effectively employed for the rapid detection of PBTC concentration.  
427 Positively charged PS particles offer promising opportunities for the practical monitoring of  
428 phosphate additives in a water medium, offering a simple process, fast detection, low cost, and  
429 reduced chemical and equipment. In the case of mixtures, the PBTC detection may be impacted  
430 depending on the nature of the compounds present in the system. However, without dedicated  
431 experiments, it is not possible to affirm to which extent the detection will be impacted at this  
432 stage.

433

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443

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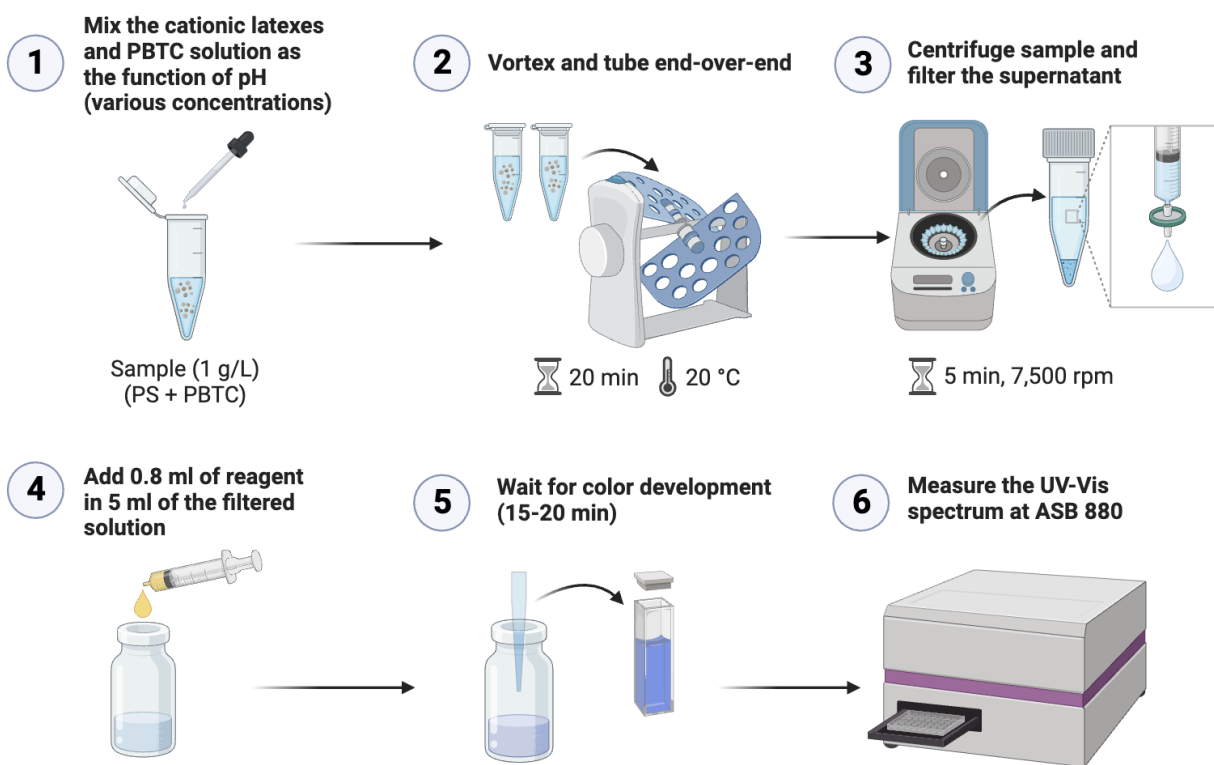
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 609 Fig 1. The adsorption process of PBTC on the cationic PS latex particles and the colorimetric  
 610 determination

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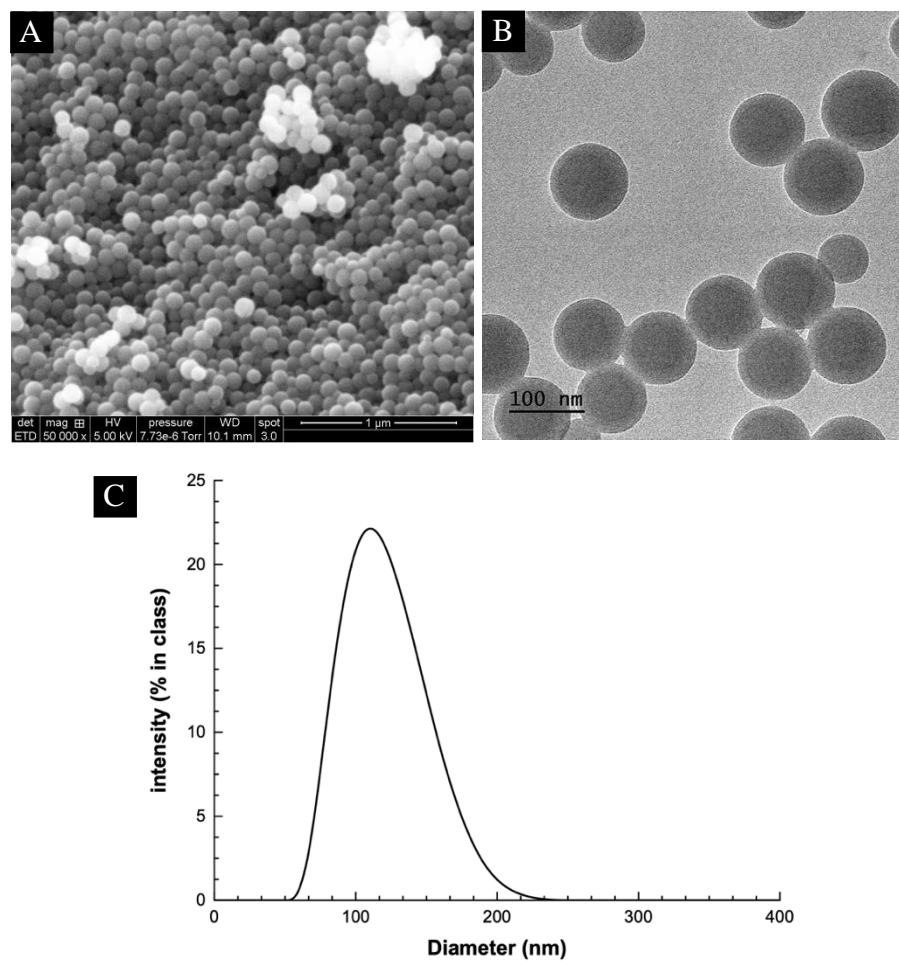
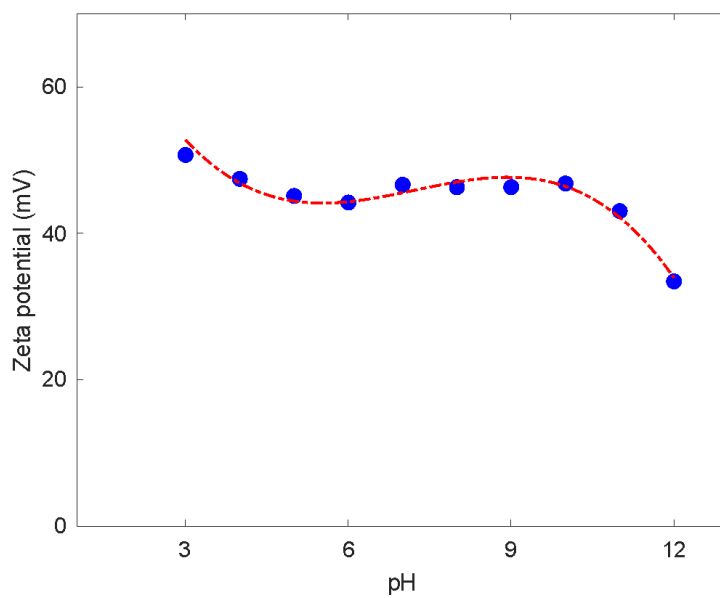


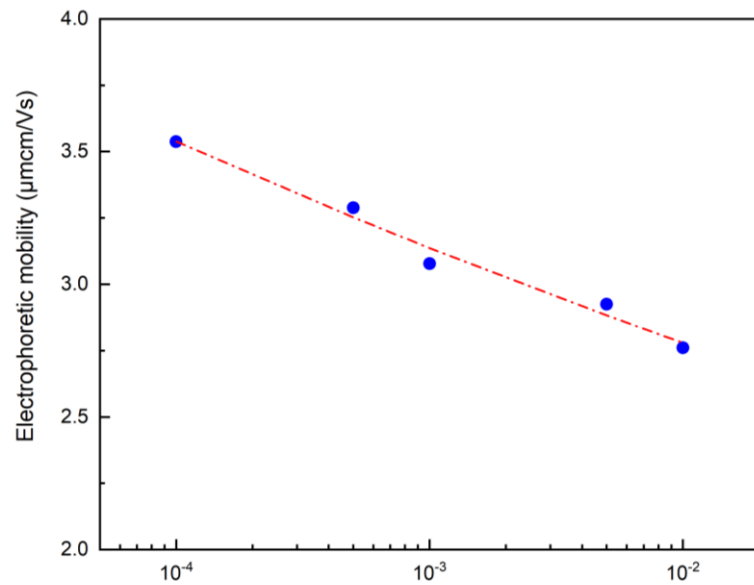
Fig 2. SEM (A) and TEM (B) images and hydrodynamic size (C) of the prepared cationic PS latex particles

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683 Fig 3. (A) Zeta potential of the prepared cationic PS latex particles as a function of pH and  
684 (B) Impact of electrolyte concentration on the electrophoretic mobility of PS latex particles

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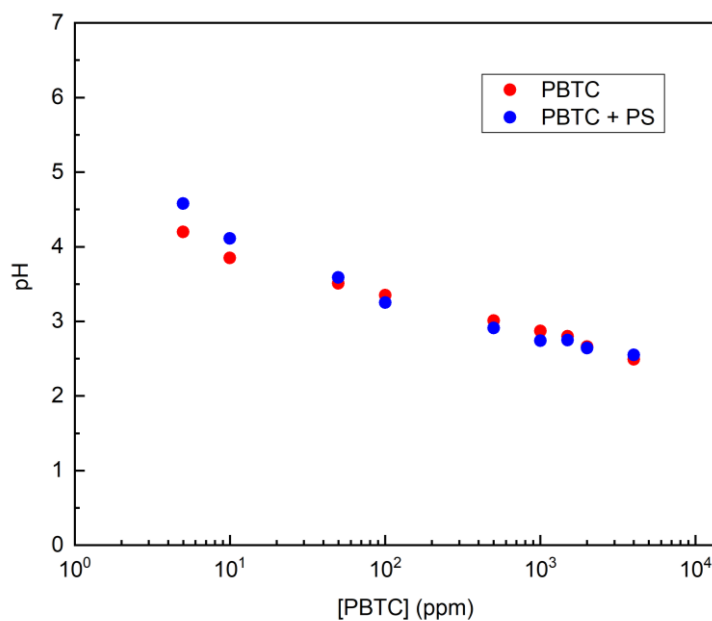
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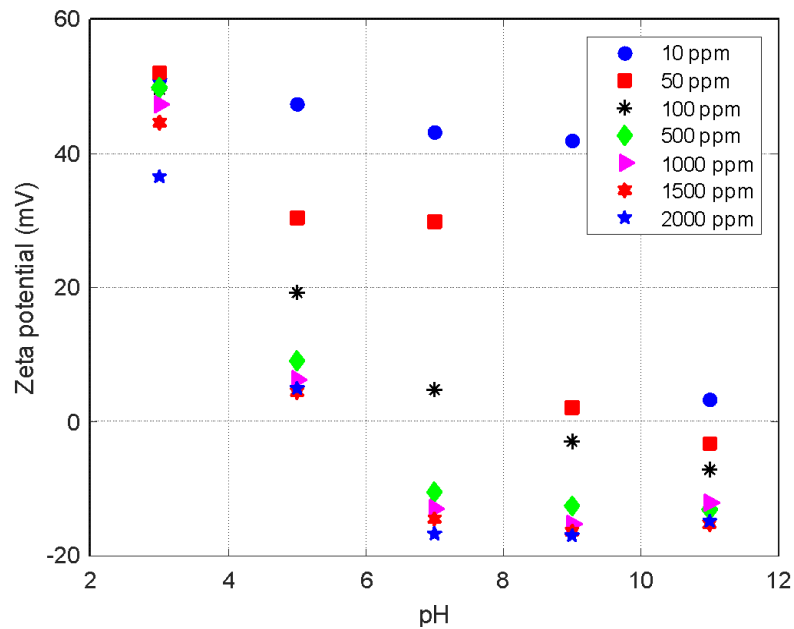
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700 Fig 4. Effect of adding PS latex particles on the pH of PBTC solutions at different concentrations

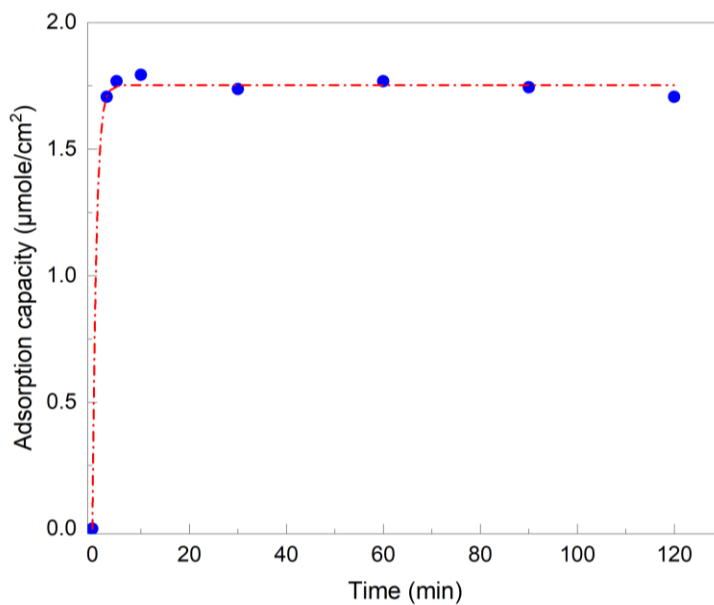
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704 Fig 5. Zeta potential of cationic PS latex particles added in PBTC solutions as a function of  
 705 PBTC concentrations at specific pH between 3-11



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707 Fig 6. The adsorption kinetics of PBTC on the PS latex particle's surfaces at an initial PBTC  
 708 concentration of 1000 ppm and pH 5

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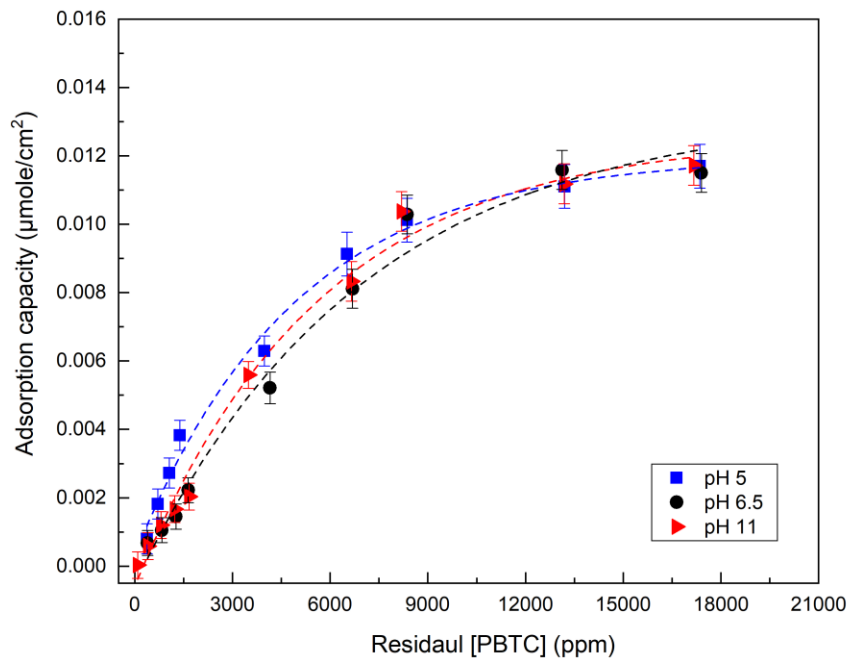
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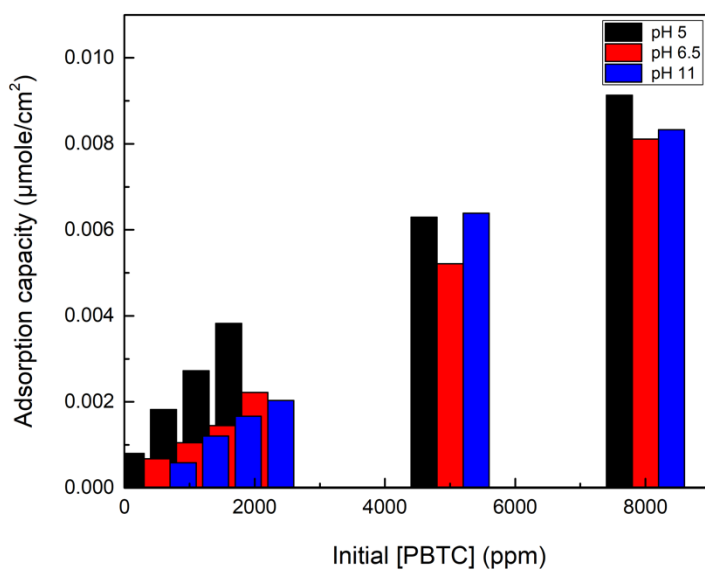
724 Fig 7. The adsorption isotherm of PBTC on the PS latex particle's surface at different pH  
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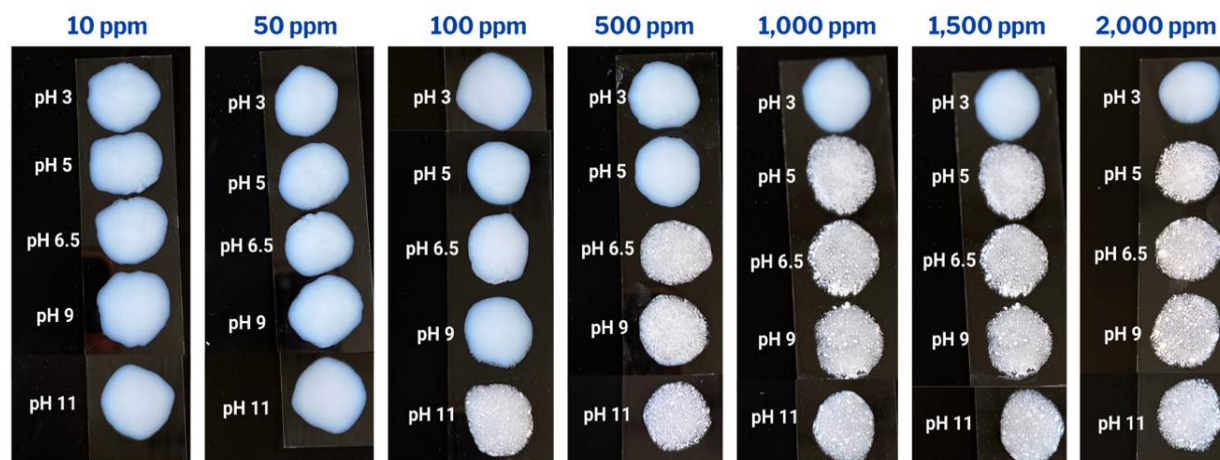
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727 Fig 8. The adsorption capacity of the anionic-charged PBTC on the particle's surface at different

728 pH and the initial PBTC concentrations

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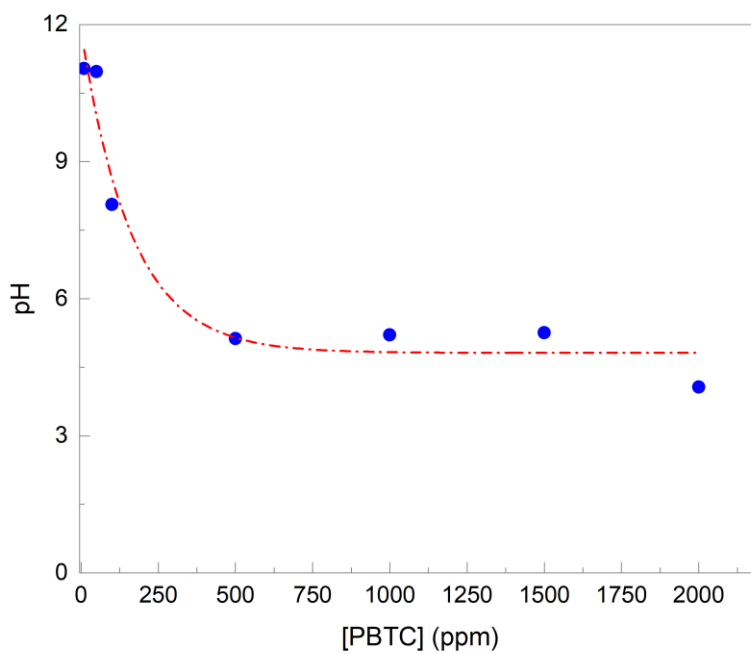
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732 Fig 9. Latex aggregation phenomenon for PBTC detection as a function of pH and PBTC  
733 concentration

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736 Fig 10. The relationship between pH and PBTC concentration at zero-zeta potential points