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# Enhanced removal of polystyrene nanoplastics by air flotation modified by dodecyltrimethylammonium chloride: Performance and mechanism

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ABSTRACT

Nanoplastics exhibit greater environmental biotoxicity than microplastics and can be ingested by humans through major routes such as tap water, bottled water and other drinking water. Nanoplastics present a challenge for air flotation due to their minute particle size, negative surface potential, and similar density to water. This study employed dodecyltrimethylammonium chloride (DTAC) as a modifier to improve conventional air flotation, which significantly enhanced the removal of polystyrene nanoplastics (PSNPs). Conventional air flotation removed only 3.09% of PSNPs, while air flotation modified by dodecyltrimethylammonium chloride (DTAC-modified air flotation) increased the removal of PSNPs to 98.05%. The analysis of the DTAC-modified air flotation mechanism was conducted using a combination of instruments, including a zeta potential analyzer, contact angle meter, laser particle size meter, high definition camera, scanning electron microscope (SEM), energy dispersive spectrometer (EDS) and Fourier transform infrared spectrometer (FTIR). The results indicated that the incorporation of DTAC reversed the electrostatic repulsion between bubbles and PSNPs to electrostatic attraction, significantly enhancing the hydrophobic force in the system. This, in turn, improved the collision adhesion effect between bubbles and PSNPs. The experimental results indicated that even when the flotation time was reduced to 7 min, the DTAC-modified air flotation still achieved a high removal rate of 96.26%. Furthermore, changes in aeration, pH, and ionic strength did not significantly affect the performance of the modified air flotation for the removal of PSNPs. The removal rate of PSNPs in all three water bodies exceeded 95%. The DTAC-modified air flotation has excellent resistance to interference from complex conditions and shows great potential for practical application.



Microplastics (MPs), which are plastic particles less than 5 mm in size, have become a major international pollutant [1]. These particles come from the decomposition of large plastic products or personal care products [2–4]. Unfortunately, MPs have been found in aquatic environments worldwide [5,6], posing significant risks to the health of aquatic plants, animals, and humans [7–9]. It is predicted that emissions of MPs will reach 10,840.18 million tons by 2030 [10]. Over time, MPs break down into even smaller particles called nanoplastics (NPs), with particle sizes of less than 1 μm, which pose more serious environmental and biological health threats [11].

The toxicity of NPs is closely related to their properties [12,13]. NPs' larger specific surface area than MPs leads to increased adsorption of various chemical contaminants and pathogens, which can be released into the open water environment [14]. Studies have shown that NPs can also damage cell membranes [15], and even enter the brain, interacting with protein fibers in neurons, thus increasing the risk of Parkinson's disease [16]. NPs had been detected in both water treatment plants and drinking water [17]. A recent study confirms that the plastic content of three best-selling brands of bottled water in the US market ranges in 110,000–370,000 pcs/L, with NPs accounting for up to 90% of the total [18]. This indicates that NPs are highly likely to be directly ingested by humans, posing a serious risk to human health [19]. However, the extremely small size of NPs presents a significant challenge in their removal, which has resulted in a paucity of studies on the subject and a complex

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process [20,21]. Therefore, there is an urgent need to develop efficient, economical, and simple techniques for separating NPs from aqueous environments.

The air flotation process is a conventional water treatment method that is widely utilized in the water treatment industry due to its high safety and effectiveness in dealing with suspended substances that are difficult to degrade naturally in water. Additionally, it does not produce new toxic substances [22,23]. MPs in water is a kind of pollutant that is difficult to degrade naturally. Due to their low density and hydrophobic properties, MPs can adhere to bubbles and form floating flocs that can be separated from water [24,25]. Therefore, air flotation has great potential for MPs separation [26,27]. Studies prove that air flotation is effective in removing Micrometer and millimeter sized MPs [28,29]. However, conventional air flotation shows poor performance in removing Nanometer sized MPs, with a removal rate of almost zero [26]. Bubbles have negative charges due to the asymmetric dipoles of water molecules at the gas-liquid interface [30,31]. Similarly, NPs in aquatic environments also exhibit negative surface potentials [32]. Therefore, the electrostatic repulsion between the two is a significant factor contributing to the low removal efficiency. Furthermore, the low probability of collisional adhesion between nanoparticles (NPs) and bubbles contributes to the extremely low removal rate [28,33].

Based on studies of removing MPs, it is hypothesized that modifying the air flotation process with polymers or surfactants has significant potential for removing NPs [34,35]. Cationic modifiers, such as cetyltrimethylammonium bromide (CTAB), dodecyltrimethylammonium chloride (DTAC), and poly diallyl dimethyl ammonium chloride (PDADMAC), can induce a positive charge on the surface of bubbles. This transforms electrostatic repulsion into electrostatic attraction [36], and causes bubbles to exhibit a positive surface potential [26,37]. Additionally, DTAC, PDADMAC, and anionic surfactants such as sodium oleate (NaOL) and sodium dodecyl sulfate (SDS) can increase the hydrophobic forces between bubbles and the object to remove [26,35,37], facilitating their separation from water [38]. Theoretically, the modified air flotation should yield positive results for NPs removal.

To summarize, the modified air flotation process has a broad application prospect in effectively separating NPs in water. However, there is still a lack of relevant research in this area. Polystyrene (PS) is considered one of the most representative MPs due to its ubiquitous and difficult-to-degrade stability [39,40]. This study focused on PSNPs and utilized five modifiers, namely DTAC, CTAB, PDADMAC, SDS, and NaOL, to conduct batch air flotation experiments. This study aimed to achieve the following objectives: (1) To compare the effectiveness of various modifiers for removing PSNPs using air flotation and to select the best-performing modifiers from among them; (2) to investigate the performance of the optimal modifier for removing PSNPs; (3) to elucidate the main mechanism of air flotation modified by the optimal modifier for removing PSNPs using a series of characterization techniques; (4) to investigate the effects of adjusting influencing factors such as modifier dosage, flotation time, aeration, pH, and ionic strength and to evaluate the stability of the system and the potential of the practical application of the DTAC-modified air flotation by simulating the real water treatment environment with the actual water body.

DTAC, PDADMAC, and NaOL were all purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Anhydrous disodium hydrogen phosphate ($Na_2HPO_4$), anhydrous sodium dihydrogen phosphate ($NaH_2PO_4$), and CTAB were sourced from Chengdu Kelong Chemical Co., Ltd. SDS was procured from Tianjin Huadong Reagent Factory. PSNPs (2.5 wt%) were purchased from Wuxi Ruige Biotechnology Co., Ltd., with an average particle size of 100±8 nm and a density of 1.05 g/cm³, characterized as monodisperse microspheres. The purity of the chemical reagents used in the experiments was analytical grade or higher. The ultrapure water used in the experimental process was prepared using the Ultrapure Fully Automatic Water Softening System purchased from Sichuan Youpu Ultra-Pure Technology Co., Ltd. The experiment employed the UV-1800 PC UV–visible spectrophotometer purchased from Shanghai Meipuda Instrument Co., Ltd. The concentration-absorbance standard curve of PSNPs was determined through full scanning, and subsequently, the concentration change of PSNPs during the treatment was measured. The pH value of the solution was measured using the FE28 pH meter (METTLER TOLEDO, FiveEasy series, USA). All solutions were used immediately after preparation.

The purchased PSNPs dispersion was added to ultrapure water to configure a PSNPs contamination solution with a 10 mg/L concentration. The flotation system (S1 in Supporting information) employed a cylindrical flotation device with an aeration plate at the bottom. Air was introduced to the aeration plate *via* an air pump (YeTing-009, Air Pump, China), generating uniformly rising bubbles at the bottom of the flotation column. Various modifiers were dissolved in ultrapure water to prepare surface modifier solutions. The prepared flotation modifier solution was extracted and added to the aforementioned PSNPs contaminated solution. After thorough mixing, flotation was initiated immediately. Each set of parallel experiments was conducted at least three times.

The determination of PSNPs concentration referenced previous studies [41]. The concentration of PSNPs was measured at a detection wavelength of 226 nm using a UV-visible spectrophotometer (UV-1800 PC). Based on the concentration of PSNPs and their corresponding absorbance, a concentration-absorbance standard curve for PSNPs was obtained over a concentration gradient of 0–10 mg/L (S2 in Supporting information), with a correlation coefficient ($R^2$) of 0.99995. The calculation formula for removal efficiency of PSNPs is detailed in S3 (Supporting information).

The characterization of NPs and flocs involved the use of a high definition camera (FDR-AX60, Sony, Japan) to capture images of the solution changes in the flotation column and the formation of surface flocs before and after conventional and modified flotation treatments. Analysis of the changes in surface potential before and after the process was conducted using a zeta potential analyzer (Nicomp 380 Z3000, PSS, USA), and the particle size distribution of the scum and supernatant before and after the process was measured using a laser particle size analyzer (AccuSizerTM 780 from Particle Sizing Systems, Santa Barbara, CA, USA). The NPs dispersion before the treatment and the floc float suspended after the air flotation treatment were collected and dried in a vacuum freeze dryer (FDU-1200, EYELA, JPN). Scanning electron microscope (SEM) was employed for the examination of surface morphology alterations, while elemental distribution was analyzed *via* energy dispersive spectrometer (EDS) to elucidate the binding interaction between PS and DTAC. Fourier transform infrared spectroscopy (FTIR, Nicolet 6700, Thermo, USA) was employed to characterize and analyze the materials before the treatment and the flocs generated after the treatment, to determine changes in chemical bonds. The detection range was set between 4000 $cm^{-1}$ and 400 $cm^{-1}$, with a wavenumber accuracy of 0.01 $cm^{-1}$ and a resolution of 0.09 $cm^{-1}$. Contact angle measurements of dried PSNPs and flocs were performed using a contact angle meter (JC2000D4B, Shanghai Zhongchen, China) to characterize changes in hydrophobicity.

In this study, CTAB, DTAC, SDS, NaOL and PDADMAC were selected as modifiers to remove PSNPs by air flotation. Meanwhile, the removal performance of conventional and modified air flotation were compared. The average maximum removal rate of PSNPs is presented in Fig. 1. The results showed that conventional air flotation removed only 3.09% of PSNPs on average. However, after the addition of five modifiers, the removal effect improved to varying degrees. The removal of PSNPs by SDS-modified air flotation increased to 7.42%. The removal rate of PSNPs by PDADMAC-modified

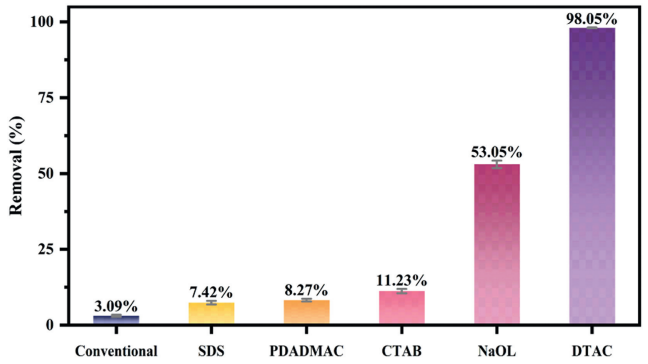


**Fig. 1.** Removal of PSNPs by conventional air flotation and modified air flotation with different modifiers. $[PSNPs]_0 = 10$ mg/L, pH ≈ 5.8 (pure water), flotation time = 20 min.

air flotation increased to 8.27%. The removal rate of PSNPs by CTAB-modified air flotation increased to 11.23%. The removal rate of PSNPs by NaOL-modified air flotation significantly increased to 53.05%. The removal of PSNPs by DTAC-modified air flotation was significantly enhanced, with the average maximum removal rate reaching 98.05%.

However, PDADMAC and NaOL, which had good performance in previous studies [26,37], did not achieve the desired results. DTAC, which had been less frequently mentioned in previous studies, exhibited exceptional performance in removing PSNPs. This study provided a comprehensive and detailed analysis of the performance of DTAC-modified air flotation in removing PSNPs. A comparison of high definition images (S4 in Supporting information) before and after the experiments of conventional air flotation and DTAC-modified air flotation revealed a significant difference between their performances in the air flotation system before and after the treatment. The conventional air flotation test yielded no discernible changes above the liquid surface of the column. However, DTAC-modified air flotation led to the formation of white flocs visible to the unaided eye, which were agglomerates of PSNPs and DTAC.

Next, the variation of the concentration of PSNPs under different DTAC dosages was explored, and the results are shown in Fig. 2a. Additionally, this study compared the performance of air flotation in removing PSNPs under different DTAC dosages, as shown in Fig. 2b. Without the surface modifier, conventional air flotation only removed 3.09% of PSNPs in 20 min. However, the mean removal of PSNPs using DTAC-modified air flotation was as high as 98.05%, representing a 95% improvement in removal.

As can be observed from Fig. 2a, the concentration of PSNPs decreases more rapidly as the dosage of modifier approaches the optimal dosage. The modified air flotation can efficiently remove PSNPs in a short time. And by observeing the concentration change curve of PSNPs, it can be found that when the dosage of DTAC is at the optimal level, the concentration of PSNPs was reduced to less than 5% of the initial concentration within 7 min. Afterward, the concentration tends to level off, and there was no significant change. That is, the DTAC-modified air flotation can remove more than 95% of PSNPs from the initial solution in only 7 min. Therefore, the duration of air flotation can be shortened to 7 min, which is favorable for cost control and practical application.

Based on the results presented in Fig. 2b, the optimal dosage of DTAC is approximately 0.5 mg/L. When the DTAC dosage was in the range of 0.25–1 mg/L, the modified air flotation can remove PSNPs up to 90% within 7 min. If the concentration exceeded this range, air flotation with other DTAC dosages cannot achieve the same removal effect within the same time frame. It should be noted that both DTAC dosages, above and below the optimal dosage, result in a decrease in removal efficiency of PSNPs to varying degrees.

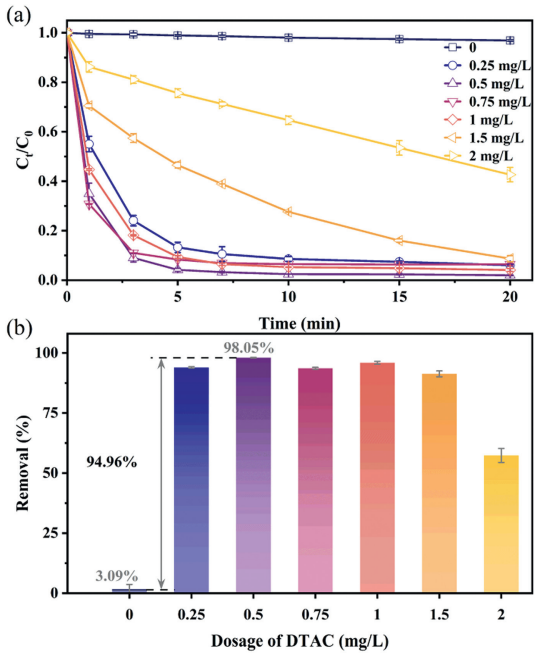


**Fig. 2.** (a) Changes in the concentration of PSNPs under different DTAC dosages. (b) Relationship between DTAC dosage and removal rate. $[PSNPs]_0 = 10$ mg/L, pH ≈ 5.8 (pure water), flotation time = 20 min.

The reason why the DTAC-modified air flotation can greatly enhance the removal of PSNPs is most likely that it is a targeted solution to the problems and limitations of the conventional air flotation in the removal of PSNPs. DTAC is a positively charged quaternary ammonium surfactant. The molecule contains a trimethylammonium chloride ion, which gives it a positive charge [42]. Additionally, the DTAC molecule has a hydrophobic dodecyl group. Alkyl chains are long chains of carbon atoms that typically exhibit hydrophobicity due to their composition of primarily carbon and hydrogen, lacking polar bonds in the molecule [43]. Therefore, it is hypothesized that electrostatic attraction and enhanced hydrophobicity may be the main mechanism of action. To systematically reveal the mechanism of removing PSNPs by DTAC-modified air flotation, a large number of experiments were conducted, and a series of characterizations were carried out.

PSNPs are negatively charged on the surface [44]. The air flotation system relies on bubbles, which also have a negative electrical charge [45]. The electrostatic repulsion between the two greatly weakened the collisional adhesion effect, which led to the low removal efficiency of PSNPs by air flotation. In contrast, DTAC is a cationic surfactant with a large number of positive charges on its surface. Due to the high interfacial potential of the bubbles, the cationic modifier will be the first to bind to the bubbles generated by the air flotation system and firmly attach to the bubble surface [46]. DTAC can correct the charge carried by the surface of bubbles, transforming the electrostatic repulsion between bubbles and PSNPs into electrostatic attraction, thus enhancing the removal effect [47]. To clarify the mechanism of DTAC-modified air flotation, it is necessary to investigate the changes in zeta potential during the process. The zeta potentials of PSNPs, DTAC, and the initial PSNPs contaminated solution modified with DTAC were measured before the start of the treatment. Simultaneously, measurements were taken on the zeta potentials of the upper suspension and upper clear solution in the flotation column after the treatment. The results are presented in Fig. 3.

The measurements show that the initial zeta potential of DTAC was 16.44 mV, while that of PSNPs was −15.64 mV, indicating

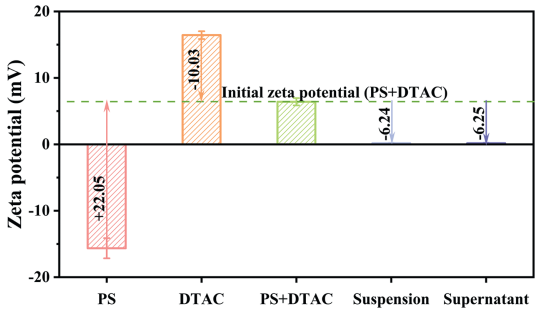


**Fig. 3.** Zeta potential before and after the treatment.

diametrically opposite zeta potentials. Upon adding the DTAC, the initial zeta potential of the PSNPs solution was found to be 6.41 mV, indicating the presence of charge attraction in the DTAC-modified air flotation treatment. The zeta potentials of the solution and scum were examined after the air flotation treatment. Both the upper suspension and the supernatant had a zeta potential of approximately 0.16 mV. It is worth noting that the PSNPs contaminated water prior to the addition of DTAC would have been significantly negatively charged. This indicates a significant charge attraction phenomenon in the DTAC-PSNPs system throughout the air flotation process. The zeta potential of the DTAC-PSNPs system was nearly zero after the experiments, indicating the presence of strong electrostatic attraction in the system. This also explains the weakening effect observed when PSNPs were removed with DTAC outside the optimal concentration range. If the DTAC dosage is lower than the optimal dosage, there is not enough positive charge to neutralize the negative surface potential carried by PSNPs. Consequently, the ideal removal rate cannot be achieved. When the dosage exceeds the optimal dosage, the excess DTAC produces more than the demand for the positive charge. This results in an interface potential between bubbles and PSNPs that is too high, causing electrostatic repulsion and difficulties in adhesion. These issues negatively impact the performance of DTAC-modified air flotation. In addition, the high dosage of surface modifier can also cause the solution surface tension to decrease, which leads to the generation of bubbles of smaller size, and thus the probability of collision adhesion between PSNPs and bubbles in the solution is lower [48,49].

Additionally, the measurement of surface charge can be used to determine the concentration of polymers or colloids [50]. Lower zeta potentials indicate a relatively low residual surface modifier concentration after the treatment. Zeta potential measurements of DTAC-modified air flotation treating wastewater, both floc float and supernatant, converged to a potential of zero, indicating a very low residual DTAC concentration in the treated water. This suggests that DTAC is a highly utilized material in the air flotation process, with minimal environmental impact. It can also indicate from the side that the adhesion between DTAC and PSNPs is very strong, and no obvious shedding phenomenon occurs. Through the detection and analysis of zeta potential, it can be seen that the electrostatic attraction effect is one of the main mechanisms for DTAC-modified air flotation to greatly improve the removal rate of PSNPs.

Another possible reason is that although MPs possess inherent hydrophobicity [26], the hydrophobicity of PSNPs is not sufficient to allow for a tight bonding with bubbles. In this way, the weaker hydrophobic force between PSNPs and bubbles leads to a low collisional adhesion efficiency between the two and a poor removal effect. Long-chain surfactants containing both hydrophilic and hydrophobic components can extend the hydrophilic groups into water, while the hydrophobic groups attach to the surface of MPs, enhancing their hydrophobicity through van der Waals and hydrophobic forces [51]. To characterize whether the hydrophobicity of PSNPs changed during the DTAC-modified air flotation treatment and the magnitude of the change, the contact angles (CA) of the freeze-dried treated PSNPs and the bubbles-DTAC-PSNPs flocs were measured and analyzed by using a contact angle meter. The results are presented in S5 (Supporting information). Characterizing the CA can more intuitively reflect the change of hydrophilicity on the surface of PSNPs before and after the air flotation.

Prior to the commencement of the experiment, the CA of PSNPs was consistently maintained at $91.8° \pm 1.6°$, indicative of a relatively slight hydrophobicity. However, after collecting and drying the bubbles-DTAC-PSNPs floc floating on the surface after the experiment, it was detected that the CA of the floating flocs increases significantly by more than 70° to $161.6° \pm 2.9°$, indicating a significant enhancement in the material's hydrophobicity. The dodecyl group in the DTAC molecule is an alkyl chain with hydrophobicity, so it can exhibit strong hydrophobicity in water [43]. Furthermore, the CA of the floating flocs has exceeded 150°, and PSNPs have transitioned from exhibiting slightly hydrophobic properties to being classified as superhydrophobic materials. In addition, both bubbles and PSNPs have negative surface potentials. Therefore, the DTAC adheres firmly to bubbles *via* positively charged trimethylammonium chloride ions and closely adheres to PSNPs *via* strongly hydrophobic dodecyl groups. DTAC's superhydrophobic groups can significantly strengthen the hydrophobic force between PSNPs and bubbles, increasing the probability of collision adhesion and enhancing the removal effect. Therefore, superhydrophobicity effect is also the main mechanism of DTAC-modified air flotation.

A high definition camera was employed to capture images and conduct a visual observation of the surface liquid level of the device following the treatment of conventional air flotation and DTAC-modified air flotation (S6 in Supporting information). In contrast to the surface liquid surface, which did not exhibit any discernible changes following the conventional air flotation treatment, a layer of white floc was observed on the surface liquid surface following the DTAC-modified air flotation test, which could be readily discerned by the unaided eye. This indicates that air flotation modified by DTAC can indeed generate bubbles-DTAC-PSNPs flocs, which subsequently rise to the liquid surface to form flotsam.

To study the combination of PSNPs and DTAC, the surface morphology of the materials before and after the air flotation treatment was analyzed by SEM (S7 in Supporting information). The surface of PSNPs was flat and smooth, and the particle size was uniform, primarily around 100 nm. Prior to air flotation, the PSNPs were dispersed throughout the solution and exhibited minimal aggregation. The surface of DTAC exhibited a rougher texture, with the presence of folds and laminar structures, which could serve as potential adhesion sites for PSNPs. The difference between the morphology of DTAC and PSNPs was readily apparent and easily distinguishable. Furthermore, it is evident that the spherical PSNPs particles, which were dispersed prior to air flotation, were arranged in a tightly stacked layer around the DTAC, forming a particle-coated structure. The SEM results corroborate the robust bonding effect of the DTAC and PSNPs in the modified air flotation process. The considerable number of agglomerated nanoplastic particles also substantiates the robust PSNPs removal capability of the modified air flotation process.

EDS was employed to investigate the elemental distribution of PSNPs, DTAC, and flocs, further validating the strong adhesion between PSNPs and DTAC. The EDS mapping revealed the distribution of C, O, Cl on the material surface before and after air flotation, as depicted in S8 (Supporting information). And illustrates the percentage of different elements. Notably, the EDS mapping characterization of PS indicated an absence of Cl on its surface, while DTAC exhibited a Cl content of 24.67%. Moreover, the EDS mapping characterization of the flocs revealed a Cl content of 3.17%. Over-

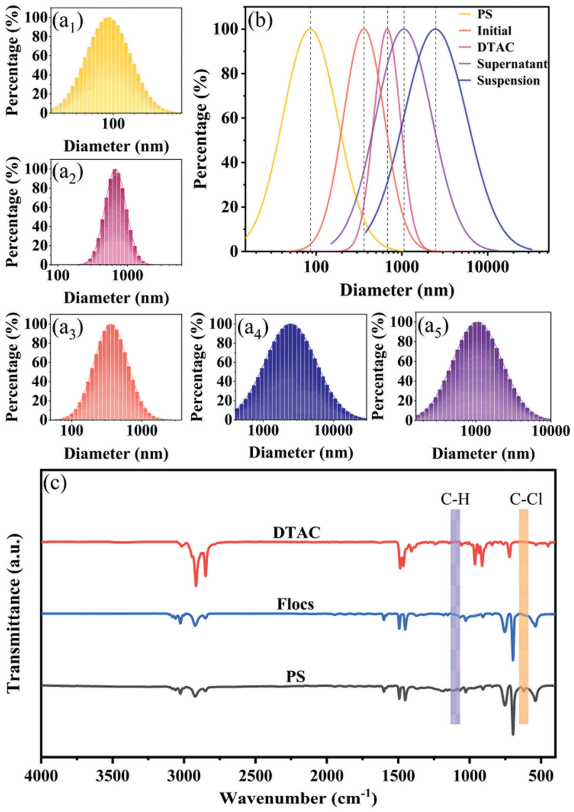


**Fig. 4.** (a) Particle size distribution: PS ($a_1$); DTAC ($a_2$); initial solution ($a_3$); suspension ($a_4$); supernatant ($a_5$). (b) Change in particle size before and after treatment. (c) FTIR spectra of PS, DTAC and floating flocs.

all, the EDS mapping elucidated the distribution of Cl, C, and O on the material surface, affirming the interaction between PSNPs and DTAC during the air flotation process.

The particle size distributions of PSNPs, DTAC and the solution before and after the air flotation experiments are shown in Fig. 4a. The average particle size of PSNPs was detected to be 111.5 nm (Fig. 4$a_1$), slightly higher than the results of the SEM (S7). This difference may be due to the tendency of spontaneous agglomeration of the NPs in the solution, leading to the formation of larger particles of PSNPs that contribute to the overall scattering [52]. The average particle size of DTAC was 716.1 nm (Fig. 4$a_2$). After the addition of DTAC, the average particle size of the initial solution of PSNPs came to 419.2 nm (Fig. 4$a_3$), which was as expected. The upper suspension and the supernatant after the modified air flotation were extracted and examined for particle size distribution, respectively. The average particle size of the upper suspension reached 3511.6 nm (Fig. 4$a_4$) and there were no more floc particles below 350 nm. The average particle size of the supernatant also reached 1400.1 nm (Fig. 4$a_5$). A comprehensive comparative analysis of the changes in the particle size distribution of the solution before and after the air flotation treatment was conducted, and the results are shown in Fig. 4b. The results of particle size detection showed that agglomerative adhesion and formation of floatable flocs with larger particle sizes occurred between DTAC and PSNPs in the modified air flotation treatment.

The FTIR spectra of PS, DTAC, and the floc float formed after the experiment are shown in Fig. 4c. No new absorption peaks appeared in the range of 609–646 $cm^{-1}$ in the floc, but the area of the corresponding absorption bands changed significantly, which can be recognized as the bending vibration of the C–Cl bond in the DTAC [53]. Moreover, the peaks were found to be altered and

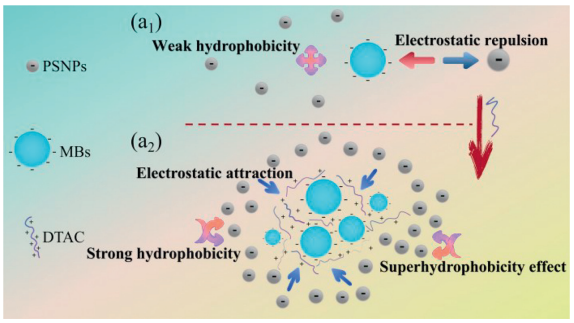


**Fig. 5.** Mechanism: conventional flotation ($a_1$); DTAC-modified flotation ($a_2$).

shifted in the range of 1087–1128 $cm^{-1}$, which was attributed to the C–H bond stretching vibration in the DTAC [54]. DTAC and PS exhibited a strong binding affinity, and it was proved that adhesion took place during the air flotation process.

The explorations confirm that the DTAC adheres to PSNPs through collision in the DTAC-modified air flotation. The dominant mechanisms are electrostatic attraction and superhydrophobicity effect. Compared to the unsatisfactory performance of the conventional air flotation in removing PSNPs (as shown in Fig. 5$a_1$), the DTAC-modified air flotation achieves a desirable removal effect through electrostatic attraction and strong hydrophobicity (as shown in Fig. 5$a_2$). The DTAC demonstrates a high positive surface potential attributed to the presence of quaternary ammonium ions. This conversion of electrostatic repulsion between bubbles and PSNPs into electrostatic attraction through charge neutralization is a significant reason in the increased removal rate of PSNPs by DTAC-modified air flotation. Superhydrophobicity is another major mechanism that dominates the efficient removal of PSNPs. The addition of DTAC can greatly strengthen the hydrophobic force between PSNPs and bubbles, forming bubbles-DTAC-PSNPs flocs. This further enhances the removal effect of PSNPs by air flotation.

To further investigate the system stability and practical application potential of the DTAC-modified air flotation, common influencing factors such as aeration volume, pH, and ionic strength were selected. And batch experiments were conducted using tap water and natural water to simulate the real water treatment environment, to explore the effect of DTAC-modified air flotation on the removal of PSNPs under different conditions.

Aeration volume is an important parameter in the air flotation [33]. The study investigated the impact of altering aeration on the efficiency of DTAC-modified air flotation in removing PSNPs. The results are shown in Fig. 6a, where it can be observed that at zero aeration, the concentration of PSNPs remained constant, indicating no flocs. The removal rate of PSNPs was gradually accelerated with the increase of the aeration volume in the flotation column, which affected the density of the bubbles and the removal capacity. However, it should be noted that the effect of aeration volume on removing efficiency is not significant and decreases with further increase in aeration volume. The final concentration of PSNPs did not differ significantly under the five aeration volume gradients.

When observing the effect of aeration volume on the final removal rate of PSNPs (as shown in Fig. 6b), it became apparent that the removal rate increased with the increase of aeration volume, albeit to a small extent. After 7 min, the removal rate of PSNPs was close to or greater than 90% for all 5 gradients of aeration volume. The final removal rate of PSNPs was 96.26% when the aeration volume was 7 L/min. Even when the aeration volume was reduced to the minimum of 3 L/min, which is less than half of the maximum aeration, the removal rate of PSNPs could reach 87.24%. The aeration volume generally affects the efficiency and effectiveness of

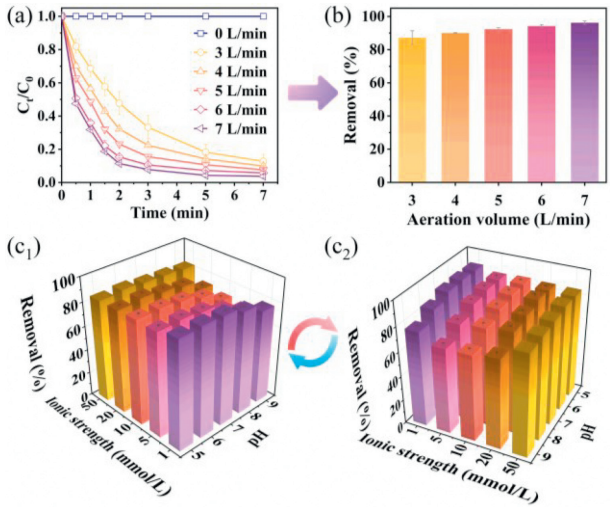


**Fig. 6.** (a) Variation curves of PSNPs concentration under different aeration levels. (b) Relationship between aeration and removal rate. (c) Effect of pH and ionic strength on removal rate. $[PSNPs]_0 = 10$ mg/L, flotation time = 7 min.

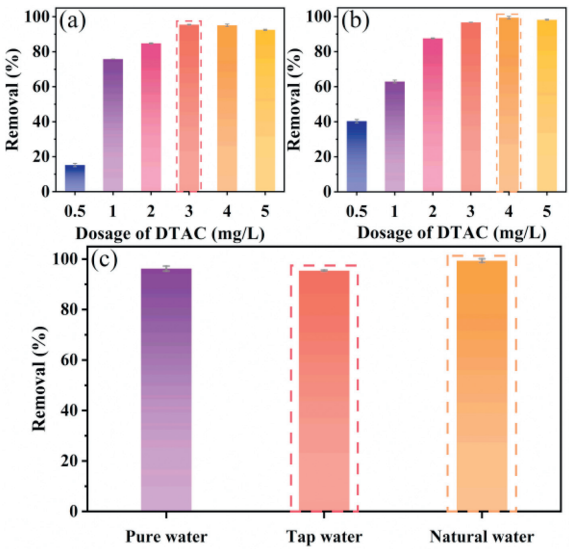


**Fig. 7.** Relationship between DTAC dosage and removal rate: tap water (a); natural water (b). (c) Removal of PSNPs by DTAC-modified air flotation in different water bodies. $[PSNPs]_0 = 10$ mg/L, flotation time = 7 min.

the DTAC-modified air flotation in removing PSNPs, but it does not significantly impact the operational performance of the process.

The results of the impact of pH and ionic strength on the performance for removing PSNPs are presented in Fig. 6c. To ensure accurate and reliable calculations, the ionic strength of the solution was determined using the Visual MINTEQ database. The presence of other anions and cations in the solution somewhat inhibited the removal effect of PSNPs under consistent DTAC dosage, compared to the removal efficiency in ultrapure water. The hydrophilicity of the PSNPs may be due to the adsorption of cations in the solution onto the surface of the electronegative PSNPs. These ions can then accumulate in the aqueous film through charge neutralization or non-covalent interactions on the surface of the PSNPs when other anions and cations are present in the solution [55]. The term "aqueous film" refers to the idea that a layer of water exists between PSNPs and the aqueous phase, which is extruded into a film [56]. Cations have a significant wetting effect by adsorbing onto the surface of PSNPs, resulting in a more hydrophilic surface and weakening the hydrophobic force. This makes it difficult for bubbles to adhere to PSNPs, ultimately reducing the removal effect [57]. Regarding the anions in solution, they may bind with positively charged DTAC and compete with PSNPs for electrostatic adsorption sites, reducing the charge attraction and resulting in lower removal efficiency. However, the presence of other anions and cations in solution did not significantly inhibit the removal performance of PSNPs, and the experimental results still showed a good removal effect.

Further observations showed that changes in pH and ionic strength changes did not significantly affect the removal performance of PSNPs by DTAC-modified air flotation. The removal rate increased with pH until pH 6 and decreased with pH above 7. However, both increases and decreases were relatively slight, with a relatively significant decrease only at pH 9. Under acidic conditions, the removal of PSNPs was more favorable, while overly alkaline environments may slightly inhibit flotation performance [26]. This differed from the findings of Jiang *et al.* [26], and it was speculated that the difference may be due to variations in the study object or the ionization or hydrolysis equilibrium of the solution. At pH 5, 6, and 7, the removal performance was not significantly affected by changes in solution ionic strength. However, at pH 8 and 9, the removal effect initially decreased and then increased with increasing ionic strength, which was an intriguing phenomenon. This may be due to a shift and balance in the charge interaction between DTAC and PSNPs caused by the change in solution ionic strength. The alteration in ionic strength had an insignificant impact on the removal performance, particularly in acidic and neutral conditions.

The performance of the DTAC-modified air flotation in removing PSNPs was tested under real water conditions using tap water and natural water. The results showed that the removal effect was somewhat reduced in both tap water and natural water, compared to ultrapure water, when the same DTAC dosing condition was applied (0.5 mg/L). This reduction is reasonable due to the presence of a large number of ions, organics, impurities, and other substances in tap water and natural water. The more complex water conditions in natural water bodies, as opposed to ultrapure water, lead to this situation. Therefore, the effects of DTAC dosage on the separation performance of PSNPs were investigated under tap water and natural water conditions, respectively. The relationship between DTAC dosage and removal rate in tap water environment is presented in Fig. 7a. The highest removal rate was achieved at a DTAC dosage of 3 mg/L. Fig. 7b presented the relationship between DTAC dosage and PSNPs removal rate in a natural water environment. The best removal effect of PSNPs was achieved at a DTAC dosing of 4 mg/L.

The removal performance of the DTAC-modified air flotation for PSNPs in ultrapure water was compared with that in tap water and natural water. The results are shown in Fig. 7c. It is easy to find that the removal performances in ultrapure water, tap water and natural water were all excellent. Specifically, the DTAC-modified air flotation removed 95.43% of PSNPs from tap water and 96.26% from ultrapure water. In natural water, the removal rate was 99.39%, effectively eliminating almost all PSNPs from the water body.

The reasons for such results are explored separately. In the case of tap water, it may be attributed to the existence of impurity ions, which have an impact on the interaction between the DTAC and PSNPs [58], leading to a slight reduction in the removal rate. For instance, monovalent cations, such as $Na^+$ and $K^+$, may impair the aggregation of PSNPs in solution. Furthermore, as the particle size of PSNPs decreases, the stability of PSNPs increases in monovalent cation system [59]. The removal of PSNPs in natural water may be enhanced by the adsorption bridging effect between PSNPs, bubbles, and DTAC, which is caused by negatively charged or hydrophobic macromolecular organic matter in the water body [46,60]. Adsorption bridging occurs when DTAC adheres to bubbles

and PSNPs, and simultaneously combines with negatively charged hydrophobic macromolecules in the water. This is similar to the bridging of particles in the aqueous environment, forming the floc network of "bubbles-DTAC-PSNPs-macromolecules". During the rising process with the bubbles, the floc network can intercept and capture free PSNPs and other particles, further enhancing the removal performance. The flocs formed in this process are larger and denser due to the adsorption bridging effect. This could be observed with the naked eye during the air flotation process.

In conclusion, this study showed that DTAC-modified air flotation was highly effective in removing PSNPs and explained its main mechanism. The average removal rate of PSNPs by DTAC-modified air flotation was 98.05%, which was significantly higher than the 3.09% removal efficiency by conventional air flotation. Furthermore, despite significantly shortening the air flotation expriment time, DTAC-modified air flotation still achieved an average removal rate of 96.26%. The air flotation is heavily influenced by electrostatic attraction and superhydrophobicity. The DTAC modified air flotation overcame the electrostatic repulsion present in conventional air flotation, and the zeta potential of the solution before and after the process confirmed charge neutralization in the system. Contact angle measurements revealed that DTAC greatly improved the hydrophobic interaction between bubbles and PSNPs, resulting in a superhydrophobic material ($161.6° \pm 2.9°$). SEM observations revealed a distinct particle-coated structure of the floc, characterized by an abundance of PSNPs particles densely adhered to the surface of DTAC molecules. This suggests a plausible bonding mechanism involving DTAC, PSNPs, and bubbles during air flotation. Complementary analyses including EDS-mapping, particle size measurements, and FTIR analyses corroborated the robust binding between PSNPs particles and DTAC molecules throughout the process, underscoring the presence of a strong interaction. The DTAC-modified air flotation was not significantly affected by aeration, pH, ionic strength, or different water bodies. In fact, natural water environments can increase the removal of PSNPs to more than 99%. The DTAC-modified air flotation has demonstrated significant potential for practical applications due to its stability and efficiency even under complex water quality conditions.

## Declaration of competing interest

The authors declare that they have no competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## CRediT authorship contribution statement

**Jinhui Xu:** Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Yanting Zhang:** Methodology, Formal analysis, Conceptualization. **Kecheng Wen:** Visualization, Software, Investigation. **Xinyu Wang:** Visualization, Formal analysis. **Zhiwei Yang:** Software, Investigation. **Yuan Huang:** Investigation. **Guozhong Zheng:** Investigation. **Lupeng Huang:** Methodology. **Jing Zhang:** Writing – review & editing, Supervision, Resources, Methodology, Funding acquisition, Formal analysis, Conceptualization.

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## Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2024.110240.

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