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Green detergent made of halloysite nanotubes

Xiaohan Yang, Jiabing Cai, Linhong Chen, Xiang Cao, Hongzhong Liu, Mingxian Liu *

Department of Materials Science and Engineering, Jinan University, Guangzhou 510632, China

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ABSTRACT

The detergent has wide range of applications and plays a critical role in daily life. However, the existing commercial detergents present the drawbacks of irreversible environmental pollution due to their discharge with wastewater. Herein, halloysite clay nanotube (HNT) with unique hollow structure was explored as a green, non-toxic, multifunctional, and cheap detergents. HNT has large aspect ratio, small size, and high adsorption ability, which provides the possibility for removing various stains from different substrates. The increased contact angle and decreased surface tension of HNT dispersion are achieved by increasing the HNT concentration, and HNT tends to stabilize oil-in-water (O/W) Pickering emulsion. The cleaning capacity of HNT on cotton fabric for dyes is almost twice that of laundry powder, indicating that highly efficient cleaning capability of HNT. HNT detergent is also effective to remove ink, tea, and chili oil from textiles with clean efficacy higher than 88%. As kitchen detergent, HNT can effectively eliminates chili oil from ceramic, stainless steel, glass, and plastic plate. Seed germination and crop growth experiment demonstrate that HNT detergent shows no toxicity towards plants and no contamination towards soil. Furthermore, the residue on the cloth of HNT detergent is negligible. Overall, HNT has great potential as an alternative detergent in the future because of its excellent cleaning efficacy and ecological friendliness.

1. Introduction

It is expected that the global market of washing detergent is growing at a rate of 4.9% from 2017 to 2025, and the global market in 2025 will reach 205.2 billion dollars [1]. This suggests a consistent high demand and usage of detergent are proceeding. However, the wastewater of traditional detergent contains phosphorus nutrient pollutants [2], which is always directly discharged into rivers and lakes through the sewer, resulting in a serious environmental pollution problems [3]. The discharge of detergent contained wastewater have an adverse influence on aquatic organisms and further disturb the growth of higher organisms, like animals and human beings. Considering that the disadvantages of artificial detergents, the natural, ecological, and sustainable detergents are on their way coming into the market. The natural detergents currently available on the market are surfactants extracted from plants [4]. For instance, detergents derived from coconut palm oil, enzyme, and lipase are useful for cleaning protein stains [4,5]. Although the natural detergents are safer than synthetic detergents, the low yields and high costs limit their application. In addition, some of them can cause skin allergies of the body, causing the potential damages [6]. Thus, new type of natural detergents with a low-cost, abundant source, and less irritating to the skin is highly demanded to be exploited. It has long been recognized that kaolin can remove oil stains on textiles or skins in daily life although few papers has been published for discussion the mechanism [7]. Recently, Pickering emulsions stabilized by nanoparticles with the benefits of lower costs, less environmental pollution, less toxic effects, and better emulsion stability have attracted increasing attentions [8,9]. For example, cellulose nanosphere from agricultural waste corncob shows higher cleaning efficiency in removing stains from various surfaces, and it is a safe, cost-effective and sustainable alternative to commercial synthetic detergents [10].

Halloysite nanotube (HNT) is a natural, bio-compatible, inexpensive, and high-performance nanomaterial [11–13]. HNT has a large aspect ratio and a tubular structure with silicon oxide tetrahedrons outside and an aluminum oxide octahedron inside of the tubes [14–17]. HNT, with the molecular formula of $Al_2(Si_2O_5)OH_4{\cdot}nH_2O$, is a hollow tube with a length of 0.02–30 μm, an outer diameter of 30–70 nm and an inner diameter of 10–30 nm [18–20]. Moreover, HNT is biocompatible and non-toxic, and previous studies proved the HNT is safe towards various cell lines and animals at certain dose [21–23]. HNT and its composites

* Corresponding author.
E-mail addresses: 1227448038@qq.com (X. Yang), 754924425@qq.com (J. Cai), 1752165934@qq.com (L. Chen), 975094609@qq.com (X. Cao), liumx@jnu.edu.cn (M. Liu).

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have been widely employed in porcelain raw materials, paper additive, wastewater treatment materials, drug delivery carrier, tissue engineering scaffold, optoelectronic material, and cosmetics [24,25]. Interestingly, HNT can be absorbed on oil–water interface to stabilize Pickering emulsions, which increase the detachment energy from the interface due to its unique hollow tubular morphology with high aspect ratio [9,26,27]. The interactions between the colloidal particles adsorbed at the oil–water interface mainly involve electrostatic force and van der Waals force [28,29]. As the particles are adsorbed at the oil–water interface, the electrostatic force between the particles repels through the water phase [30], and the dipole force through the oil phase, and the van der Waals force through the water phase and the oil phase [31]. Pickering emulsion system stabilized by bentonite and montmorillonite has been identified as having a three-dimensional network structure [30,32]. In recent research, Pickering emulsions stabilized by HNT for oil spill remediation and bioremediation technologies has been discussed [33]. Therefore, the particles can effectively slow down or inhibit the delamination of the emulsion [34–36]. Moreover, the network structure can prevent the droplets from approaching and colliding [36,37], reducing the occurrence of coalescence between emulsion drops. To allow solid particles to effectively stabilize the emulsion, the solid particle stabilizer can be partially wet by both liquids [38,39]. The wettability of the particles is usually described by the three-phase contact angle θ which determines the type and stability of the emulsion [36,40,41]. HNT is partially amphipathic to oil and water with a negative surface ζ-potential [13]. Furthermore, the size and shape of HNT are appropriated for their organizing at the oil–water interface. Additionally, it have shown that HNT-stabilized Pickering emulsions are much safe to marine bacteria than standard detergents used in petroleum industry [42].

In this study, HNT is utilized as a stabilizer at the oil–water interface of the Pickering emulsion. The basic physical and chemical properties of HNT, the stabilizing mechanisms in Pickering emulsion, the staining clean efficiency on different substrates, the toxicity of HNT towards plant, and the residue on textile were studied. Attributed to the unique structure of HNT, it shows decreased surface tensions and increased stabilization performance in Pickering emulsion. The results of the cleaning stains on the different substrates demonstrated that HNT has an attractive cleaning capacity on the dye stains. For example, the cleanliness of HNT in the removal of dyes on the cotton is nearly 1.8 times higher than that of conventional detergent. HNT was found to be harmless towards plant, while the regular detergent has a higher inhibitory effect on seed germination and crop growth. The few HNT residue indicated that the risk of human skin irritation is negligible during the process. This work demonstrated the feasibility of using natural clay nanoparticles as a high effective, safe, and cost-effective green detergents, which shows promising application in laundry and kitchen detergents.

2. Experimental

2.1. Materials

Halloysite nanotube (HNT) (mined from Yunan province, China) was obtained from Guangzhou Runwo Materials Technology Co., Ltd., China. Different dyes (gentian violet, basic fuchsin, and methylene blue) were obtained from Chengdu Aikeda Chemical Reagent Co., Ltd., China. Tea, peanut oil, ink and chili oil, cotton, Dacron, ceramic, stainless steel, glass, and plastic plate (Polystyrene, PS) were obtained from the local supermarket. Wheat and lactuca sativa seeds were acquired from Sunong Seed Industry Co., Ltd. (Jiangsu, China). Sodium dodecyl sulfate (SDS), Dodecyltrimethylammonium bromide (DTAB), and Triton X-100 were provided from Tianjin Fuyu Fine Chemicals Co., Ltd., China. Deionized water was used in all the experiments.

2.2. Preparation of the Pickering emulsions

Peanut oil/HNT Pickering emulsions was prepared by ultrasonic treatment for 20 min to get the Pickering emulsion with oil/water volume ratio of 1:10. The emulsification of emulsion was insufficient with the shorter time, while HNT was over ultrasonicated with longer time, which reduced the effect of HNT in the emulsion. O/W Pickering emulsions were stabilized by HNT at different concentrations (0, 0.5, 1, 5, 10 wt%).

2.3. Characterization

The morphology of HNT was analyzed using a transmission electron microscope (TEM) (JEM-2100F, JEOL Ltd., Japan). The HNT aqueous dispersion concentration for the TEM test was 0.05 wt%. The surface morphology of HNT and the freeze-dry Pickering emulsion sample were conducted by a scanning electron microscope (SEM) (Ultra 55 SEM instrument, ZEISS, Germany) at a voltage of 5 kV. The macro-graphs and micro-graphs of the Pickering emulsions were characterized by polarizing microscope (BX51, OLYMPUS, Japan). Atomic force microscopy (AFM) (Bioscope Catalyst Nasoscope-V, Broke Instruments Ltd., USA) was used to test the surface roughness of HNT with a scanning area of 2 μm × 2 μm. X-ray diffraction (XRD) patterns of HNT were obtained on an X-ray diffractometer (MiniFlex-600, Rigaku Corporation, Japan) with a scan rate of 5°/min ranging from 5 to 60°. Fourier transform infrared spectroscopy (FTIR) spectra of HNT was characterized by a Thermo FTIR instrument (Nicolet iS50, Thermo Fisher Scientific Ltd., USA) ranging from 4000 to 500 cm^{-1}. To determine the specific surface area and pore size of the raw HNT, the powder was verified by automated surface area and pore size analyzer (BeiShiDe 3H-2000, Instrument-ST. Co., Ltd., China). The adsorption and desorption curves were recorded. Particle size was measured with a Nano-ZS instrument (Malvern Instruments Ltd., UK). The concentration of HNT is 0.05 wt% by dispersing in the ultrapure water by ultrasonication for 30 min. The thermal stability of HNT was analyzed by a TGA instrument (Mettler Toledo, Switzerland) from 50 to 700 °C at a heating rate of 10 °C/min under an N_2 atmosphere. Zeta potentials of 0.1% HNT dispersion at different pH values and NaCl concentrations of HNT were characterized by a solid surface zeta potential analyzer (Surpass 3, Austria).

2.4. Measurement of contact angle

To measure the contact angle, the peanut oil (1 mL) was released and spread uniformly over different substrates (plastic, glass, cotton, Dacron) to completely wet the surfaces of the substrate. Then, 4 μL of different concentrations of HNT dispersion droplets were injected with a syringe with a needle tube diameter of 0.5 mm to drop onto the surface of different substrates soaked in oil. The contact angle of different HNT dispersion on the different substrates was recorded in 30 s when the HNT dispersion was touched the substrates. The value of contact angle was observed and recorded by a contact angle analyzer (DSA 100, DataPhysics, OCA-25, Germany).

2.5. Surface tension of HNT dispersion

A syringe with a diameter of 0.5 mm was used to inject 10 μL of the liquid to be tested (0.5 wt% HNT dispersion, 0.5 wt% SDS, DTAB, and Triton X-100 aqueous solution), and slowly squeezed the liquid to create droplets. The droplet pictures were analyzed to obtain the d_e (d_e is the maximum diameter of the hanging drop) and d_s (d_s is the diameter of the cross section of the hanging drop at the distance from d_e to the vertex) to calculate its surface tension by using the built-in software based on the instrument (DSA 100, DataPhysics, OCA-25, Germany). To obtain the relationship between the time and the surface tension of each test solution, d_e was measured every 180 s.

2.6. Cleaning efficiency on different textile cloths and plates

Different types of textile fabrics (Dacron and cotton) were utilized to demonstrate the cleaning effects of HNT on the elimination of stains from cloths surfaces. The cloths were cut into 5 × 5 cm^2 pieces and polluted with different dyes (gentian violet, basic fuchsin and methylene blue), black ink, tea, and chili oil to simulate stains on clothes. The stained cloth was dried in the air. The stained cloths were soaked in 10 mL of distilled water, HNT dispersion (0.5, 1, 5 and 10 wt%) and 1 wt% laundry powder (LP) solution were employed as the blank control and experimental groups. The fabrics were then placed into an ultrasonic cell cleaner for 30 min at room temperature to simulate the washing process. The samples were manually scrubbed for 15 min at the same angle and speed just like practical cleaning process, and then rinsed 3 times with deionized water to remove the remaining HNT and LP. The cleaned fabrics were naturally air-dried at room temperature. In order to measure the cleaning efficiency of the different formulations on the stains, the photographs were recorded before and after the cleaning process.

To investigate the clean ability of HNT detergent towards oils in kitchen, chili oil was selected as model for determining the clean efficacy from different plates. Various types of plates, including ceramic, stainless steel, glass, and plastic plates, have been stained with chili oil to imitate daily plates after use. Then, the dirty plates were put in an ultrasound cleaner with deionized water, HNT detergent, and dishwash liquid (DWL) for 5 min at 240 W at room temperature. The dirty plates were photographed before and after the cleaning. The photographs were analyzed by comparing the average gray value of the different stains in the photos by Image J software. The cleaning efficiency of HNT to stains in different substrates (cloth and plates) were calculated by the following equation:

$$\text{Cleaning efficiency } (\%) = \frac{G_2 - G_1}{G_0 - G_1} \times 100\%$$

where G_0, G_1 and G_2 are the average gray value of the original (G_0) and soiled cloths and plates before (G_1) and after (G_2) washing.

The whiteness retention ratio which reflected whiteness change before and after cleaning was determined as follows.

$$\text{Whiteness retention } (\%) = \frac{W_2 - W_1}{W_0 - W_1} \times 100\%$$

where W_0, W_1 and W_2 are the whiteness (%) of the original (W_0) and the soiled cloths before (W_1) and after (W_2) washing. The whiteness was measured using a whiteness meter (Datacolor ELREPHO, USA).

2.7. Toxicity evaluation of HNT on crop

Wheat and lactuca sativa seeds were firstly soaked in distilled water for 24 h. The seeds were then transferred to the container with 10 mL HNT dispersion (1 and 10%) and LP (1%) for germination and growing. The germination rate of the different groups has been calculated. Besides, the average length of shoot in different groups were counted after 7 days of cultivation.

3. Results and discussion

3.1. Characterization of HNT

Fig. 1 provides a basic characterization of the used HNT mined from Yunan province, China. As it can be seen in Fig. 1A, HNT has a hollow tubular structure with a thinner tube wall and a uniform tube

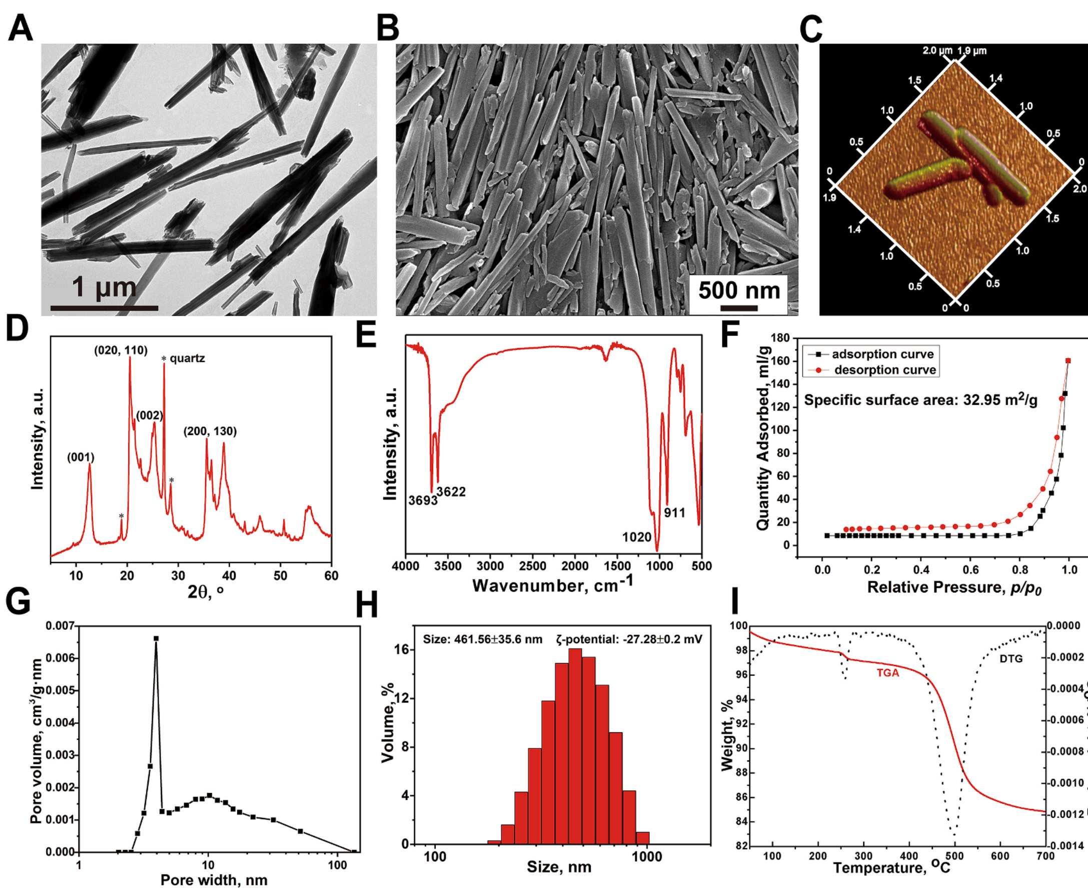

Fig. 1. Characterization of the used HNT. TEM (A), SEM (B), AFM (C), XRD (D), FTIR (E), specific surface area (F), pore size distribution diagram (G), particle size distribution (H), TGA curve (I).

morphology. The length and diameter of the used HNT have a wide distribution, while the length of tube is in 0.5–2.5 μm with external diameter is in 60–160 nm. HNT with longer tubes showing high reinforcing effect can be used for polymer fillers [43], while the different length of HNT have the advantages for cleaning different dimensional stains. SEM images in Fig. 1B clearly shows that HNT sample exhibits typical rod-shaped structure with few plate-like kaolin impurities, which are consistent with the TEM results in Fig. 1A. The AFM image of HNT in Fig. 1C shows that shorter tubes appearance, and the aspect ratio is obviously smaller than those in 1A and 1B. This may be due to the excessive ultrasound power during sample preparation process, which caused the tube to be broken. The XRD pattern of HNT illustrates that 2θ = 12.2, 20.24, 24.98 and 30-40° belong to the flections of (0 0 1), (002, 110), (0 0 2) and (200, 130) planes, respectively. It has also been found that some quartz impurities exist in the HNT sample, which is difficult to completely remove especially during the industrial process.

Fig. 1D shows the FITR spectra of HNT. The absorption peaks at 3693 and 3622 cm^{-1} are attributed to the stretching vibrations of the inner surface hydroxyl and inner hydroxyl groups of HNT, respectively. The peak at 1020 cm^{-1} is assigned to the Si-O-Si asymmetric stretching vibration, and the absorption of the hydroxyl vibration connected to Al is located at 911 cm^{-1} [44]. No peak attributed to impurities has been detected, illustrating high purity of the HNT. Fig. 1F demonstrates the specific surface area and adsorption–desorption curve. HNT has a specific surface area value of 32.95 m^2/g. As shown by the nitrogen adsorption curve in Fig. 1F, the adsorption–desorption curve of HNT shows the type II adsorption behaviour [45]. From the pore distribution curve in Fig. 1H, the pore size of HNT is 2–110 nm with a sharp peak around 4 nm and a convex peak around 10 nm, suggesting that HNT has both mesopores and macropores. Fig. 1G depicts the particle size of HNT. The average particle size of the HNT is 461.6 nm with a zeta potential of −27.28 mV at pH = 7.

Fig. 1I depicts the thermogravimetric behavior of HNT. The remaining mass of HNT at 700 °C is 84.8% of the initial mass. The differential thermogravimetric curve (DTG) curve shows that the maximum weight loss rate of HNT appears at 499.2 °C, which is attributed to the dehydration structural hydroxyl groups. The weight loss (0.55%) at 250 °C is attributed to the degradation of additives during industrial purification process of HNT (such as sodium hexametaphosphate). The changes of zeta potentials of HNT with pH value and salt concentration are then determined in order to study the stability of Pickering emulsion (Figure S1). When the pH is 2, the zeta potential of HNT is −9.6 mV, indicating a negative charge. As the pH value increases, the surface potential drops to –32.3 mV (pH = 7). As the ion concentration increases, the absolute value zeta potential of HNT gradually decreases. A high zeta potential absolute value has been reported to be beneficial to the dispersion stability of HNT dispersion [46].

3.2. The oil de-wetting mechanism of HNT

As the concentration of HNT increases, the three-phase contact angles of HNT dispersion in plastic, glass, Dacron, and cotton increase gradually (Fig. 2A). Specifically, when applied in the Dacron, the contact angle of HNT (10%) is 78.5°, which is three times more than that of

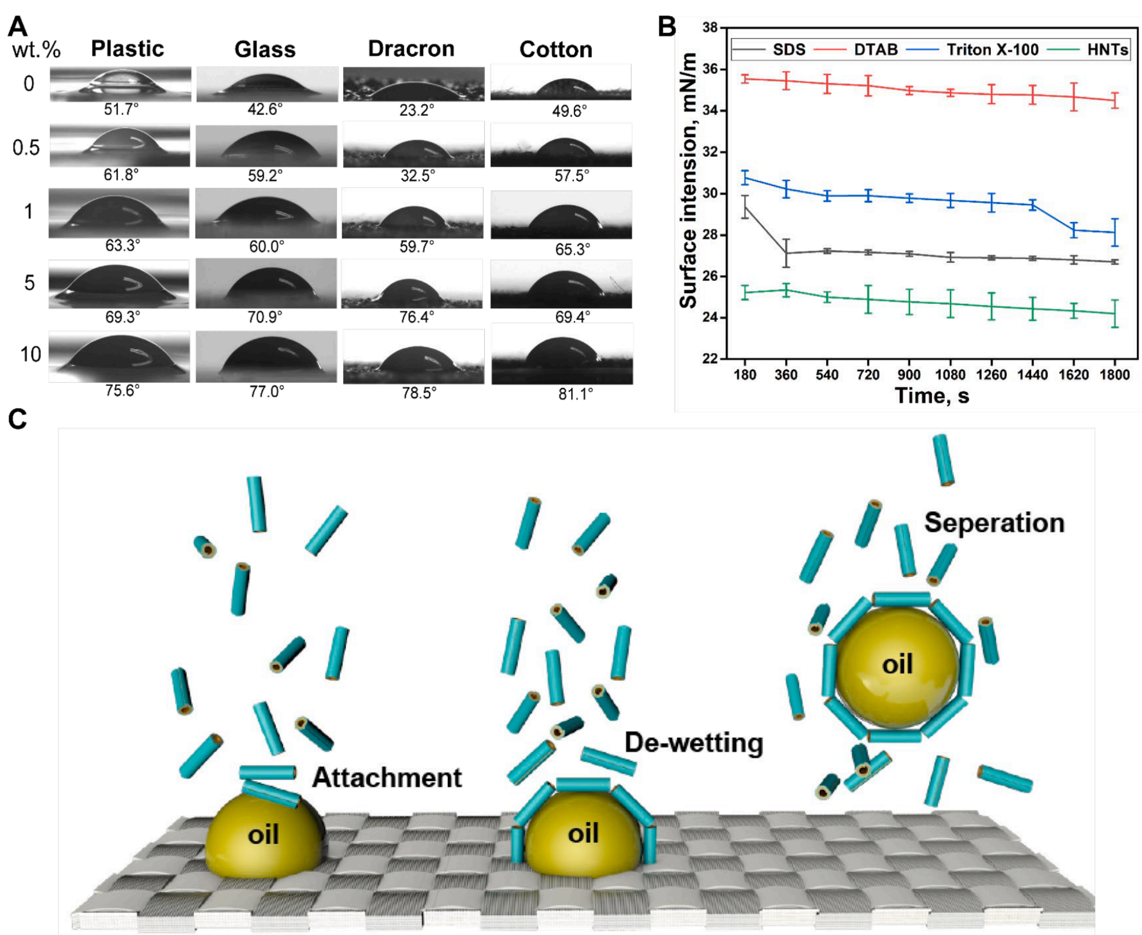

Fig. 2. The oil de-wetting mechanism of HNT. Three-phase contact angle of oil droplet in water stabilized by different concentrations of HNT on different surfaces (Plastic, Glass, Dacron, and Cotton) (A), the surface tension of SDS, DTAB, Triton X-100, HNT aqueous dispersion versus time (the surface tension was measured every 180 s for 30 min until equilibrium was reached) (B), the removal process of oil on cottons by HNT (C).

the pure water group (23.3°). The contact angles on the glass and cotton in the control group change from 49.6° and 42.6° to 81.1° and 77°, respectively. The results indicate that HNT is capable of de-wetting the oil. Furthermore, HNT in high concentration has a more effective de-wetting ability to oil compared to HNT in low concentration on the surface of textiles and plates.

The HNT de-wetting process to oil attached to the surface of the substrate is described in Fig. 2C. Firstly, as a Pickering emulsion stabilizer, HNT is absorbed at the oil–water interface gradually, and the convection force generated by the washing movement greatly conquers the adhesion between the oil and the substrate surface during the cleaning process, and the oil was removed from the surface of substrate. Additionally, after the oil releasing from the surfaces, HNT as a stabilizer is closely arranged at the oil–water interface to stabilize the oil droplets, making it difficult for the oil droplets to reattach to the surface of the substrate to achieve a good removal effect.

The surface tension of HNT and the different types of common surfactants in water were further tested. The results show that HNT has a lower surface tension compared to SDS, DTAB and Triton X-100 (Fig. 2B). The surface tensions of HNT and the three surfactants tend to decrease over time [47]. Only by reducing the surface tension of the water, can the stains and fibers be wetted better, resulting in a better decontamination and cleaning effect [48]. The reduction of the surface tension of HNT implies that HNT has a powerful capacity of being applied in detergent industry.

3.3. *HNT-stabilized Pickering emulsion*

HNT with small size, as a solid particle stabilizer in Pickering emulsion, were irreversibly adsorbed on the interface of oil–water and makes it possible to form a more stable system [37,49,50]. Besides, the irregular shape of HNT limits the particle rotation movement and allows a better emulsification. Fig. 3 shows the HNT- stabilized Pickering emulsion stored for 4 weeks. The results in Fig. 3 imply HNT tends to stabilize oil-in-water (O/W) Pickering emulsion due to the smaller size and uniform dispersion of the emulsified drops, which is an indication of the good stabilization ability of solid particles [41]. HNT are hydrophilic nanoparticles which can adsorb onto the hydrophobic oil droplet surfaces and increase the oil-in-water emulsion stability.

As the concentration of the HNT dispersion goes up, the oil droplets become smaller, illustrating that the increase of the concentration of HNT tends to stabilize the Pickering emulsion (Fig. 3A), which allows the most of particles to be adsorbed on the interface. HNTs concentration has an important influence on the droplet size and emulsion stability. The droplet size of Pickering emulsions decreases with the increase of the concentration of the solid particles. When it reaches a minimum value, the droplet size remains basically unchanged. Low particle concentration will cause the emulsion to be unstable, and high particle concentration may affect the hydrodynamic properties of the continuous phase and improve the stability of the emulsion. It is also clear that the Pickering emulsion is more stable at pH = 7 and at low ion concentrations (Fig. 3B and 3C). The negative charge of HNT increases as the pH value rises, and when the absolute value of the zeta potential rises, the electrostatic repulsion between the droplets goes up, and the stability of the emulsion is declined. While the Pickering emulsion is at neutral condition, the greater charge-induced stabilization occurs, making it more stable. As the ion concentration rises, the size of emulsion droplets decreases at lower concentration. However, the droplets tend to be larger in size gradually and the density decreases after the concentration is greater than 1 mmol/L. This is ascribed to the flocculation of HNT at low ion concentrations by making the system more stable, while HNT is more distributed with the increasing zeta potential caused by the higher ion concentration. Consequently, the Pickering emulsion becomes more stable under low ion concentration.

Figure S2 demonstrates that as the temperature increases, the size of the emulsion droplets become smaller, more uniform, and denser. It shows that as the temperature increases, the emulsifying ability of HNT gradually increases, making the oil droplets smaller and easier to be removed. With the temperature of the two phases increases, the thermal energy will be transformed into the thermal kinetic energy of the HNT in the phase, which will intensify the motion that leads to more HNT adsorption on the oil–water interface, thus improving the emulsification of the system. It suggests that the efficiency of HNT improves with the slight rise of temperature. The results implies that HNT in a proper concentration, neutral state, low ion concentration, and slightly higher temperature is more stable at the oil–water interface. Furthermore, HNT was packed at the oil–water interface, suggesting HNT was absorbed from the oil droplet surface according to the SEM images (Figure S3) for

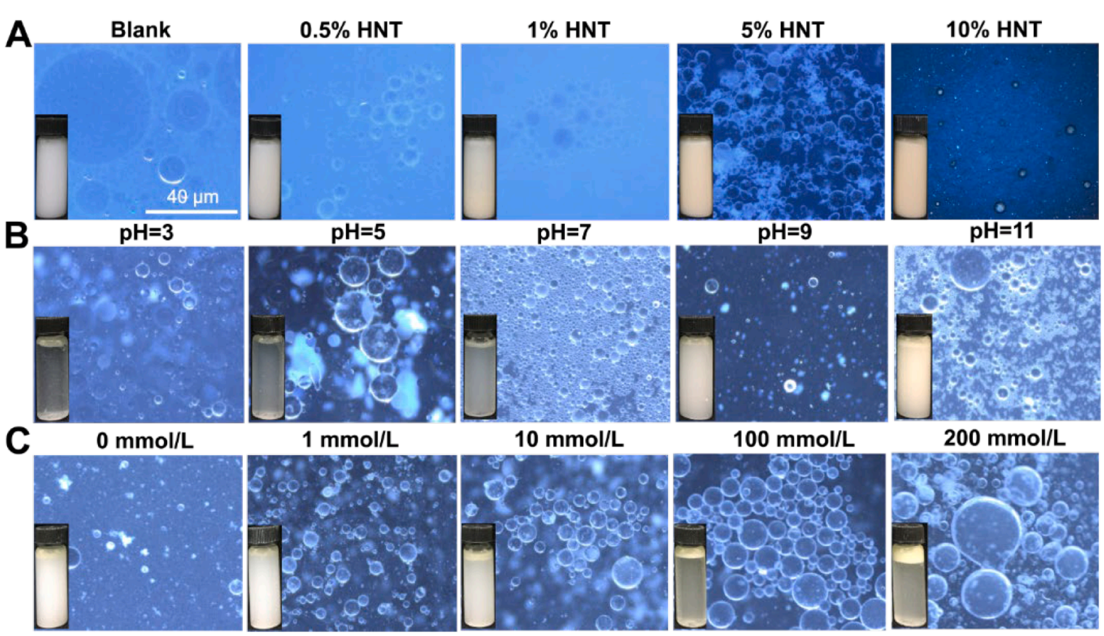

Fig. 3. HNT-stabilized Pickering emulsion stored for 4 weeks. The micrograph image of O/W Pickering emulsions stabilized by HNT. Digital photographs of the emulsion are shown in the inset, Stability comparison of O/W emulsions emulsified by different concentrations of HNT, 0, 0.5, 1, 5, 10% (A) stability comparison of O/W emulsions of 0.1% HNT dispersed in water at different pH (B) and at different NaCl concentrations (C).

the freeze-dried Pickering emulsions. Overall, HNT as O/W Pickering emulsion stabilizer exhibits a good potential for applying as detergent.

3.4. Cleaning capacity of HNT

Since HNT plays a role as a good stabilizer in the Pickering emulsion from the results above, and it is also known from other studies that the potential of emulsion stabilizer in detergent industry [51]. These inspired us that one can make use of HNT as a detergent to clean dyes and other daily stains from common textiles. Therefore, the cleaning efficiency of HNT is investigated together with the commercial LP. HNT exhibits a better cleaning ability in the removal of stains such as dyes (gentian violet, basic fuchsin and methylene blue) and tea from cotton than LP from Fig. 4A and Figure S4. For example, the cleaning efficiency of the lowest concentration (0.5%) of HNT on cotton for three dyes is very close to that of LP. When the HNT concentration increases to 10%,

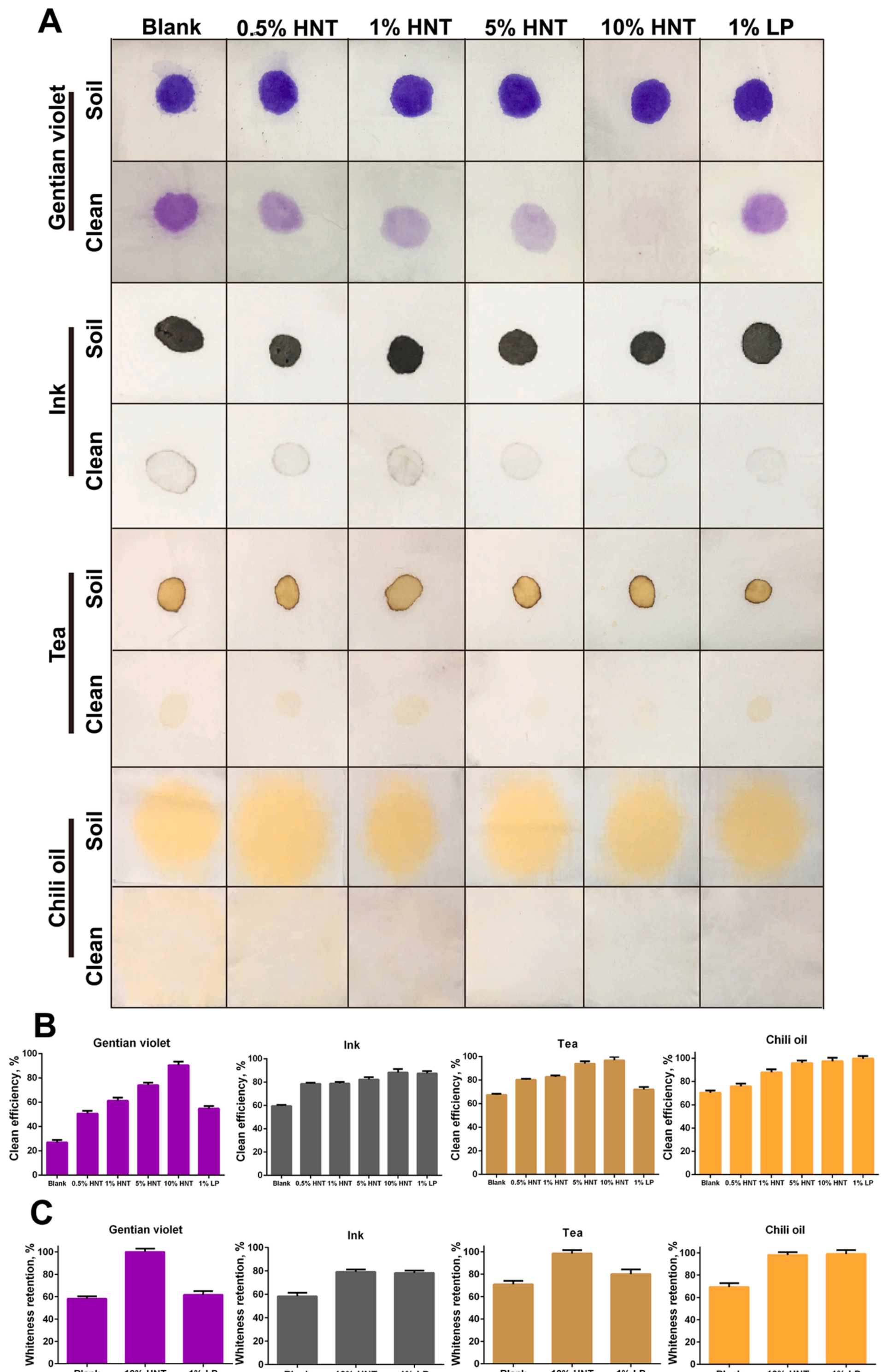

Fig. 4. Cleaning capacity of different concentrations of HNT compared to LP to remove different stains from cotton by ultrasonic cleaner. Removal of different dyes, ink, tea, and chili oil from white cotton fabric (A), cleaning efficiency (B) and whiteness retention (C).

the cleaning efficiency is twice more than that of LP. The increased cleaning efficiency is attributed to the following reasons. HNT has the good ability to stabilize the Pickering emulsion, meanwhile it shows high adsorption capability due to its unique hollow tubular structure, rich pore structure and high surface activity. These allow the dyes to be adsorbed on them for achieving high cleaning effects. Moreover, the different chemical composition and charging properties of the inner and outer walls of HNT make it possible to adsorb both anion and cation dyes, greatly enriching its application range. The existing evidences has confirmed that the dye stains can be mainly absorbed in the lumen of HNT [52,53]. Besides, the high cleaning efficiency was also associated with the increased friction forces between the solid clay material and the textiles during cleaning process. Similarly, the high-concentration HNT cleaning effect towards tea stains is also stronger than commercial detergent on stained cotton cloth (Fig. 4A). The possible reason is that HNT has the high adsorption effect towards coloring matter in tea as dyes. HNT and LP have basically equal cleaning efficiency for ink on cotton cloth, while the cleaning effect of HNT and LP on Dacron fabrics is relatively poor due to the strong force of ink and Dacron. (Fig. 4A and Figure S5). When removing chili oil stains on cotton and Dacron cloth, high concentrations of HNT have shown the same highly efficient cleaning capability as commercial detergents. These results suggest that HNT can be used as an effective laundry detergent in daily life.

To further investigate the cleaning effect of HNT detergent, tableware made of different materials was stained by chili oils. Fig. 5 compares the cleaning efficiency of HNT and DWL. The cleaning effect of the two detergent is nearly equivalent, and there is no obvious residue on the cleaned dishes after washing. The advantages of HNT detergent are highly effective and non-toxic. Additionally, we compared HNT with other clays in Figure S6, the tubular HNT is found to be more efficient for dye cleaning. The possible reason is that HNT has special tubular structure, which provides the larger adsorption areas than the sheet-like clay [54]. Besides, the high surface negative charges of HNT makes it more efficient when applied as detergent to remove the cationic dyes and so on. In addition, the high surface activities make it has a stronger binding force with the dyes than other clays. Besides, the stained fabrics after treatment by HNT detergent has a high whiteness retention (Fig. 4C), which demonstrates HNT has a high capacity that prevents the reattaching of the stains on the surface of textiles. In total, HNT detergent (10 wt% concentration) has a better cleaning effect than commercial detergent especially at higher concentration, which makes it a potential alternative to synthetic detergents.

3.5. Toxicity studies of HNT

The LP powder residues will enter the environment such as river, soil, and ocean with the water flow after the use, so the LP sewage has a negative effect on the growth of plants [2,55]. In previous studies, HNT was found with high compatibility with the cell and tissue of animals [21,23,51], which suggests that HNT is not harmful to animals at normal dose. To study the effects of HNT detergent on plant growth, two typical plant models were applied. The wheat and lactuca sativa seeds were immersed in deionized water (blank group), 1% LP, 1 and 10% HNT dispersion for 24 h, separately. The germination rate, the root length, and the digital pictures of the wheat and lactuca sativa on the 7th day are shown in Fig. 6. Wheat and lactuca sativa seeds from the 1% LP group does not germinate at all, while the seed germination rate of the HNT treated group is 100%. Moreover, it can be found in Fig. 6 that the growth trend of the 1% HNT group is better than that of blank group. So, a low concentration of HNT is effective to promote plant growth.

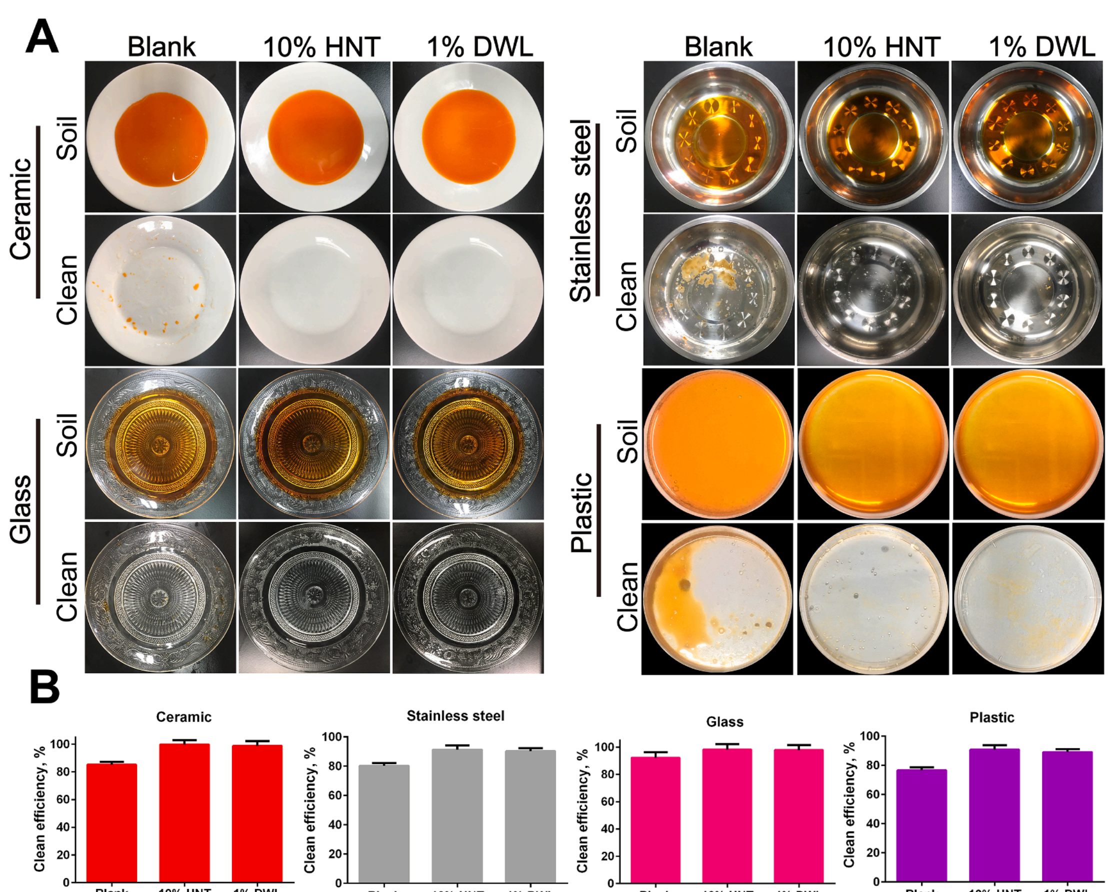

Fig. 5. Cleaning effect of different concentrations of HNT compared to LP to remove chili oil from ceramic, stainless steel, glass, and plastic plate (A) and cleaning efficiency (B).

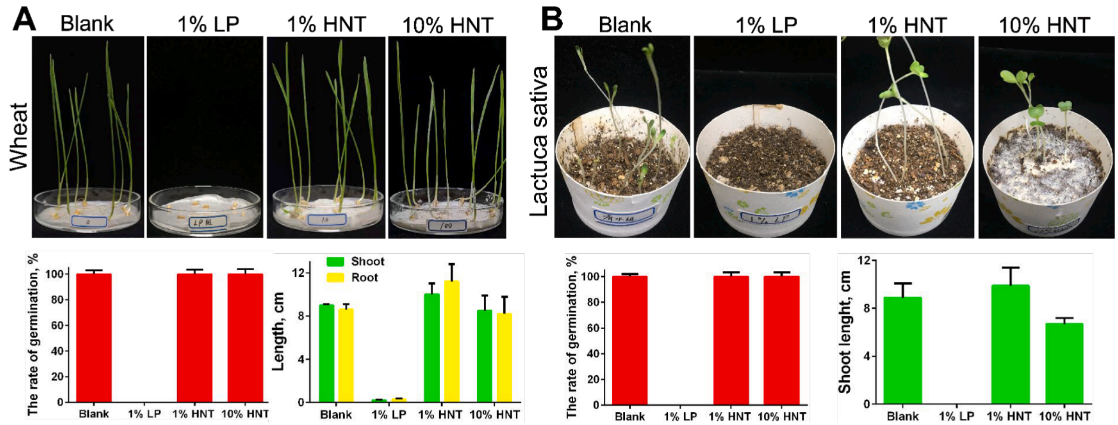

Fig. 6. Toxicity studies of HNT and LP (Day 7). Wheat (A) and lactuca sativa (B).

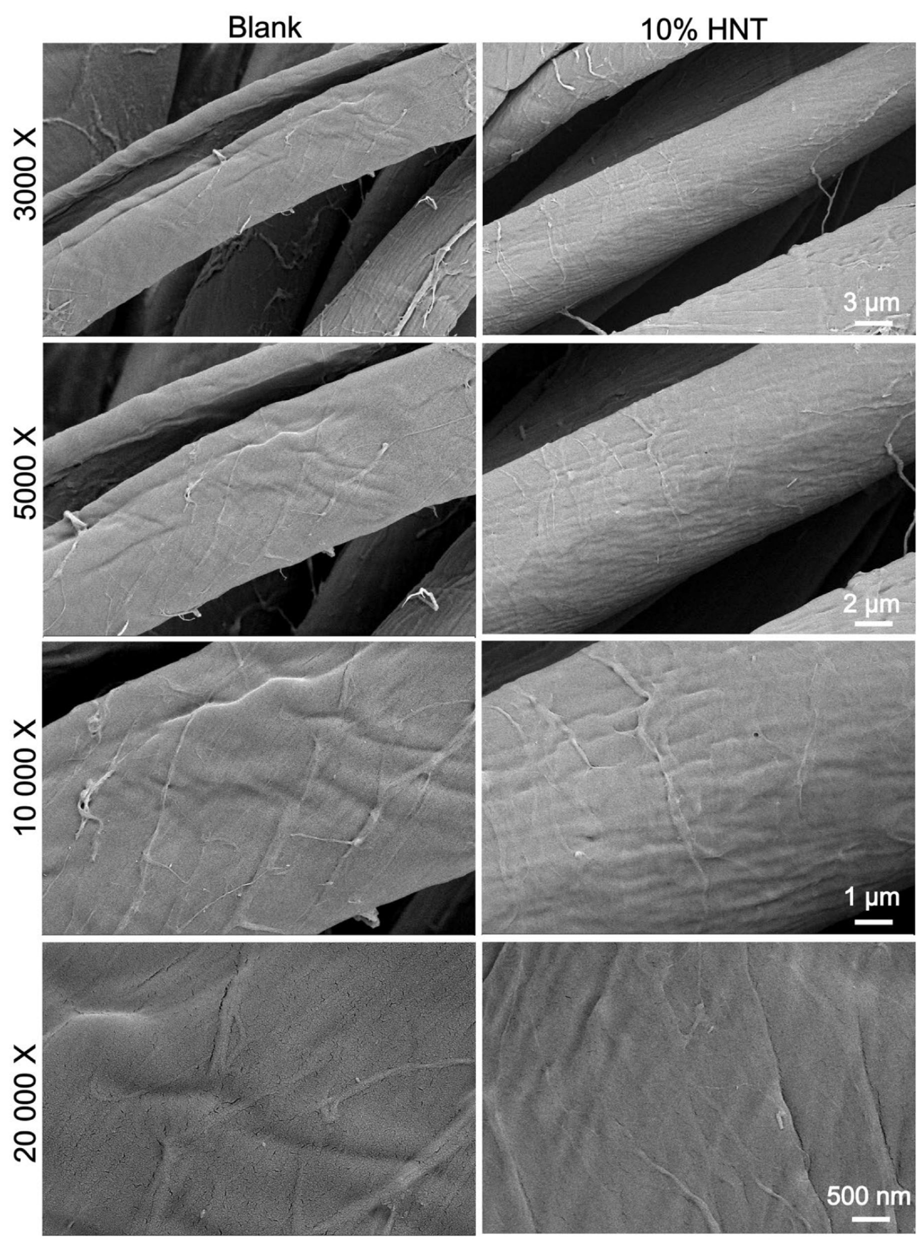

Fig. 7. SEM of cotton cloth stained with gentian violet solution in the blank group (deionized water) and HNT (10 wt%).

However, HNT at a high concentration suppress the plant growth, suggesting high concentration of HNT may have certain phytotoxicity. In total, the plant experiment results imply that HNT nearly has no harm on plant germinate and growth, while LP powder is very harmful to the plants. So, the green and environmental-friendly HNT clay detergent makes it a better choice than the synthetic LP which has higher toxicity to the organisms. Previous studies have shown that the concentrations of HNT below 0.05 mg/L are safe for nematodes and no in vivo toxicity effect occurs on nematodes. Moreover, HNT will not affect the fertility and lifespan of nematodes [21,56]. The zebrafish model also illustrated that different concentrations of HNT have no acute toxicity on zebrafish embryos and larvae. Additionally, the concentration of HNT under 25 mg/L can also promote zebrafish hatching, although HNT was enrich on the zebrafish embryo egg membrane. However, the long-term eco-toxicity of HNTs should be further evaluated [23].

3.6. The residue on the cloth after HNT cleaning

It is evident that HNT exhibits great efficiency in stabilizing O/W Pickering emulsion, excellent adsorption capacity and non-toxic performance, which can be applied in the detergent industry. It is important for practical application to consider whether there is any residue on the washed substrates, since the HNT residue can contact and enter the body, which may bring potential risk. The cotton cloth washed with 10% HNT and deionized water were observed by SEM separately in order to investigate whether HNT residues will remain on the clothes (Fig. 7). It demonstrated that the surface of the cotton washed with deionized water and that of the 10% HNT dispersion is equally clean, with no tubular HNT particle residue on the cloth. So, HNT does not damage the fiber structure and nearly has no residue on the cottons, which represents the best potential of applying in the detergent industry.

4. Conclusions

HNT, as an eco-friendly, low-cost, natural material, has large aspect ratio and is partially amphipathic to oil and water, which makes it to become a high efficiency green detergent. HNT shows good stabilization effect towards O/W Pickering emulsion, since HNT exists on the oil–-water interface at a high concentration. The capability of removing stains (dyes and daily stains) of HNT on cloth and the dishes is fairly better than that of common LP and DWL. HNT shows no negative effect on the germination and growth of wheat and lactuca sativa at low concentration, but LP solution completely inhibits the plant germination. It is also satisfied that no HNT residues on the fabrics after rinsing in the deionized water. This study designed a highly effective, safe, and low-cost clay materials with applications in the fields of detergents.

CRediT authorship contribution statement

Xiaohan Yang: Investigation, Methodology, Writing - original draft. **Jiabing Cai:** Visualization. **Linhong Chen:** Investigation, Validation. **Xiang Cao:** Investigation. **Hongzhong Liu:** Investigation. **Mingxian Liu:** Funding acquisition, Project administration, Supervision, Writing - review & editing.

Declaration of Competing Interest

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

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Appendix A. Supplementary data

Zeta potentials of 0.1% HNT aqueous dispersion at different pH and NaCl concentrations of Yunnan HNT; Stability comparison of O/W emulsions of HNT aqueous dispersion at different temperature; The dispersion of HNT in Pickering emulsion; Cleaning capacity of different concentrations of HNT compared to LP on cotton and Dacron; Cleaning capacity of different clay compared to HNT (PDF). Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2021.130623.

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Supporting Information

Green detergent made of halloysite nanotube

*Xiaohan Yang, Jiabing Cai, Linhong Chen, Xiang Cao, Hongzhong Liu, Mingxian Liu**

Department of Materials Science and Engineering, Jinan University, Guangzhou 510632, China

*Corresponding author. Email: liumx@jnu.edu.cn

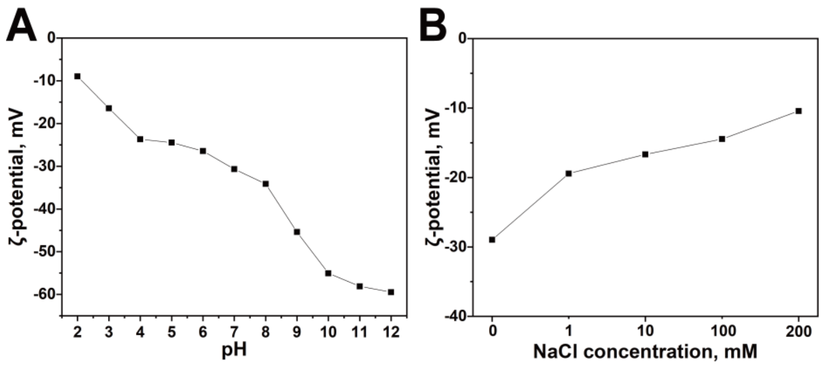

Figure S1. Zeta potentials of 0.1% HNT dispersed in water at different pH (A) and NaCl concentrations (B) of Yunnan HNT.

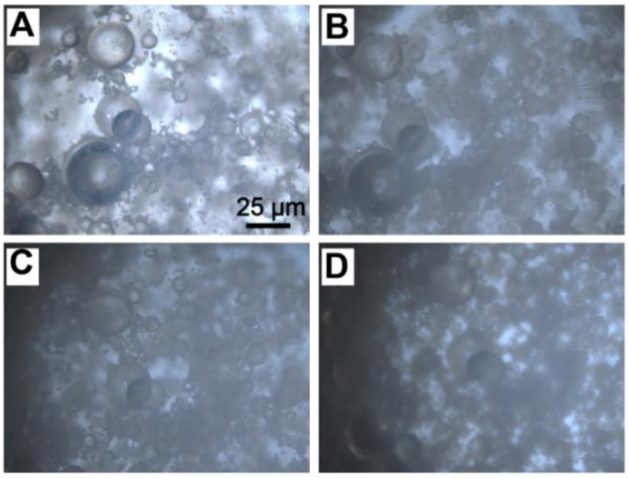

Figure S2. HNT-stabilized Pickering emulsion. Stability comparison of O/W emulsions of 1% HNT dispersed in water at different temperature, 25^{o}C (A), 30^{o}C (B), 35^{o}C (C) and 40^{o}C (D).

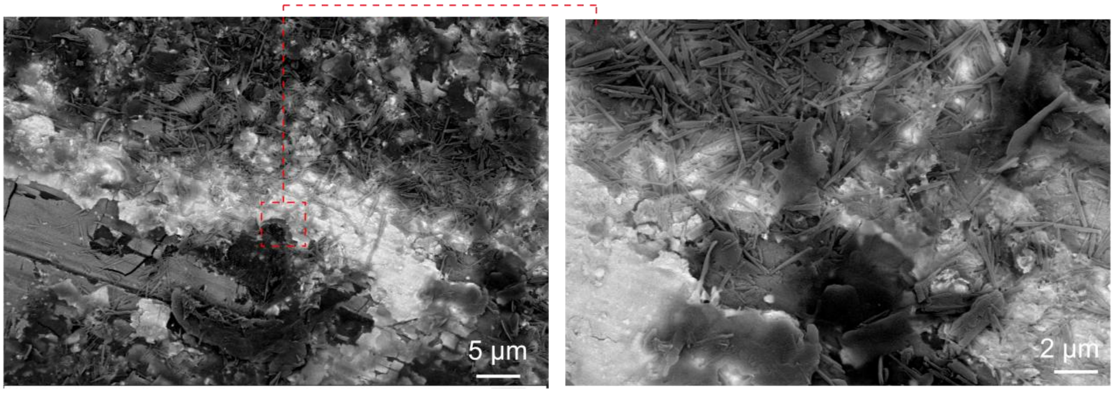

Figure S3. The dispersion of HNT in Pickering emulsion.

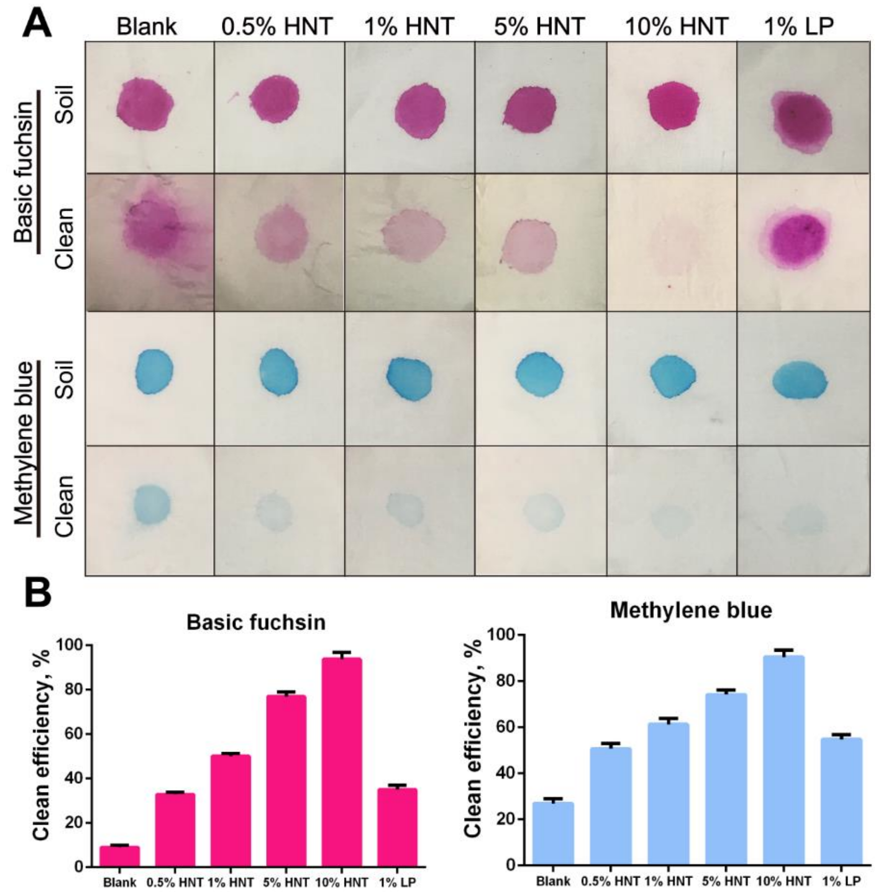

Figure S4. Cleaning capacity of different concentrations of HNT compared to LP for removal of different stains from cotton by ultrasonic cleaner. Removal of different dyes from cotton (A) and cleaning efficiency (B).

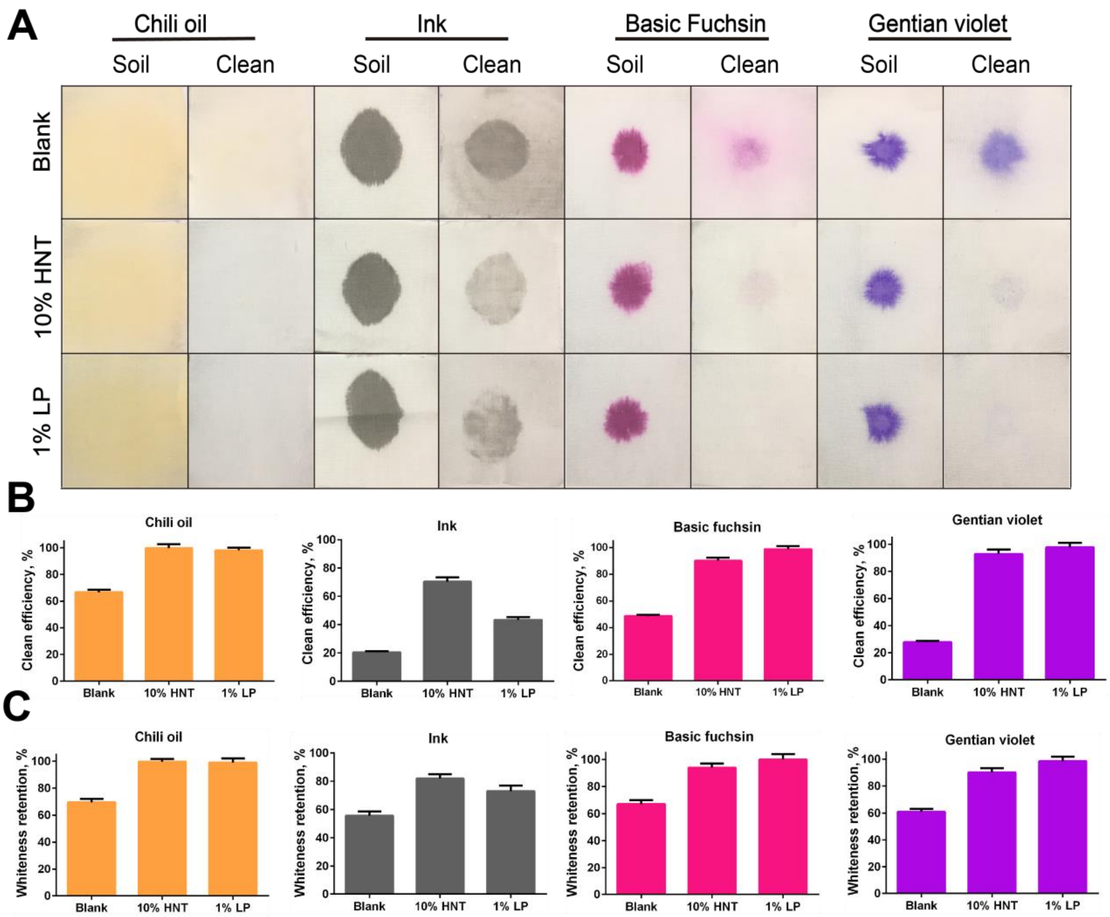

Figure S5. Cleaning capability of HNT compared to LP for removal of different stains from Dacron by ultrasound cleaner. Removal of chili oil, different dyes, and ink from white Dacron (A), cleaning efficiency (B) and whiteness retention (C).

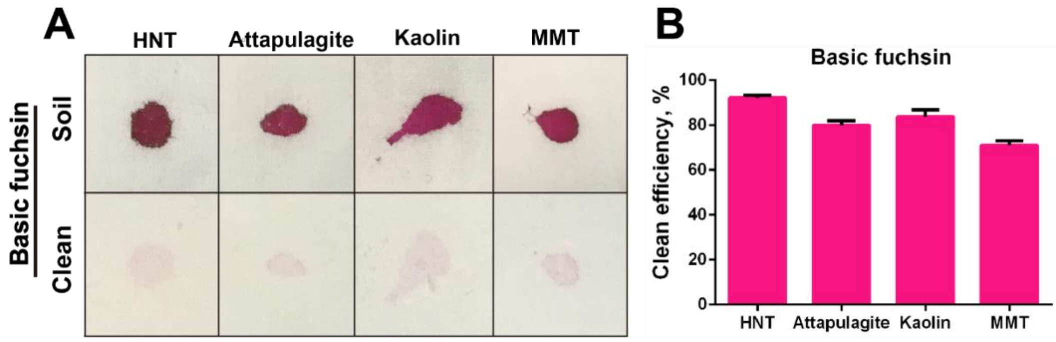

Figure S6. Cleaning capacity of different clays compared to HNT for removal of basic fuchsin dye from cotton by ultrasonic cleaner. Removal of basic fuchsin dye (A) and cleaning efficiency (B).