

Article

# Removal of Emulsified Oil from Aqueous Environment by Using Polyvinylpyrrolidone-Coated Magnetic Nanoparticles

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**Abstract:** In recent years, a large amount of emulsified oily wastewaters were produced from petroleum and food industries, resulting in severe environmental problems. In this study, a series of polyvinylpyrrolidone (PVP)-coated Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles (MNPs) were prepared via one-step solvothermal method by introducing various amounts or types of PVP. The synthesized MNPs were characterized by multiple techniques, and their demulsification performances were evaluated in petrochemical and vegetable oil wastewaters, respectively. Results showed that the introduction of PVP in solvothermal process could significantly enhance the demulsification efficiency of MNPs, although excessive addition of PVP could not further increase its efficiency. Moreover, the effects of pH, surfactant concentration of wastewater, and the recycle number of MNPs on the demulsification performance were investigated in detail. It was found that the demulsification efficiency decreased with the increase of pH and surfactant concentration, and the synthetic MNPs were still effective after being reused for 5 cycles under acidic and neutral conditions. It is expected that the development of the PVP-coated MNPs can provide a simple and powerful route for the oily wastewater treatment.

**Keywords:** magnetic nanoparticles; polyvinylpyrrolidone; magnetic separation; demulsification performance; reusability

## 1. Introduction

In recent years, a large amount of emulsified oily wastewaters were produced from petroleum and food industries, resulting in severe environmental problems [1]. The oily wastewater should be strictly treated to meet the requirements of the wastewater discharge. However, the emulsified oil droplets are highly stable due to the presence of surface-active substances, which are either naturally existed or intentionally added [2], making it hard to deal with the emulsified oily wastewaters. Conventional techniques, such as flotation [3], chemical flocculation [4,5] and membrane separation [6–8], were used to break emulsions. However, flotation was ineffective to treat the nanosized oil droplets, chemical flocculation was effective but time-consuming, and membrane separation was limited by the high energy consumption and membrane fouling in actual application [9]. As a consequence, there remains an urgent need to develop easy and powerful techniques or demulsifiers to achieve efficient emulsified oil-water separation.

Recently, oil-water separation by using Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles (MNPs) has attracted considerable attention [10–13], due to its good biocompatibility and easy surface modification.

The  $\text{Fe}_3\text{O}_4$  MNPs were usually modified with surface-active substances to improve their interfacial activity and water dispersibility. After introduction into the oil-in-water emulsion, the surface-modified  $\text{Fe}_3\text{O}_4$  MNPs can be well dispersed in the aqueous media and then assemble to the emulsified oil-water interface, imparting the magnetic responsiveness to the emulsified droplets [14,15]. Thus, the MNPs-coated oil droplets could be rapidly separated from the water phase under an external magnetic field. For example, the MNPs were previously modified with oleic acid [2,11], polyethyleneimine [12], poly(N-isopropylacrylamide) [16,17], poly(2-dimethylaminoethyl methacrylate) [18], (3-aminopropyl)triethoxysilane [14], chitosan [19–21], and so on, and these modified MNPs exhibited good demulsification performance. However, there is still a demand to develop more magnetic demulsifiers and understand the influences of environmental parameters on their demulsification performance.

In the present work, polyvinylpyrrolidone (PVP)-coated  $\text{Fe}_3\text{O}_4$  MNPs were prepared by one-step solvothermal method and used to remove emulsified oil from aqueous environment. Previously, Lead et al. studied the evolution of residual organic component in water phase during the demulsification process by using PVP-coated MNPs; the MNPs showed superior oil removal performance, which was enhanced with increasing ionic strength but reduced in the presence of natural organic macromolecule [22–24]. However, the influences of pH, surfactant and recycle number of MNPs on the demulsification efficiency were not examined; moreover, the effect of PVP in solvothermal reaction system on the demulsification performance of the synthesized MNPs was also not investigated. Consequently, in this study, a series of PVP-coated MNPs were synthesized in the presence of various amounts or types of PVP. The synthesized MNPs were characterized by various techniques, and their demulsification performances were evaluated in petrochemical and vegetable oil wastewaters, respectively. The effects of pH, surfactant concentration on the demulsification performance were investigated in detail. Subsequently, the reusability of the PVP-coated MNPs was further assessed at various pH levels. It should be noted that larger PVP-coated  $\text{Fe}_3\text{O}_4$  MNPs were prepared in this work, and different oils and experimental conditions were used as compared with previous study [22–24], and therefore the obtained results cannot be directly compared. However, the influence of the environmental parameters or recycle number of MNPs on the demulsification performances can be still used for reference.

## 2. Materials and Methods

### 2.1. Materials

Iron chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), anhydrous sodium acetate (NaAc), ethylene glycol (EG), n-hexane, sodium dodecyl sulfate (SDS), and sodium hydroxide (NaOH) were purchased from Aladdin Chemistry. Polyvinylpyrrolidone (PVP, with a molecular weight of 10 k and 1300 k, respectively) was purchased from Shanghai Macklin Biochemical Co. Ltd (Shanghai, China). Hydrochloric acid (HCl) was supplied by Zhejiang Sanying chemical reagent Co. Ltd (Lanxi, China). Ethanol was purchased from Hangzhou Gaojing fine chemical Co. Ltd (Hangzhou, China). A commercially available diesel was obtained from Sinopec, and the soybean oil was obtained from supermarket. Deionized water was used throughout the experiment. All chemicals were of analytical grade and used without further purification.

### 2.2. Synthesis of $\text{Fe}_3\text{O}_4$ MNPs

$\text{Fe}_3\text{O}_4$  MNPs were prepared by a modified solvothermal method [25]. Briefly, a certain amount of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , NaAc and PVP were completely dissolved in EG (Table 1). The resultant solution was then introduced into a Teflon-lined autoclave and kept at 200 °C for 6 h. The product was collected and washed with ethanol and water three times. Subsequently, a portion of synthetic  $\text{Fe}_3\text{O}_4$  MNPs was dried at 50 °C under vacuum for 24 h, and the rest of MNPs were dispersed in water for further use.

**Table 1.** Recipes for the synthesis of PVP-coated Fe<sub>3</sub>O<sub>4</sub> MNPs.

Sample Number	FeCl <sub>3</sub> ·6H <sub>2</sub> O (g)	NaAc (g)	PVP (g)	EG (mL)
S0	2.0	6.0	0	65
S1	2.0	6.0	1.5 (10 k)	65
S2	2.0	6.0	3.0 (10 k)	65
S3	2.0	6.0	4.5 (10 k)	65
S4	2.0	6.0	1.5 (1300 k)	65

### 2.3. Characterization

Size and morphology of MNPs were observed by transmission electron microscopy (TEM, JSM-1200EX, Tokyo, Japan) with a voltage of 80 kv. The MNPs was dispersed in neutral deionized water, and the concentration was kept at about 0.2 g/L; thereafter, a drop of nanoparticle dispersion was cast on the copper net and dried at room temperature for TEM examination. Zeta potential of MNPs and oil droplets at various pH levels was measured with a zeta potential analyzer (Nano ZS90, Malvern Instruments Company, Malvern, UK), the nanoparticle or oil droplet concentration of aqueous dispersion was also kept at around 0.2 g/L. Herein, dried samples of MNPs were used throughout the characterization of X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Thermogravimetric analysis (TGA), and physical property measurement system (PPMS). X-ray powder diffraction patterns were determined by using an X-ray diffractometer (XRD, D8 Discover) in the 2θ range of 10°–90°. FTIR of MNPs was performed using a FTIR spectrometer (Nicolet 6700, Thermo Fisher Scientific, Boston, MA, USA) from 400 to 4000 cm<sup>-1</sup>, and the samples were prepared by using KBr pellet technique. TGA was performed on a thermal gravimetric analyzer (TGA/DSC 1, Mettler Toledo, Zurich, Swit) under nitrogen atmosphere from 25 to 800 °C at a heating rate of 10 °C/min. Magnetization measurements were taken on a PPMS (PPMS-9, Quantum Design, San Diego, CA, USA) at room temperature; prior to examination, the nanoparticle power was bonded with each other to form a globule by using adhesive, and its size was no more than 3 mm. Water transmittance of emulsion before and after oil separation was determined by means of a UV-vis spectrometer (UV-2450, Shimadzu, Kyoto, Kyoto Prefecture, Japan) at a wavelength of 610 nm. The microscopic image of the mixture of emulsion and MNPs was examined by using a digital optical microscope (KH-7700, Hirox, Tokyo, Japan).

### 2.4. Demulsification Test

Oil-in-water emulsion was prepared by powerful sonication under magnetic stirring for 5 min, and the concentration of diesel or soybean oil was kept at 2.7 g/L. A certain amount of SDS was introduced following by short ultrasound treatment to make majority of surfactant assemble at the oil-water interface. pH of emulsion was regulated by using HCl or NaOH solution. The SDS concentration and pH were kept at 0 mol/L and 7.0, respectively, except as otherwise indicated. The demulsification experiment was performed at room temperature. A certain amount of MNPs were added to the emulsion, and the mixture was shaken just by hand (without sonication) to let the MNPs attach to the oil droplets. The MNPs-coated oil droplets were rapidly separated by using a magnet within 5 min. The water transmittance after magnetic separation was determined to assess the demulsification efficiency. The initial transmittance of emulsion was closed to zero.

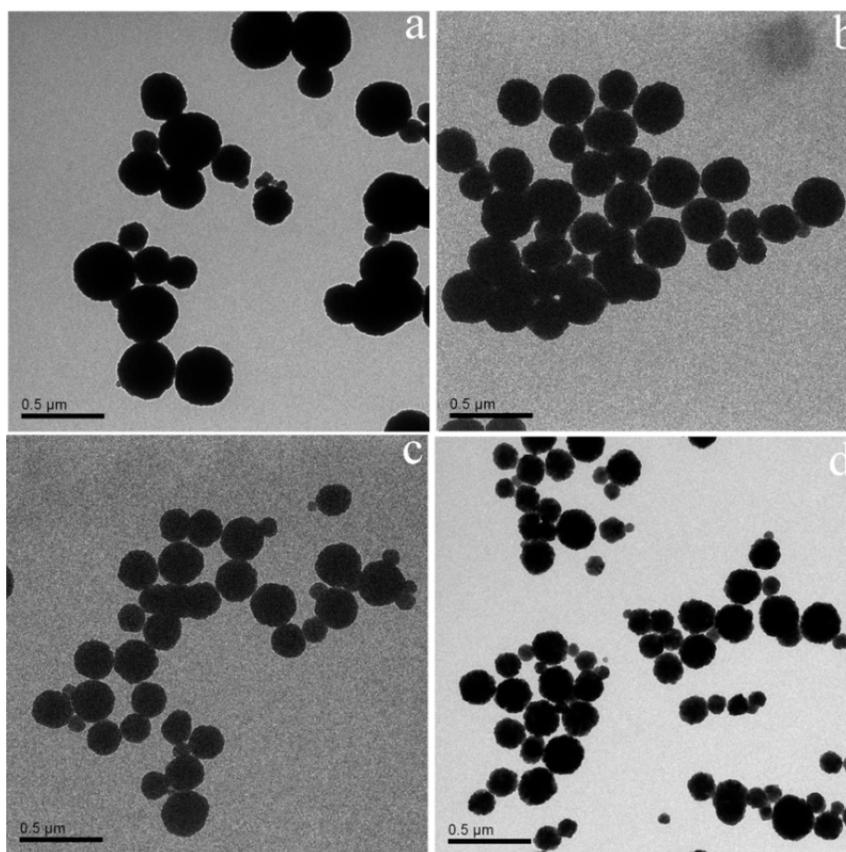
### 2.5. Recycle Tests

After the demulsification test, the spent MNPs were regenerated by washing with ethanol to remove the attached diesel oil and washing with n-hexane and ethanol to remove the attached soybean oil. The regenerated MNPs were re-dispersed in water and then reused in the next cycle of demulsification test. The recycle of MNPs was carried out for 7 times to evaluate their recyclability.

### 3. Results and Discussion

#### 3.1. Characterizations

TEM images of PVP-coated  $\text{Fe}_3\text{O}_4$  MNPs are shown in Figure 1. Without addition of PVP, the synthesized  $\text{Fe}_3\text{O}_4$  MNPs could not be well dispersed in water. However, after the introduction of PVP (1.5 g) into the solvothermal system, the water dispersibility of synthetic MNPs was significantly improved. As shown in Figure 1a, the spherical MNPs were polydisperse, and their size ranged from about 90 to 410 nm. XRD patterns of the synthesized MNPs are shown in Figure 2a. Diffraction peaks at  $2\theta$  values of  $30.3^\circ$ ,  $35.5^\circ$ ,  $43.2^\circ$ ,  $53.6^\circ$ ,  $57.3^\circ$ , and  $62.9^\circ$  can be indexed to the indices (220), (311), (400), (422), (511), and (440) of standard  $\text{Fe}_3\text{O}_4$  [25], suggesting the successful preparation of  $\text{Fe}_3\text{O}_4$  MNPs. Meanwhile, no obvious difference of diffraction peaks was observed between bare  $\text{Fe}_3\text{O}_4$  and PVP-coated  $\text{Fe}_3\text{O}_4$  MNPs, indicating that the crystal structure of  $\text{Fe}_3\text{O}_4$  was not varied after PVP addition.

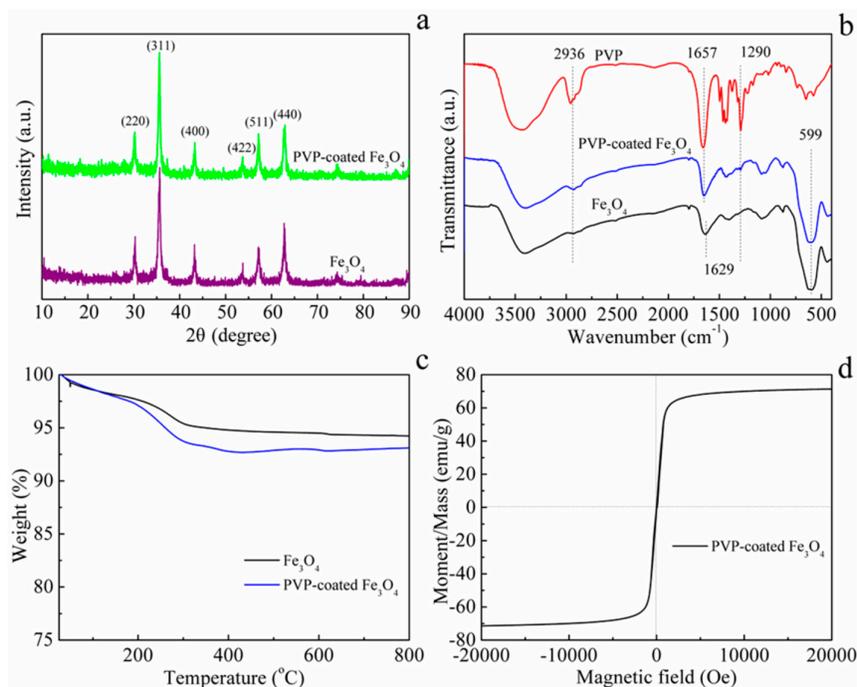


**Figure 1.** TEM images of PVP-coated  $\text{Fe}_3\text{O}_4$  MNPs ((a): S1; (b): S2; (c): S3; (d): S4).

Figure 2b shows the FTIR spectra of PVP, bare  $\text{Fe}_3\text{O}_4$  and PVP-coated  $\text{Fe}_3\text{O}_4$  MNPs. The intense absorption peak at around  $599\text{ cm}^{-1}$  corresponded to the Fe-O vibrations [20]. As compared with the bare  $\text{Fe}_3\text{O}_4$ , the stretching vibration of C=O in PVP-coated  $\text{Fe}_3\text{O}_4$  MNPs moved from  $1629$  to  $1657\text{ cm}^{-1}$ ; moreover, the peak at around  $1290\text{ cm}^{-1}$  ascribed to the vibrations of C-N appeared, and the peak at around  $2936\text{ cm}^{-1}$  due to the C-H stretching became notable in PVP-coated  $\text{Fe}_3\text{O}_4$  MNPs. These results confirmed that PVP was indeed coated on the surface of  $\text{Fe}_3\text{O}_4$ . In order to estimate the PVP content in the synthetic MNPs, TGA experiment was performed on the bare  $\text{Fe}_3\text{O}_4$  and PVP-coated  $\text{Fe}_3\text{O}_4$  MNPs (Figure 2c). The evaporation of physically absorbed water was usually found below  $120\text{ }^\circ\text{C}$ , while the decomposition of organic component was mainly observed between  $120$  and  $650\text{ }^\circ\text{C}$  [22].

Obviously, the weight loss of MNPs increased after introduction of PVP, and the increase in organic component decomposition could be attributed to the PVP coated on  $\text{Fe}_3\text{O}_4$  MNPs. Accordingly, the PVP content was estimated to be about 1.4% based on the weight of  $\text{Fe}_3\text{O}_4$  MNPs. Furthermore, the magnetic property of MNPs was measured at room temperature (Figure 2d).

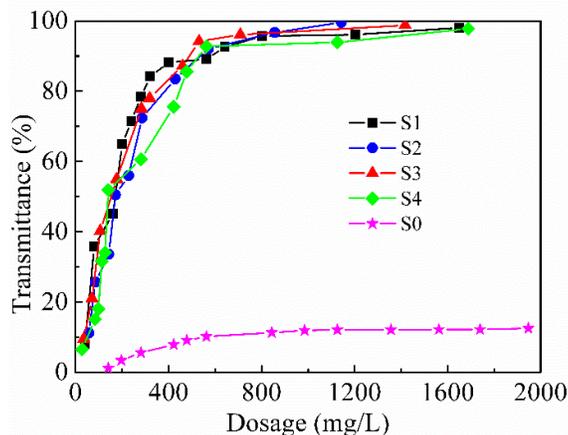
The saturation magnetization of PVP-coated  $\text{Fe}_3\text{O}_4$  MNPs was determined to be 71.4 e mu/g; meanwhile, negligible hysteresis of magnetism was observed. The superparamagnetic behavior can be explained by the fact that each  $\text{Fe}_3\text{O}_4$  microsphere prepared via solvothermal method was composed of many nanosized primary particles, which are usually smaller than 30 nm [18]. This result indicated that the synthesized PVP-coated  $\text{Fe}_3\text{O}_4$  MNPs could be well dispersed in water in the absence of magnetic field and rapidly collected from aqueous media by applying magnetic field.



**Figure 2.** XRD patterns (a), FTIR spectra (b), TGA curves (c), and magnetic hysteresis loop (d) of the synthesized MNPs ( $\text{Fe}_3\text{O}_4$ : S0, PVP-coated  $\text{Fe}_3\text{O}_4$ : S1).

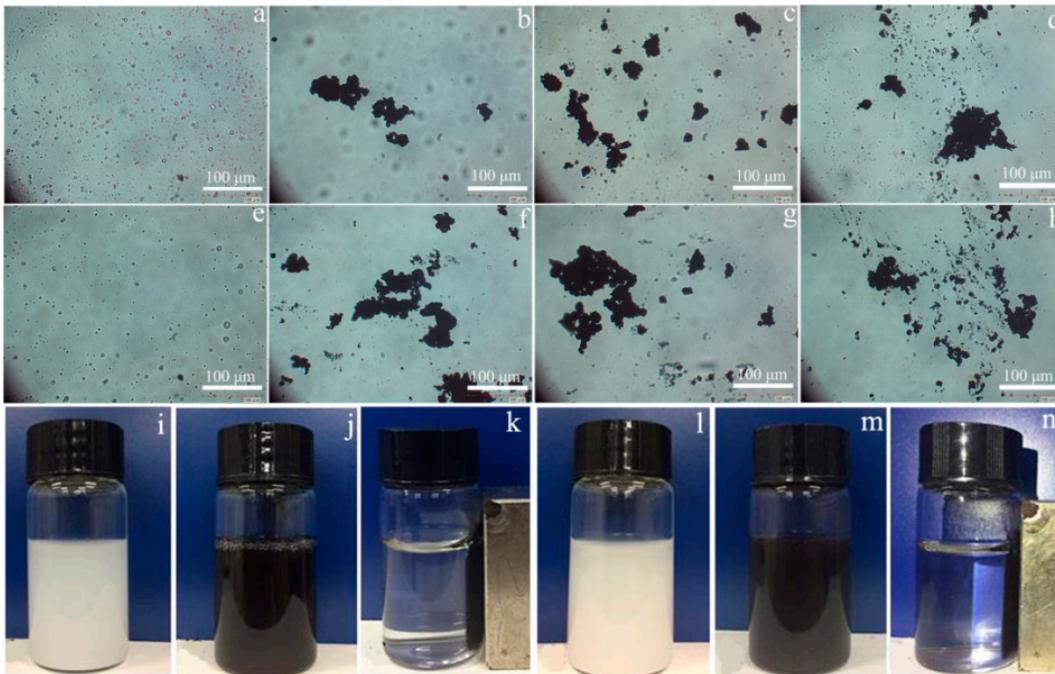
### 3.2. Demulsification Performance

Figure 3 shows the demulsification performance of the  $\text{Fe}_3\text{O}_4$  MNPs prepared with various amounts or types of PVP. As mentioned earlier, the bare  $\text{Fe}_3\text{O}_4$  MNPs could not be equably dispersed in water and was too hydrophilic to attach to the oil droplets [2,12], thereby showing negligible demulsification effect. After introduction of 1.5 g PVP, the synthesized PVP-coated  $\text{Fe}_3\text{O}_4$  MNPs exhibited good dispersibility and certain interfacial activity due to the amphiphilic nature of PVP [26], and hence their demulsification efficiencies were significantly enhanced. When the PVP amount increased from 1.5 to 4.5 g or the PVP molecular weight increased from 10 k to 1300 k, the size of synthesized PVP-coated  $\text{Fe}_3\text{O}_4$  MNPs decreased slightly (Figure 1); however, their demulsification effects were not further enhanced and nearly kept constant (Figure 3). As a result, the PVP-coated  $\text{Fe}_3\text{O}_4$  MNPs prepared with addition of 1.5 g PVP (10k) were further applied to treat the petrochemical and vegetable oil wastewaters under various conditions.

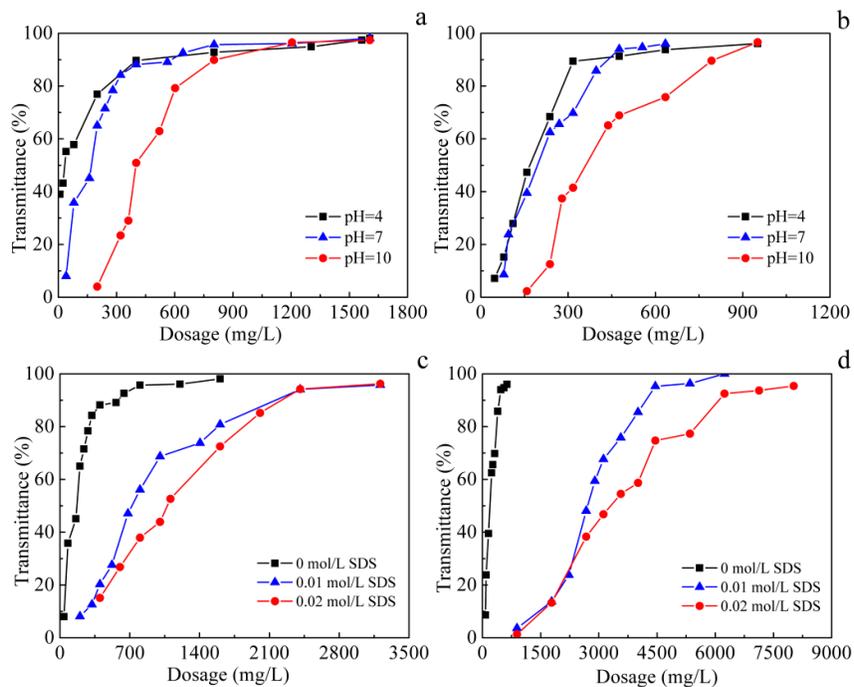


**Figure 3.** Demulsification effect of various  $\text{Fe}_3\text{O}_4$  MNPs in diesel oil-in-water emulsion.

pH is usually regarded as an important parameter affecting the oily wastewater treatment efficiency [4], and hence the demulsification performance of the MNPs was evaluated at various pH levels. Figure 4 shows the micrographs of the diesel (soybean) oil-in-water emulsion and its mixture with MNPs at pH 4.0, 7.0, and 10.0, respectively. The emulsified oil droplets with a size of less than  $10\ \mu\text{m}$  could be easily observed in the microscopic image (Figure 4a,e). However, after addition of MNPs to the emulsion, free oil droplets almost disappeared in the microscopic view; instead, some aggregated MNPs were found under different pH conditions (Figure 4b–d,f–h). The disappearance of free oil droplets and aggregated morphology of MNPs indicated the oil sorption onto the MNPs [24]. In other words, the synthesized PVP-coated  $\text{Fe}_3\text{O}_4$  MNPs attaches to the oil droplets once it is added to the emulsion. Therefore, the emulsified oil droplets could be rapidly separated from the water phase by applying magnetic field (Figure 4i–n). The detailed effect of pH on the demulsification efficiency was shown in Figure 5a,b. It was found that the demulsification efficiency declined with pH rising in both diesel and soybean oil-in-water emulsions. As shown in Figure 6, both emulsified oil droplets and PVP-coated  $\text{Fe}_3\text{O}_4$  MNPs were negatively charged at various pH levels, and hence, the electrostatic interaction between MNPs and oil droplets was repulsive. However, the PVP-coated MNPs could still attach to the oil droplets mainly via hydrophobic effect, which was also proposed by Lead et al. [23]. The zeta potential decreased with pH rising (Figure 6), and therefore the electrostatic repulsion between MNPs and oil droplets became stronger at high pH level. Thus, the MNPs became difficult to attach to the oil droplets, resulting in a reduction in demulsification efficiency. Besides, it can be seen in Figure 5a,b that the demulsification efficiency did not show significant difference between diesel oil-in-water emulsion and soybean oil-in-water emulsion at the same dosage of PVP-coated MNPs. When the dosage reached  $400\ \text{mg/L}$  at pH 7.0, the water transmittance exceeded 85%, indicating the oil removal ratio exceeded 99% [12]. In other words, the PVP-coated MNPs are capable of effectively removing emulsified oil from a synthetic wastewater ( $2.7\ \text{g/L}$  oil) at a ratio (oil:MNPs) of 6.75:1 under neutral conditions. The oil absorption capacity of synthetic PVP-coated MNPs seems to be lower than that in previous reports [22–24], presumably due to the much larger size of MNPs and shorter magnetic separation time in this study.



**Figure 4.** Microscopic images of diesel oil-in-water emulsion (a) and its mixture with MNPs (S1) at pH 4.0 (b), 7.0 (c), and 10.0 (d); soybean oil-in-water emulsion (e) and its mixture with MNPs (S1) at pH 4.0 (f), 7.0 (g), and 10.0 (h); photographs of diesel oil-in-water emulsion (i), its mixture with MNPs (S1) at pH 7.0 (j) and water solution after magnetic separation (k); photographs of soybean oil-in-water emulsion (l), its mixture with MNPs (S1) at pH 7.0 (m) and water solution after magnetic separation (n).



**Figure 5.** Demulsification effect of MNPs (S1) at various pH levels in diesel oil-in-water emulsion (a) and soybean oil-in-water emulsion (b); demulsification effect of MNPs (S1) at various SDS concentrations in diesel oil-in-water emulsion (c) and soybean oil-in-water emulsion (d).

Emulsified oily wastewater usually contains surface-active substances, which either naturally exist or are intentionally added [2]. Therefore, it is important to examine the influence of surfactant on the demulsification performance. Herein, SDS was used as the surface-active substance. As shown in Figure 5c,d, the demulsification efficiency decreased significantly with the addition of SDS in both diesel and soybean oil-in-water emulsions. It is well known that the oil droplet was attached to PVP-coated MNPs via hydrophobic interaction [23]. After introduction of SDS, majority of SDS would be distributed on the surface of oil droplets; meanwhile, part of SDS might also attach to PVP-coated MNPs, since the SDS molecule would be bound to a hydrophobic site of PVP molecules due to the attractive force of the hydrophobic association [27]. The SDS adsorption not only increased the hydrophilicity of the oil, thereby decreasing the hydrophobic driver but also increased the electrostatic repulsion between MNPs and oil droplets. Both factors did not favor the sorption of oil to PVP-coated MNPs, and therefore, their demulsification effect declined remarkably with addition of surfactant. This phenomenon is similar to the impact of natural organic macromolecules on the oil separation efficiency as previously studied [23].

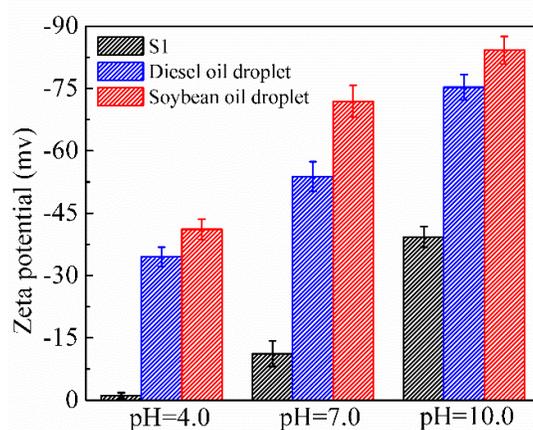
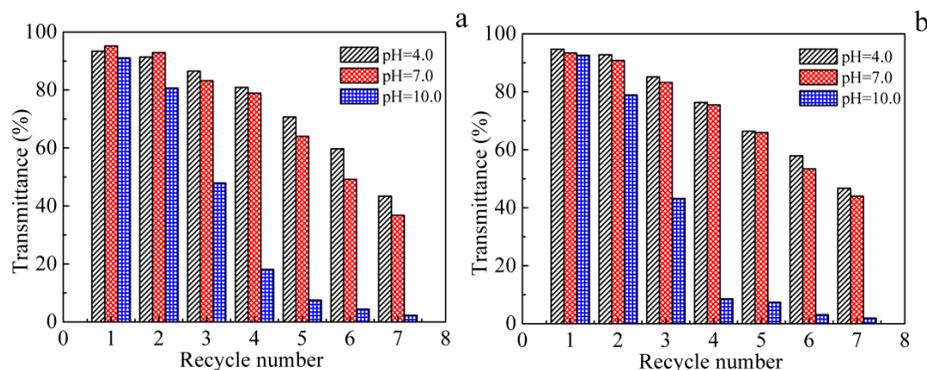


Figure 6. Zeta potential of MNPs (S1) and oil droplets at various pH levels.

### 3.3. Recyclability of MNPs

As compared with traditional flocculants and demulsifiers, another advantage is that the MNPs can be recycled in addition to their high demulsification efficiency. The reusability of PVP-coated  $\text{Fe}_3\text{O}_4$  MNPs was evaluated by treating the diesel (soybean) oil-in-water emulsion at various pH levels (Figure 7). It was found that the water transmittance still exceeded 60% after 5 cycles of magnetic demulsification under acidic and neutral conditions. According to our previous study [12], the oil removal ratio was higher than 95% when the water transmittance reached 60%, suggesting that the PVP-coated  $\text{Fe}_3\text{O}_4$  MNPs were still efficient after 5 cycles at low and middle pH levels. However, under alkaline condition, the demulsification efficiency declined dramatically during the reutilization process. This can be presumably explained as follows. As discussed earlier, electrostatic repulsion was the negative factor for oil absorption onto MNPs. During the recycle process of MNPs, some substances in wastewater would partly contaminate the MNPs, thereby competitively blocking the potential for oil sorption to some extent. At this time, the effect of negative factor (electrostatic repulsion) on the oil attachment to MNPs was significantly magnified. As indicated by the zeta potentials, the electrostatic repulsion between oil droplets and MNPs at high pH level was much stronger than that at low and middle pH levels. Therefore, the PVP-coated  $\text{Fe}_3\text{O}_4$  MNPs exhibited evident slowdown in demulsification performance under alkaline condition during their recycle process. Besides, as mentioned earlier, the PVP-coated MNPs are able to remove emulsified oil at a ratio (oil:MNPs) of 6.75:1 at medium pH level. Accordingly, 80 g of MNPs was required to treat a ton of synthetic emulsified oily wastewater (2.7 g/L oil, without surfactant) in this laboratory, assuming that the MNPs can be recycled for 5 times.



**Figure 7.** Reusability of MNPs (S1) at various pH levels in diesel oil-in-water emulsion (a) and soybean oil-in-water emulsion (b).

#### 4. Conclusions

In summary, the PVP-coated  $\text{Fe}_3\text{O}_4$  MNPs prepared via solvothermal method exhibited good demulsification performance toward treating petrochemical and vegetable oil wastewaters. Demulsification efficiency of MNPs was significantly enhanced due to the surface coating with PVP. Increasing PVP content or molecular weight in solvothermal process resulted in a slight decrease in nanoparticle size, whereas their demulsification performance was not further improved and nearly kept constant. Moreover, pH and surfactant significantly influence the demulsification performance of PVP-coated  $\text{Fe}_3\text{O}_4$  MNPs. It was found that their demulsification efficiency decreased markedly with increasing pH or surfactant concentration. Recycle experiment indicated that PVP-coated  $\text{Fe}_3\text{O}_4$  MNPs showed good recyclability under acidic and neutral conditions but poor reusability under alkaline conditions. It is believed that use of PVP-coated MNPs is a facile and reliable technique for removing emulsified oil from aqueous environment at low and medium pH conditions.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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