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Acceleration of floc-water separation and floc reduction with magnetic nanoparticles during demulsification of complex waste cutting emulsions

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ABSTRACT

Waste cutting emulsions are difficult to treat efficiently owing to their complex composition and stable emulsified structure. As an important treatment method for emulsions, chemical demulsification is faced with challenges such as low flocs–water separation rates and high sludge production. Hence, in this study, Fe_3O_4 magnetic nanoparticles (MNPs) were used to enhance chemical demulsification performance for treating waste cutting emulsions under a magnetic field. The addition of MNPs significantly decreased the time required to attain sludge–water separation and sludge compression equilibrium, from 210 to 20 min. In addition, the volume percentage of sludge produced at the equilibrium state was reduced from 45% to 10%. This excellent flocculation–separation performance was stable over a pH range of 3–11. The magnetization of the flocculants and oil droplets to form a flocculant–MNP–oil droplet composite, and the magnetic transfer of the composite were two key processes that enhanced the separation of cutting emulsions. Specifically, the interactions among MNPs, flocculants, and oil droplets were important in the magnetization process, which was controlled by the structures and properties of the three components. Under the magnetic field, the magnetized flocculant–MNP–oil droplet composites were considerably accelerated and separated from water, and the sludge was simultaneously compressed. Thus, this study expands the applicability of magnetic separation techniques in the treatment of complex waste cutting emulsions.

Introduction

Metalworking fluids (MWFs) are widely used for cooling and lubrication during machine production, polishing, and cleaning processes. After usage, the MWFs are discarded as waste metalworking emulsions (Cheng et al., 2005). These effluents comprise a complex mixture of water, oil, and various additives, such as emulsifiers, biocides, rust inhibitors, corrosion inhibitors, and antifoaming and extreme

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pressure agents, which are toxic to the environment. They are listed on the National Catalogue of Hazardous Waste in China (HW09) and must be treated before disposal because of the toxic nature of the components. Among various waste metalworking emulsions, cutting emulsions are some of the most difficult to treat because of their extremely high concentrations of oils and surfactants. These waste cutting emulsions contain emulsified oil at concentrations of 1500–90,000 mg/L, chemical oxygen demands (COD) of 50,000–200,000 mg/L, and high surfactant concentrations (Cheng et al., 2006). Because anionic surfactants are the most commonly used surfactants, the emulsion droplets are negatively charged. The surfactant film layer on the oil–water interface and the electrostatic repulsion between oil droplets makes the emulsion structure extremely stable (Benito et al., 2010).

Common separation processes such as centrifugation, flotation, and gravity sedimentation are ineffective in separating complex emulsions (Talbi et al., 2009). Although membrane filtration offers high separation efficiency, membrane fouling remains a major drawback (Gutiérrez et al., 2011; Matos et al., 2016). Chemical demulsification is an important treatment method for these emulsions. Flocculants such as metallic salts containing Al^{3+} and Fe^{3+} are the most commonly used agents for demulsification, owing to their ability to reduce the surface charges of oil droplets, promoting droplet coalescence or flocculation that facilitates oil–water separation (Pinotti and Zaritzky, 2001; Zhang et al., 2017b). However, this type of emulsion treatment requires a large amount of flocculants, with dosages as high as 6–8 g/L (Ahmad et al., 2006; Lee et al., 2014). Furthermore, this process produces large volumes of sludge, and the sludge–water separation requires a certain residence time that could reach several hours. To accelerate the separation of the two phases, the post-breakdown emulsion is usually processed using a centrifuge or ultrafiltration module (Benito et al., 2002). While flocculants are commonly used in demulsification, high flocculant consumption, low separation rates, and sludge disposal are significant concerns associated with this method. Therefore, the development of more efficient demulsification–separation methods is essential.

Recently, magnetic nanoparticles (MNPs) have attracted widespread interest because they can be conveniently separated from complex multiphase systems under an external magnetic field. Functional MNPs, including MNPs coated with oleic acid (Liang et al., 2014), ethylcellulose (Peng et al., 2012a), and demulsifier 5010 (Li et al., 2014), have been synthesized to treat assorted emulsions, with demulsification ratios reaching 90% within a few minutes. In addition, MNPs can be reused more than five times without any deterioration in their demulsification performance. However, MNPs are limited to the treatment of model emulsions characterized by a low internal phase volume (Chen et al., 2015; Peng et al., 2012b) and low surfactant content (milligrams per liter or even surfactant-free (Zhang et al., 2016)). Furthermore, the oil phases are predominantly short-chain hydrocarbons having low viscosity, such as hexane, toluene, and kerosene (Li et al., 2014; Chen et al., 2015). As emerging demulsifiers, MNPs have not been as widely used as chemical flocculants in waste emulsion treatment, but they show great advantages in terms of fast oil–water separation and excellent recyclability. According to the characteristics of chemical flocculants and MNP demulsifiers, flocculants and MNPs show complementary demulsification and separation behaviors. A combination thereof can provide a new approach for efficient emulsion treatment.

MNP-aided separation, also known as magnetic separation, is growing in popularity in the removal of both non-magnetic and weakly magnetic materials from water (Ambashta and Sillanpää, 2010; Tang and Lo, 2013). Magnetic separation has been extended to the treatment of drinking water (Chang et al., 2006), surface water (Hatamie et al., 2016; Wang et al., 2016), and industrial wastewater (especially for eliminating turbidity) (Chen et al., 2016). The target pollutant removal process is conceptually divided into two stages: (1) "seeding" MNPs in a fluid suspension where they flocculate with target pollutants, and (2) removing the resulting "seed–pollutant" agglomerates from the suspension via a magnetic field (Relle and Grant, 1998). These studies mainly involved magnetic separation of solid particles. For solid-particle removal, the flocculation process is of primary importance. The floc morphology, size, and zeta potential are used to analyze the floc formation–breakage–reformation process, as well as the flocculation mechanism (Chin et al., 2006; Sakaguchi et al., 2010; Zhao et al., 2015). However, particle removal and oil droplet removal differ significantly under magnetic separation, and the interactions between MNPs and target pollutants have not been clarified in previous studies. For oil droplets, the density is lower than that of solid particles, and thus, aggregated oil droplets are more difficult to separate under gravity; this separation process becomes the rate-limiting step in the overall scheme. Magnetizing the flocculants and oil droplets, therefore, is critical for accelerating the overall floc separation process. Because of the different properties of solid particles and oil droplets, interactions among MNPs, flocculants, and oil droplets during the flocculation and separation processes are important for discovering the mechanism of magnetic flocculation–separation for emulsions.

Inspired by the separation process of MNPs, we considered a method to "seed" the MNPs in the emulsion system, wherein the MNPs would combine with droplets or flocculants, quickly separating the oil flocs from the continuous phase in a magnetic field. In this study, the effects of Fe_3O_4 MNPs on enhancing the separation performance of the flocculants, and the mechanism of separation are investigated.

1. Materials and methods

1.1. Synthesis and characterization of MNPs

Fe_3O_4 MNPs were synthesized through chemical co-precipitation. Briefly, 11.6 g of $FeCl_3 \cdot 6H_2O$ and 5.56 g of $FeSO_4 \cdot 7H_2O$ were dissolved in 300 mL of deionized water under an atmosphere of nitrogen gas. A total of 30 mL of ammonium hydroxide (25%) was then added rapidly, and the resulting suspension was stirred for 2 hr.

The morphology and elemental composition of the MNPs were characterized using transmission electron microscopy (TEM, JEM-2100F, Tokyo, Japan). X-ray diffraction (XRD) patterns were recorded using a Bruker D8 Advance diffractometer (Bruker, USA) with a copper target at 40 kV and 40 mA, with 2θ values of 20–80°. The magnetic hysteresis loops of the samples were measured using a Physics Property Measurement System (Quantum Design, California, USA) at 25 °C. Saturation magnetization was performed by applying a magnetic field from −20,000 to +20,000 Oe. The zeta potential of the MNPs was measured using a zeta potential analyzer (Malvern Instruments, Malvern, UK).

1.2. *Characterization of emulsions*

The practical waste cutting emulsion (HW09) was obtained from a waste emulsion treatment center in Changzhou (Jiangsu Province, China). The emulsion sample was collected from a storage tank containing mixed emulsions discharged from several metalworking factories. The oil content of the waste cutting emulsion was measured to be 12,850 mg/L, using an oil content analyzer (Spectro Scientific, USA). The emulsions were further characterized based on COD and zeta potential. The COD was measured using an ultraviolet spectrophotometer after digestion treatment with a Hach COD device (HACH, USA), and the zeta potential was measured using a zeta potential analyzer (Malvern Instruments, UK).

1.3. *Flocculation–separation experiments*

Flocculation–separation experiments were performed by adding flocculants polyaluminum chloride (PAC), polyacrylamide (PAM) and MNPs to emulsions, followed by mixing and sedimentation. Before each experiment, a stock solution of PAC and PAM was prepared by dissolving 10 g of PAC and 0.1 g of PAM in 100 mL of water. The waste emulsion (20 mL) was transferred into a 100-mL beaker, and the stock solution was then pipetted into the emulsions. The samples were mixed rapidly at 250 r/min for 120 s, followed by slow stirring at 60 r/min for 5 min and sedimentation for 0–240 min, either naturally or with an NdFeB magnet (1.0 T). After reaching sedimentation equilibrium, supernatant samples were collected from 1 cm below the water surface of the samples to measure the COD (HACH, USA).

During the flocculation–separation experiments, five different flocculant dosages (800, 2000, 4000, 6000, 8000, 14,000, and 20,000 mg/L), five MNP dosages (0, 480, 1200, 2400, and 4800 mg/L), and five pH values (3, 5, 7, 9, and 11) were considered to determine the optimum dosage and applicable pH range for efficient oil–water separation. To determine the optimal dosages, the best COD removal ratio and highest quality of separated water would have to be obtained. On the premise of effective treatment, the dosages of the agent (PAC or MNP) and the production of flocs have to be the lowest. The volume percentage of flocs, which represents the proportion of floc volume to the original emulsion volume, was used to evaluate sludge production. To calculate this percentage, the flocculation layer volume was obtained according to the interface of flocculation and water layers, and was divided by the total volume of the liquid.

1.4. *Morphology and composition analysis of flocs*

The oil droplet behavior, floc morphology, and distribution characteristics of MNPs in the emulsion during flocculation were evaluated using cryo-scanning electron microscopy (Cryo-SEM, Phenom ProX). Samples were prepared from the flocculation experiment. A PAC solution was pipetted into the emulsions, which were then mixed rapidly at 250 r/min for 2 min, followed by the addition of PAM (or Fe_3O_4 MNPs) and slow stirring at 60 r/min for 5 min. The oily flocs formed by flocculants and Fe_3O_4 MNPs composited with PAC were collected in plastic tubes and frozen *in situ* using liquid nitrogen. One piece of a frozen sample was imaged in a frozen chamber at −25 °C. To determine the elemental composition of the flocs formed by PAC and Fe_3O_4 MNPs, an elemental analysis was performed using energy-dispersive X-ray spectroscopy (EDS, Phenom EDS). The size distributions of the flocs shaped by PAC and by PAC composited with Fe_3O_4 MNPs were measured using a Malvern 3000 particle sizer (Malvern Instruments, UK).

1.5. *Transmission analysis of flocculation–separation process*

Emulsion transmission during the flocculation–separation process was characterized using a Turbiscan TOWER (Formulaction, L'Union, France). The Turbiscan measures the transmission (T) and backscattered (BS) light as a function of time and the distance along the axis of a tube, based on the multiple light scattering (MLS) technique. Samples were prepared in the same way as for the flocculation–separation experiment. Each sample (20 mL) was transferred to a flat-bottomed glass cylindrical cell (6 cm in height and 2.5 cm in diameter) for T and BS measurements within 3 h at 25 °C. The T detector received the light passing through the sample at 0° from the incident beam, while the BS detector received the light scattered backward by the sample at 135° from the incident beam. The entire length of the sample cell was scanned every 40 μm to acquire T and BS flux data. Because the response extent of T was more significant for the phase separation process, T was used to analyze the flocculation–separation principles.

2. Results and discussion

2.1. *Effect of flocculant dosage on flocculation–separation performance*

Different amounts of PAC were added to the emulsions to evaluate the influence of PAC dosage on the COD removal ratio, sedimentation rate of flocs, and volume percentage of flocs. The COD removal ratio and transmission of separated water improved significantly when the PAC dosage was increased to 4.0 g/L and then gradually decreased (Appendix A Fig. S1). At lower flocculant dosages, only some of the oil droplets were captured by flocculants. However, for dosages exceeding the optimal value, the effluent quality was reduced again. The time needed to reach sedimentation equilibrium was used to determine the sedimentation rate of flocs; this time increased from 10 min to 240 min as the PAC concentration was increased from 0.8 to 8 g/L, and then decreased to 180 min as the PAC concentration was increased to 20 g/L (Fig. 1a). The volume percentage of flocs at the sedimentation equilibrium state increased to 80% as the PAC dosage was increased to 8.0 g/L. The differences in flocculation–separation performance caused by the PAC dosage are shown in Fig. 1b. Therefore, the optimal PAC dosage is 4.0 g/L, for the most efficient flocculation and separation, exhibiting a high pollutant removal ratio and low floc volume ratio at a low agent dosage. At this optimal dosage, the time needed for flocs to reach sedimentation equilibrium is 210 min, and the floc volume percentage of is 45%.

Although flocculation exhibited good demulsification of the waste emulsion at the optimal dosage, certain challenges remain when treating emulsions, especially in practical applications. Flocculation is primarily used for removing suspended particles during wastewater treatment, which could achieve nearly 99% particle removal under optimized conditions after 10–60 min (Suopajärvi et al., 2013; Xu et al., 2016). However, compared with solid particle removal, oil droplet removal is more difficult via flocculation. In this study, the optimal COD removal ratio was 75% for cutting emulsions, agreeing well with reports from previous studies (30%–70%) (Lee et al., 2014). In addition, the separation process usually requires a certain runtime reaching several hours (240 min in this study). The floc volume can reach 80%, considerably hindering sludge post-treatment (Amuda and Amoo, 2007; Karhu et al., 2012, 2014). Hence, to address the drawbacks of flocculation, alternative methods should be developed. Using magnetic nanoparticles and magnetic fields may be one way to solve these problems.

2.2. Enhancement of flocculation–separation performance with MNPs

Fe_3O_4 MNPs were used to improve the performance of the flocculants to treat waste-cutting emulsions. The MNPs were 15–20 nm in size; their morphology, structure, and magnetic properties are given in Appendix A Fig. S2. Different amounts of Fe_3O_4 MNPs were added to the emulsions to determine the optimal dosage for enhancing flocculation and separation performance at the PAC dosage of 4.0 g/L. The Fe_3O_4 MNPs had a slight effect on improving the COD removal efficiency over the dosage range of 0.48–4.8 g/L (Appendix A Fig. S3). However, the addition of Fe_3O_4 MNPs accelerated the sedimentation process significantly, shortening the time needed to reach sedimentation equilibrium from 210 to 20 min (Fig. 2a). Furthermore, as the dosage of MNPs was increased, the volume percentage of flocs decreased from 45% to 10%. These results indicate that the Fe_3O_4 MNPs significantly enhance the flocculation and separation process (Fig. 2b). This is because the function of the MNPs is to accelerate the separation of the flocs and the water and reduce the volume of the former; therefore, the faster the separation rate, the higher the treatment efficiency. In terms of separation efficiency, the time required for the separation to reach equilibrium was 50 and 20 min, respectively, when MNP concentration was 1.2 and 2.4 g/L. The separation efficiency was higher under the latter condition; therefore, 2.4 g/L of Fe_3O_4 MNP is determined to be the optimal dosage for efficient separation. At this optimal dosage, the time needed for the flocs to reach sedimentation equilibrium is shortened by more than 10 times compared to condition without MNP and the volume percentage of the flocs is reduced by more than 4 times.

The initial pH of the reaction system is an important factor that affects the flocculation process. The effects of pH on PAC flocculation-separation and magnetic flocculation-separation at a PAC dosage of 4.0 g/L and a Fe_3O_4 MNP dosage of 2.4 g/L are described in Fig. 3. The time required for PAC to reach sedimentation equilibrium increased from 10 to 90 min as the pH increased (Fig. 3a), while the time for magnetic flocculation-separation remained 20 min (Fig. 3b). The volume percentage of flocs increased from 20% to 90% as the pH increased to 11 during PAC flocculation, while the volume percentage of flocs remained below 20% for magnetic flocculation-separation. The effects of pH on the volume percentage of flocs produced by PAC/PAM and PAC/Fe_3O_4 MNPs were observed by comparing Fig. 3c and Fig. 3d. The separation efficiency of the flocculants clearly relies greatly on pH; as the latter increases, the separation rate decreases and the volume of floc sludge produced increases. The magnetic flocculation-separation can overcome the effect of pH on flocculation-separation, permitting broader pH ranges in practical applications.

The MNPs had an excellent effect on accelerating floc-water separation and reducing floc volume. In addition, they had great advantages in terms of reducing agent dosage and having a strong anti-interference ability and reusability. As shown in Fig. 4a, when the PAC addition was 4.0 g/L, floc

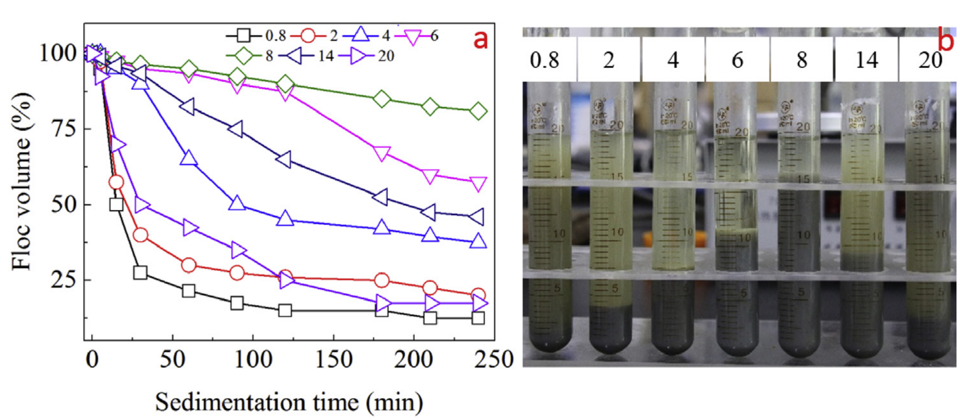

Fig. 1 – Flocculation–separation performance with initial PAC dosages from 0.8 to 20 g/L. (a) volume percentage of flocs produced over 240-min sedimentation, (b) photographs of final emulsion states after 240-min sedimentation.

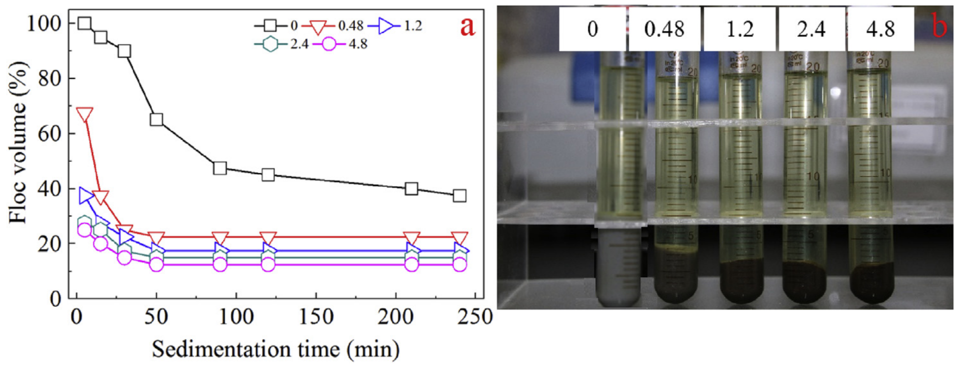

Fig. 2 – Effects of MNP dosage on enhancing the separation performance of PAC. (a) Volume percentage of flocs produced at PAC dosage of 4.0 g/L and Fe_3O_4 MNP dosage of 0–4.8 g/L, (b) final state of emulsions worked on by different MNPs dosages.

separation was slow and floc volume was up to 50%. When PAM was added, the settling rate of the flocs accelerated and the final floc volume was reduced by 10%. Therefore, PAM has a slight effect on accelerating floc separation and compressing it. After the MNPs were added and a magnetic field was applied, the flocs separated in 20 min and their volume dropped to 10%. These results show that MNPs can replace PAM in terms of improving the floc-water separation efficiency (Fig. 4c). The flocs were broken up to investigate re-flocculation-separation, and it was found that the separation rate decreased and the floc volume increased after the flocs that formed were separated under the action of PAC. However, under the effect of MNPs, the flocs can still maintain their separation rate and efficiency (Fig. 4b). The results show that the magnetic flocculation-separation has a strong anti-interference ability in the flocculation separation process. After recovering MNP that is used once, it can be used for demulsification at least three times (Fig. 4d).

The Fe_3O_4 MNPs mitigated the problems of low floc-water separation rates, high sludge production, and strong pH dependence shown by the flocculants when treating emulsions. In this study, the separation time was shortened more than tenfold, which is extremely important for the treatment of small flocs when flocculation occurs at low temperatures or when producing fragile flocs. To handle such practical situations, anionic and non-ionic polymeric flocculants are often used to agglomerate slow-settling micro-flocs into larger and denser flocs, better facilitating their removal in the subsequent sedimentation, flotation, and filtration stages (Lee et al., 2014). The Fe_3O_4 MNPs were more advantageous for this than

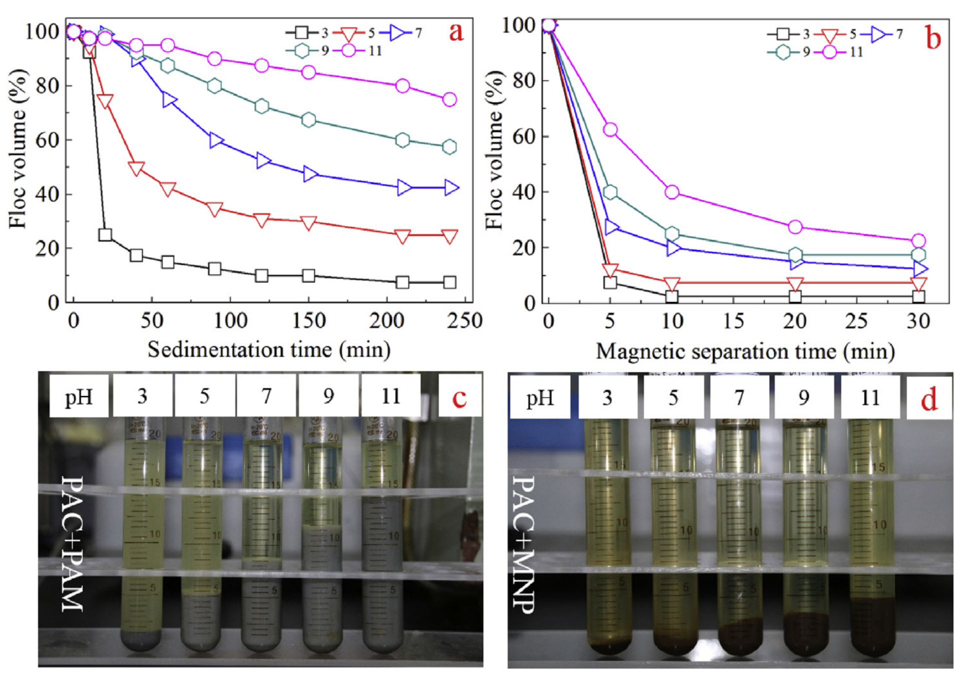

Fig. 3 – Flocculation separation performance of PAC and PAC composited with MNPs at a PAC dosage of 4.0 g/L and an Fe_3O_4 MNP dosage of 2.4 g/L under different pH levels. (a) Volume percentage of flocs produced over 240 min of sedimentation, (b) volume percentage of flocs produced over 30 min of magnetic separation, (c) final state of emulsions with PAC, (d) final state of emulsions worked on by PAC composited with MNPs.

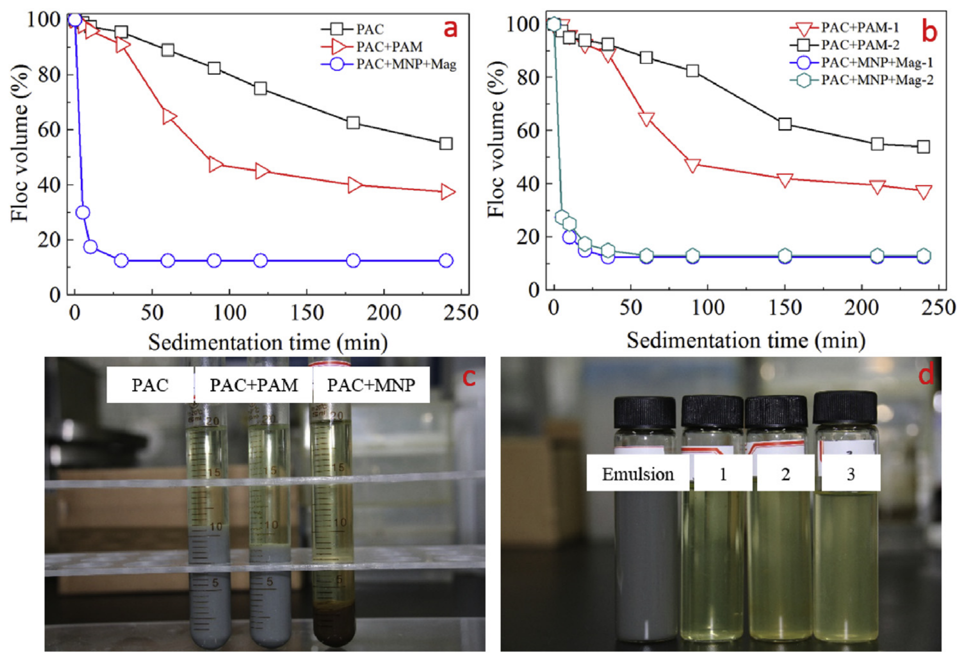

Fig. 4 – Flocculation separation performance of PAC and PAC composited with MNPs at a PAC dosage of 4.0 g/L and an Fe_3O_4 MNP dosage of 2.4 g/L. (a) Volume percentage of flocs produced over 240 min of sedimentation by PAC, PAC/PAM, and PAC/Fe_3O_4 MNPs, (b) volume percentage of flocs produced from the flocculation and re-flocculation of PAC/PAM and PAC/Fe_3O_4 MNP, (c) final state of emulsions worked on by PAC, PAC/PAM and PAC/Fe_3O_4 MNPs, (d) separated water recovered from Fe_3O_4 MNPs.

polymeric flocculants, thus possibly yielding the reduced overall treatment costs. In addition, the floc volume—which would greatly decrease the burden of sludge storage and post-treatment—was reduced by more than 4 times. The effectiveness of the MNPs would be more obvious in the treatment of emulsions with high concentrations of emulsified oils. In practical applications, pH control requires special equipment with strong corrosion resistance and thus entails high operating costs. In this case, both the floc separation rate and sludge volume production remain excellent under a broad pH range with the effect of MNPs. Here, the addition of MNPs enhanced the floc separation rate, reduced floc volume, and broadened the pH range applicable.

2.3. *Efficient mechanism for magnetic flocculation and separation*

To develop the efficient mechanism for magnetic flocculation and separation, Cryo-SEM and the analyses performed by Turbiscan were conducted to determine the interactions among MNP, flocculants, and oil droplets during the seeding and separation processes.

2.3.1. *Magnetization of flocs*

In an emulsion system, magnetic particle seeding is performed to render flocculants and oil droplets magnetically responsive for their easy separation from water later in the separation process. One common way of magnetic seeding involves direct addition of magnetic components to the target; this approach is related to the complex interactions among MNP, flocculants, and oil droplets. Because metalworking emulsions contain high concentrations of anionic surfactants, oil droplets in these emulsions are negatively charged. PAC neutralizes some of the negative charge on the oil droplets and weakens the repulsive forces between droplets under electrostatic interaction, causing droplet aggregation. The morphology of the flocculated oil droplets was determined via Cryo-SEM. As shown in Fig. 5a, the aggregated droplets were trapped into stereo structures shaped by PAC. To distinguish PAC structures from oil droplets, the elemental analysis of different components was conducted. Figs. 5b-1 and b-2 show EDS spectra corresponding to spots one and two, as noted in Fig. 5a. On comparing the main elements from the two spots, it can be seen that spot one has a higher mass of carbon (37.75%) compared to spot two (11.06%), indicating concentrated oil at spot one. The aluminum (5.13%) and chloride (4.38%) contents at spot one are notably higher than those at spot two (3.85% and 1.41%), demonstrating a combination of PAC and oil droplets.

For successful seeding, the interactions among MNPs, oil droplets, and flocculants are very important. As can be seen from the Cryo-SEM images, the MNP were actually distributed on the flocculants. The PAC structure has a large specific surface area and high density of reactive surface which could easily adsorb Fe_3O_4 MNPs. As such, the Fe_3O_4 MNPs were evenly distributed over the PAC structure and were shaped into an intact and firm net structure (Fig. 5c). EDS analysis revealed the elemental composition of the composite structure shaped by PAC and Fe_3O_4 MNPs. Figs. 5d-1 and 5d-2 show EDS spectra corresponding to spots one and two, as noted in Fig. 5c. As shown, spot one has a higher mass of iron (15.65%) than spot two (4.66%), confirming that the small particles are

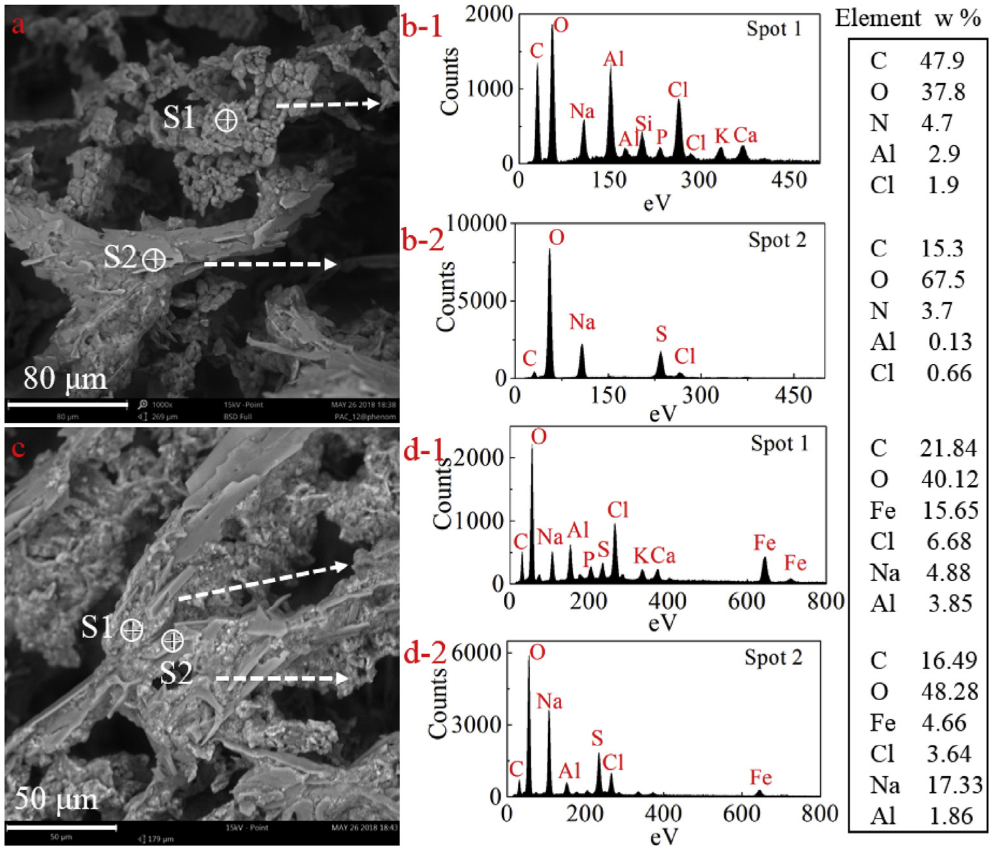

Fig. 5 – Morphology and elemental composition of flocs as determined by Cryo-SEM. (a) Morphology of flocs shaped by PAC, (b1-b2) EDS spectra of flocs shaped by PAC, (c) morphology of flocs shaped by PAC composited with Fe_3O_4 MNPs, (d1-d2) EDS spectra of flocs shaped by PAC composited with Fe_3O_4 MNPs.

Fe_3O_4 MNPs. From the imaged areas, it can be seen that Fe_3O_4 MNPs are distributed evenly throughout the composite structure, indicating the successful magnetization of the flocs.

The interactions among the MNPs, flocculants, and oil droplets also explained the efficient flocculation and separation performance under a wide pH range, as explained in Section 2.2. The oil droplets exhibited a strong negative charge, and the flocculants presented a strong positive charge in the pH range from 3 to 11 (Appendix A Fig. S4). Under electrostatic interaction, the flocculants captured the oil droplets. In contrast, the MNP exhibited a slight positive charge in the pH range from 3 to 7, and a negative charge in the pH range from 9 to 11. Theoretically, it would be difficult for the MNP to attach onto PAC due to the electrostatic repulsion force when the pH is below 9. However, because the positive charge of the MNP was not high and PAC had the ability to capture particles under the nano-size and nuclear condensation effects, the MNP could combine with PAC successfully under low pH conditions. As the pH increased from 9 to 11, the MNP became negatively charged and the electrostatic attraction contributed to MNP adsorption on PAC.

Previous studies mainly focused on species distribution analysis of ferromagnetic nanoparticle-seeded PACs during the flocculation process and changes in floc properties during separation (Zhang et al., 2012; 2017a). However, the conditions for the successful magnetization of flocs were not clearly illustrated. In this study, the interactions among flocculants, Fe_3O_4 MNPs, and oil droplets were identified as a major factor for controlling successful magnetization, especially the slight surface charge of Fe_3O_4 MNPs and special structure of PAC. Fe_3O_4 MNPs with slight positive charges were not strongly repelled by PAC and were distributed evenly in the PAC structure because PAC formed structures with a large specific surface area and could effectively absorb MNPs under the nano size effect. The oil droplets exhibited a strong negative charge and the flocculants presented a strong positive charge. With electrostatic interaction, the flocculants captured the oil droplets and finally formed a composite structure of oil droplets-flocculants-MNP. The successful seeding of magnetic particles into emulsions under the synergetic interactions among flocculants, Fe_3O_4 MNPs, and oil droplets ensured the quick separation of flocs in the later stages of the process.

2.3.2. *Separation and compression of flocs due to magnetic force*

The transmission of light through emulsions during the flocculation and separation processes was investigated by Turbiscan to determine the effect of MNPs on acceleration of the sedimentation process. At the beginning of sedimentation stage, the intensities of light transmitted through the emulsions under three different flocculant combinations were nearly zero, and all increased with increasing sedimentation time from 0 to 180 min, indicating that the continuous phase became cleaner. For emulsions flocculated by PAC and PAM (Fig. 6a), the width of the dewatering zone along the tube axis increased slowly from 0 to 17,000 μm over 180 min (94 μm/min). However, emulsions flocculated by PAC composited with Fe_3O_4 MNPs (Fig. 6b) showed an increase in the sedimentation rate from 0 to 19,000 μm over 130 min (146 μm/min). The most significant sedimentation performance was achieved by PAC composited with Fe_3O_4 MNPs in a magnetic field (Fig. 6c), where the width of the dewatering zone increased from 0 to 27,000 μm in 40 min (675 μm/min). The results imply that the Fe_3O_4 MNPs and magnetic field significantly accelerate the sedimentation process. Water separated by Fe_3O_4 MNPs in a magnetic field demonstrates the highest light intensity transmitted (64%), followed by those separated by Fe_3O_4 MNPs (47%) and by PAC (36%) (Fig. 6d). These results indicate that the Fe_3O_4 MNPs and the magnetic field notably accelerate the separation process and improve the quality of the separated water. The separation occurs owing to diverse colloidal forces acting on the magnetic matter under an external field; these forces include magnetic attraction, gravitational forces, and inter-particle forces such as the van der Waals forces, electrostatic forces, hydrodynamic resistance, and magnetic dipole attraction forces. The magnetic tractive force (F_m) overcomes other competing forces and yields a field one order of magnitude stronger than ordinary gravity sedimentation, which can be more efficient in separating flocculants when combined with MNPs (Li et al., 2010).

The effects of MNP and the magnetic field compression can be seen in Fig. 6a–c, based on the data from the study by Turbiscan. The heights of the flocs produced by PAC, PAC composited with Fe_3O_4 MNPs, and PAC composited with Fe_3O_4 MNPs in a magnetic field are 23,000, 20,000, and 11,000 μm, respectively, demonstrating that the Fe_3O_4 MNPs and magnetic field compresses the flocs to a greater extent than PAC settled by gravity. This may be due to the strong inter-particle magnetic forces affecting the formation of compact flocs, thereby enhancing the collision efficiency and frequency of the MNPs and flocs (Wang et al., 2015, 2018). For flocs formed by PAC, gravity is the only driving force that compresses the flocs. For the MNP-composited condition, the magnetic force is stronger than gravity, compressing the flocs to a greater extent than that in the case of PAC. Therefore, the volume of the flocs is reduced significantly in the case of Fe_3O_4 MNPs.

The morphology of flocs under the effect of a magnetic field was characterized using Cryo-SEM. As can be seen from Fig. 7a, the flocs are arranged directionally under the action of a magnetic field. Due to the extrusion between the flocs, the reticular structure is deformed and compressed. After a certain period of time, the flocs are compressed to the maximum extent possible and the volume is reduced, finally resulting in the formation of dense flocs (Fig. 7b).

In this study, the magnetization of flocs and the separation and compression of flocs were identified as the two key stages of the enhanced separation process. The magnetization of flocs was primarily a pre-condition for rapid separation and strong compression of flocs, where the nano-size effect and surface charge balance among the flocculants, Fe_3O_4 MNPs, and oil droplets may be critical in controlling successful magnetization. The interactions among the flocculants, Fe_3O_4 MNPs, and oil droplets were confirmed by a related morphological analysis of the flocs and a surface charge analysis. In the latter separation process, gravity and magnetic forces quickly transferred and compressed the flocs, eventually inducing an efficient separation. The sedimentation rates caused by the MNP and MNP in a magnetic

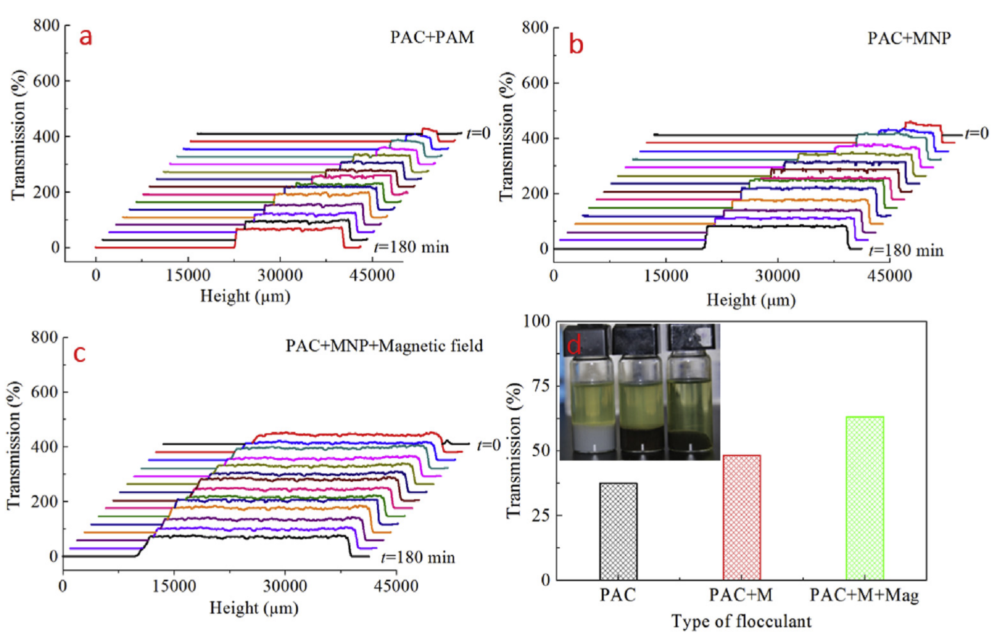

Fig. 6 – Light transmission through emulsions flocculated with different flocculant combinations. (a) PAC, (b) PAC composited with Fe_3O_4 MNPs, (c) PAC composited with Fe_3O_4 MNPs in a magnetic field, (d) average intensities transmitted through emulsions with different flocculant combinations.

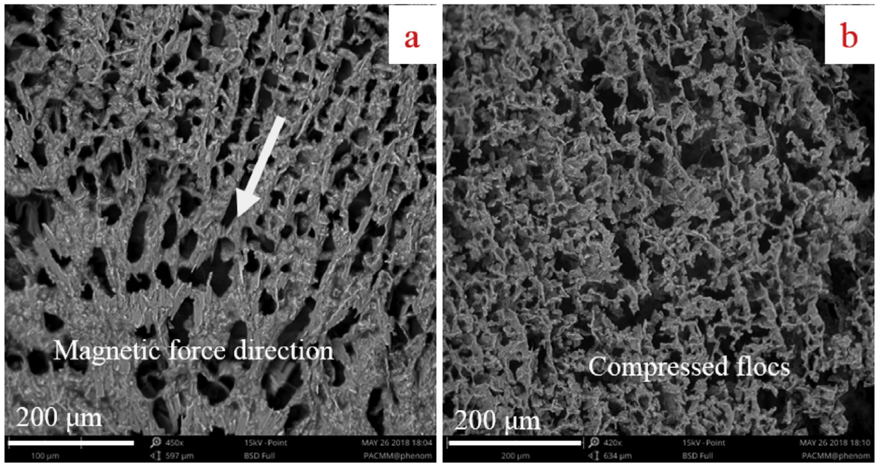

Fig. 7 – Morphology of flocs formed by PAC/Fe_3O_4 MNP, as determined by Cryo-SEM. (a) Migration of flocs under the effect of a magnetic field, (b) morphology of compressed flocs.

field were calculated by Turbiscan, which indicated that the additional gravitational force induced by the presence of the MNPs accelerated the transferring of flocs by 1.5 times, and the magnetic force accelerated it by 7 times, meaning that the magnetic force was the predominant driving force for the acceleration of the separation process. For solid, rigid, and non-compressible particles, the production of large volumes of sludge was not a problem. For the flexible liquid oil droplets, the extent of floc compression was important, reflecting the efficiency of separation. The heights of the floc layer and dewatering zone obtained from Turbiscan demonstrated that the floc compression caused by the MNPs and magnetic field was higher than that by PAC. To conclude, nano size effect and electrostatic interactions drove the magnetization of flocs in a wide pH range, while magnetic force drove the rapid separation and great volumetric compression of flocs.

3. Conclusions

In this study, Fe_3O_4 magnetic nanoparticles were used to enhance the efficiency of flocculants for treating hazardous waste cutting emulsions. The following important conclusions can be drawn: (1) compared to typical flocculants, the addition of Fe_3O_4 MNPs accelerated the flocs–water separation rate by 10 times, reduced the volume of flocs from 45% to 10%; (2) the enhanced magnetic flocculation and separation process was completed in two steps: flocs were magnetized by MNPs, and then transferred from the water by a magnetic force; (3) during the transfer process, the magnetic force compressed the oil flocs, reducing the volume of the produced flocs. This research solves the problems facing the use of flocculation in treating hazardous waste emulsions. The addition of MNPs exhibits great advantages in improving sludge-water separation efficiency and reducing the total cost of treatment, which represents a promising technique for hazardous waste reduction and disposal.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jes.2019.10.011.

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