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Poly(vinylpyrrolidinone)-Iron Magnetic Nanocomposites as Sorbents for Effective Oil Removal from Water

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Abstract. Poly(vinylpyrrolidinone)-iron magnetic nanocomposites (PVP-Fe NCs) were synthesised and used as sorbents for the removal of cooking oil from synthetic polluted water. The synthesised nanocomposites (NCs) contained particles with average grain size of 20 to 30 nm and possessed magnetic properties, as evidenced by field emission scanning electron microscopy (FESEM) and vibration sample magnetometer (VSM) analyses. The oil sorption studies revealed that the NCs are capable to remove up to ca. 80% of oil, and this remained constant irrespective of the total oil loading. Significantly, the oil-coated NCs were easily separated from “cleaned” water through a magnetic attraction using a N50 magnet. This approach, therefore, holds great potential to be scaled up and expanded to various water systems in Malaysia such as sea and river.

INTRODUCTION

Housekeeping activities, like cleaning, cooking and home maintenance, are very likely to discharge effluents into sewage system and possibly into the river. Cooking oil, either fresh or used, is a common organic substance found in the effluents. Unfortunately, existing methods for removing oil from polluted water seem ineffective and not eco-friendly. For example, the mechanical skimmers are limited to oil spilled near the deployment area, while the use of dispersants can add to water contamination when using in excessive amount [1]. Thus, there is necessity to develop a new approach that is more effective and environmental benign.

Iron oxide is a type of material known for its remarkable characteristics, including inherent low toxicity and more importantly magnetism property [2]. The latter characteristic enables the material to be strongly attracted to an external magnet, and magnetite (Fe_3O_4) is an example of iron oxides that exhibits such behaviour [3]. Interestingly, hybridising Fe_3O_4 and a hydrophobic polymer can create a smart composite that can remove oil from polluted water and be quickly separated from the “cleaned” water by an external magnet. As an example, Calcagnile *et al.*, demonstrated that a piece of floating composite foams, derived from Fe_3O_4 coated with polytetrafluoroethylene (PTFE), sorbed 13 times its own or volume of oil within 10 min [4]. Unfortunately, the method of Calcagnile *et al.* casts serious doubts with respect to its practicality, in particular in an incident where massive quantities of oil are fortuitously released.

Recently, there has been a growing interest in using poly(vinylpyrrolidinone) (PVP) as an alternative polymer to the PTFE. This is mainly because the PVP contains a hydrophilic component (the pyrrolidone moiety) and a considerable hydrophobic group (the alkyl group) [5], meaning that the polymer can attract oil molecules besides miscible in water [5, 6]. A number of studies have employed PVP-coated Fe nanocomposites (NCs) for the separation of oil and water [1, 2, 4, 7]. As an example, Mirshahghassemi *et al.* used PVP-Fe₃O₄ NCs and found that each particle of NCs sorbed 30 times its own mass or volume of oil. This is likely to be associated with the high surface area of NCs that enhances the oil sorption process [2].

In Malaysia, the utilisation of polymer composite in oil spills remediation is a relatively new research field. Thus, this study aims at demonstrating that poly(vinylpyrrolidinone)-iron magnetic nanocomposites (PVP-Fe NCs) can remove oil effectively, and be separated from “cleaned” water quickly by applying an external magnetic field. The outcomes of this study could potentially revolutionise the oil remediation industry in the country.

METHODOLOGY

Synthesis of PVP-Fe NCs

The synthesis followed a protocol reported by Mirshahghassemi *et al* [2]. An amount of PVP (MW 40 kDa, 1.8 g, 0.045 mmol) was dissolved in distilled water and then heated at 80 °C in a shaking water bath. Then, FeCl₂·4H₂O (0.198 g, 1 mmol) and FeCl₃·6H₂O (0.540 g, 2 mmol) salts were added to the solution. After mixing the resultant mixture at 80 °C for 10 minutes, an additional quantity of the PVP (1.2 g, 0.05 mmol) was loaded. Finally, 0.18 M of NH₄OH (6.25 mL) was added dropwise into the mixture under vigorous stirring at room temperature, forming black precipitates containing the desired nanocomposites. After further mixing at 90 °C for 25 min, the precipitates were recovered through a magnetic decantation with a cubic neodymium magnet (N50 block cuboid, 50 mm x 25 mm x 10 mm) followed by drying under vacuum at 50 °C overnight. The following analytical tools were employed to characterise the recovered nanocomposites (NCs): field emission scanning electron microscopy (FESEM), energy dispersed x-ray (EDX) and vibration sample magnetometer (VSM).

Oil Sorption Studies by PVP-Fe NCs

A reported protocol was referred [2]. As summarised in Fig. 1, the PVP-Fe NCs (0.2 g) was transferred into a glass vial containing an amount cooking oil (a Malaysian brand containing refined and deodorised palm olein, peanut oil and sesame oil) in distilled water (10 ml). The vial was inverted several times within 10 min. The separation of oil-coated-PVP-Fe NCs and “cleaned water” was conducted by placing a N50 magnet onto the glass for 30 min. The oil-coated-PVP-Fe NCs was then soaked in methyl tert-butyl ether (MTBE), desorbing oil molecules from the PVP-Fe NCs. The “cleaned” PVP-Fe NCs were then recovered through a magnetic decantation using the N50 magnet. Next, the desorbed oil molecules were recovered by evaporating MTBE using a rotary evaporator. All the experiments were conducted in duplicate. The percentage of oil adsorbed by the PVP-Fe NCs was determined by the following equation:

$$\text{Oil adsorbed (\%)} = W_f / W_i \times 100$$

Where

W_i = initial quantity of cooking oil used for the experiment, and;

W_f = quantity of oil adsorbed by the PVP-Fe NCs.

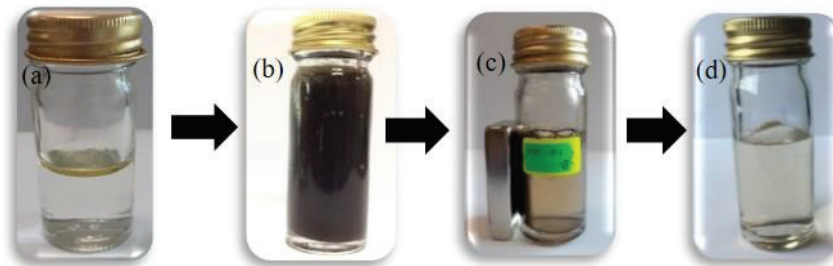


FIGURE 1. Step-by-step procedure of cooking oil sorption by the PVP-Fe NCs: (a) a mixture of cooking oil and water; (b) cooking oil-water loaded with the PVP-Fe NCs; (c) attraction of oil-coated- PVP-Fe NCs to the N50 magnet, and; (d) the resultant “cleaned” water following magnetic decantation

RESULTS AND DISCUSSION

Characterisation of PVP-Fe NCs

Examination of Surface Morphology and Composition

Figure 2 displays the surface morphology of the PVP-Fe NCs captured by FESEM. The NCs constituted of spherical-shaped particles with the average grain size about 20 to 30 nm, as shown in Fig. 2.

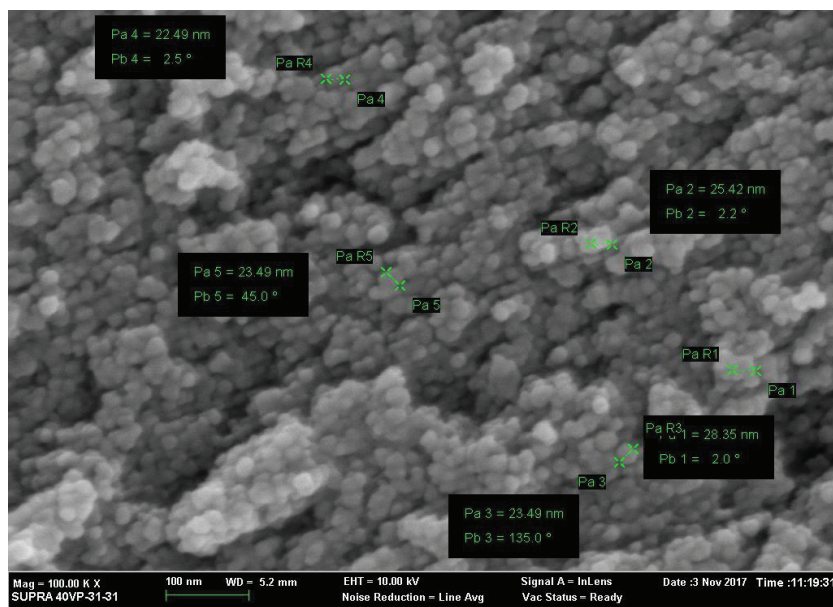


FIGURE 2. Surface morphology of PVP-Fe NCs

EDX analysis was then performed on the surface of the PVP-Fe NCs (Fig. 2). As shown in Fig.3, all the expected elements were detected in atomic %; carbon (11.8%), iron (52.2%), and oxygen (29.5%). Meanwhile, gold was used to coat NCs for better conductivity; this is the reason why the element appeared in the EDX spectrum (Fig. 3). The presence of carbon, an element of PVP, is a positive sign indicating that Fe particles had been successfully coated with PVP. However, the detection of iron in a substantial quantity suggests that some fractions of Fe particles remained uncoated. It is important to emphasise that obtained elemental composition through EDX analysis should be treated with the utmost caution. This is because EDX can only analyse very narrow segments of a specimen at a time with high detection limit (around 1% or higher) [8]. Therefore, the EDX results do not represent the actual elemental composition of the PVP-Fe NCs.

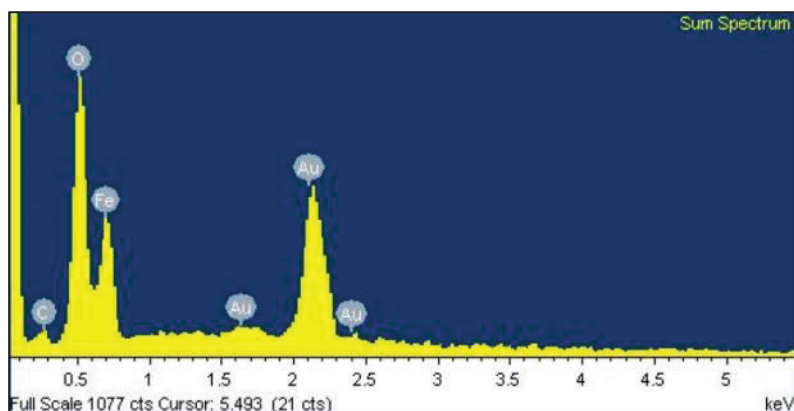


FIGURE 3. Surface elemental composition of PVP-Fe NCs

Magnetic Characteristics

The PVP-Fe NCs were further analysed by VSM, and the recorded hysteresis curve is shown in Fig. 4. The loop matched with the general shape of ferromagnetic. From the curve, the values of saturation magnetization (M_s), remanence magnetization (M_r), and coercivity force (H_c) are to be 51.2 emu/g, 2.15 emu/g, and 16.1 G, respectively. Above all, the most important information to highlight is that the NC was saturated (M_s) by an applied magnetic field of ca.1.3 T; this value is about three order of magnitudes lower than maximum magnetic field supplied by the N50 magnet, meaning that the NCs are able to be strongly attracted to the N50 magnet.

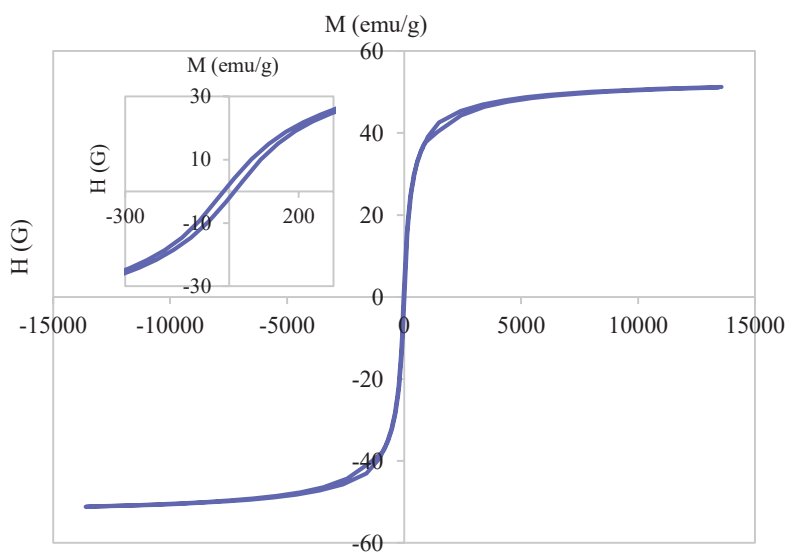


FIGURE 4. Hysteresis curve of the PVP-Fe NCs by VSM

Oil Sorption Studies

Figure 5 shows the oil sorption by the PVP-Fe NCs against different oil loadings, at a fixed quantity of the NCs. Interestingly, the NCs were able to remove up to ca. 80% of oil, irrespective of the oil loading. The oil sorption by the NCs was likely to occur via hydrophobic interactions between the alkyl group of PVP molecules and the hydrocarbon chains of FAME compounds, which present in the cooking oil (GC-FID spectrum, Fig. 6).

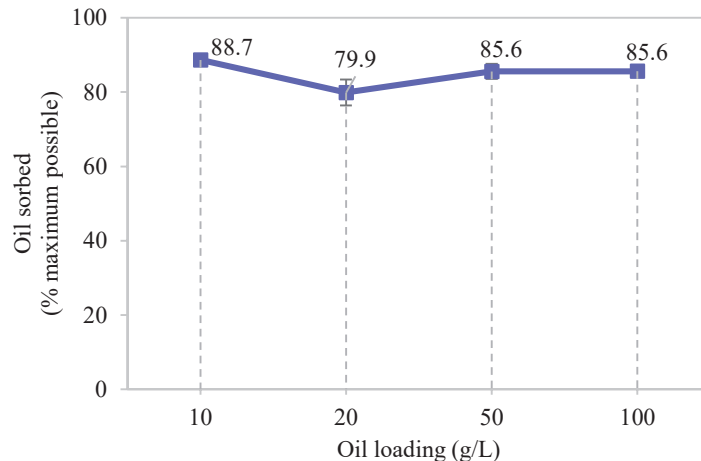


FIGURE 5. Oil sorbed against oil loading. The applied conditions were: 0.2 g of the PVP-Fe NC; contact time 10 min, and; magnetic decantation time of 30 min. Error bars are standard deviations of duplicate trials

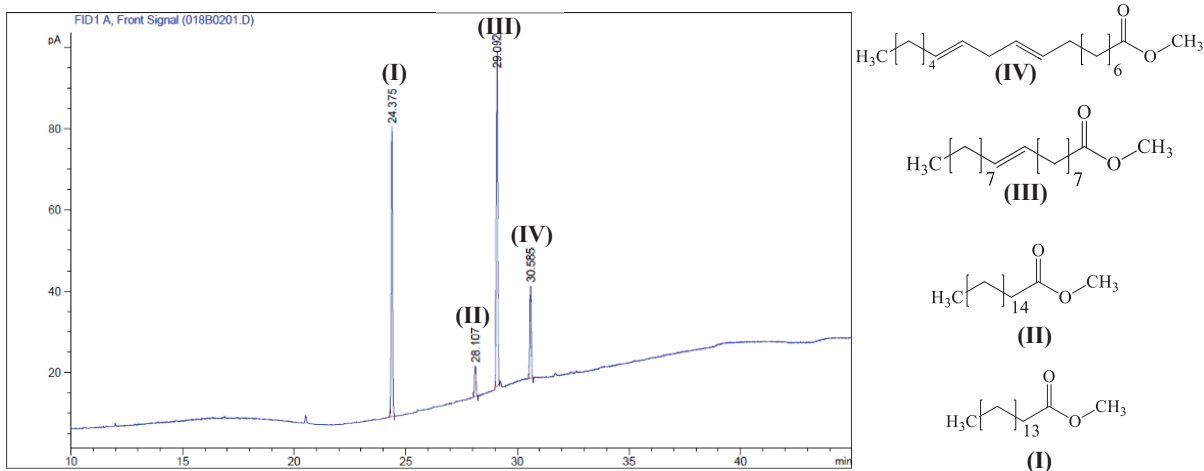


FIGURE 6. Fatty acid methyl ester (FAME) compounds present in the cooking oil recorded by GC-FID: (I) palmitic acid methyl ester, (II) stearic acid methyl ester, (III) oleic acid methyl ester, and (IV) linoleic acid methyl ester. The analysis was conducted under the conditions specified by the Supelco™ Catalog. No. 47885-U (for Component FAME Mix)

The outcomes of this study (Fig. 5), appear to strongly correlate with the preceding analyses. They supports EDX results implying that the adsorption of oil molecules was likely due to the presence of PVP coating the Fe particles, as indicated by the detection of carbon in the EDX spectrum (Fig. 3). Another important correlation is with VSM analysis confirming that the N50 magnet could supply sufficient strength of magnetic field required to saturate the core Fe particles, as determined by VSM curve (Fig. 4). This permitted the oil-coated-Fe particles to be attracted to the N50 magnet, separating them from the “cleaned water”.

CONCLUSIONS

In summary, the PVP-Fe NCs exhibit excellent performance towards oil sorption. All the components of the PVP-Fe NCs work synergistically, and each of them provides individual contribution. The PVP attracts oil molecules, and such an action is enhanced by high surface area to volume ratios of the nano-sized PVP-Fe NCs. The use of ferromagnetic Fe compound as core-particles affords magnetic effect to the NCs, enabling the oil molecules, sorbed on the surface of the PVP-Fe NCs, to be easily separated from “cleaned” water by a magnetic interaction using an external magnet. Significantly, this study demonstrates that the maximum oil sorbed by the PVP-Fe NCs remains

constant despite an increase in the oil loading. Thus, this approach is very promising to be scaled up for future oil remediation applications particularly in Malaysia.

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