

Treatment of Oil from the Oil Industry Wastewater by the Production of a Hydrophobic Magnetic Polymer Nanocomposites

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Abstract

A novel, economic and environment-friendly composite material based on magnetic hollow magnetite (Fe_3O_4) nanoparticle coated with a polyvinyl pyrrolidone (PVP) was produced to treat the oil from the oil industry wastewaters. The oils were readily removed via hydrophobic PVP -magnetite nanocomposite. In this study the physicochemical properties of the produced PVP-magnetite nanocomposite were investigated with Fourier transform infrared spectrophotometer (FTIR), X-ray diffraction (XRD) and thermogravimetric analysis (TGA) analysis. The effects of increasing PVP -magnetite nanocomposite concentrations, the effects of separation time, effect of pH on the removal of oil were investigated. The removals of individual oil types with different carbon (C) ring numbers (from C 9 up to C 25) were investigated during oil removal. The reusing capacity of PVP-magnetite nanocomposite was investigated after 40 cycling for oil removal. The removal yields for all pollutants in the oil industry was investigated. FTIR analysis results showed that in the spectrum of PVP-coated magnetite nanocomposite the peak at 2500 $1/cm$ can be attributed to the stretching vibration of C–N and C=O. XRD spectrum of the synthesized PVP–magnetite composite nanoparticle exhibited that the dominant phase of the composite nanoparticle is magnetite with a particle size of 16.8 nm. TGA analysis showed that about 69% weight loss was observed at 500°C and this is attributed to decomposition of PVP. Nonane (9 C rings) and undecane (11 C rings) have high removal yields like 99.99% while the oils with high carbon rings such as, 80% ducosene (22 C rings) and 72% pentacosane (25 C rings) exhibited low yields. The aforementioned nanoparticle can be used 29 times to remove the oil with a yield of 99.99%. The maximum CODdis, COD, TSS and oil removal efficiencies were 99%, 99.5%, 99% and 99.90% respectively, via adsorption with 3 mg/l hydrophobic PVP- Fe_3O_4 / Polimer nanocomposite.

Keywords: Magnetic hollow magnetite (Fe_3O_4) nanoparticle; oil industry wastewaters; polyvinyl pyrrolidone (PVP); fourier transform infrared spectrophotometer (FTIR); X-ray diffraction (XRD); thermogravimetric analysis (TGA).

Introduction

Environmental pollution originates from different sources including industrial effluents and wastewaters discharge in surface waters, pollutant discharge by refineries and plants, pollutant leakage from underground oil reservoirs and fueling stations as well as accidents of oil tankers [1-4]. Formation of oil in water emulsion due to release of pollutants has a significant role in oil dispersion and leakage as well as intensified physical pollution and biodegradation. Oil pollutions have irreparable effects on the environment thus elimination of oil pollutants has been one of the serious environmental problems in oil and petrochemical industries where the polluted effluents must be cleared from these contaminations [2].

Clearing oil-polluted effluents is mainly categorized into biological methods and biodegradation, application of absorbents, booms, skimmers, and in-situ burning as well as use of solid substances. As absorbents are highly selective, environmental friendly, chemical inert, have low operational costs as well as great absorption capacity, and can be easily recovered, they have been recently employed as appropriate options to clean oil pollutants and wasted oils. Despite the extensive use of porous absorbents such as zeolites, porous polymers, activated carbon, carbon aerogel, wood, clay, cane bran and straw, as oil absorbents, they suffer from low absorption, selectivity, and recyclability. In addition to, selecting the ideal absorbent with facile operation, low cost, high flexibility

and recyclability, good selectivity with excellent adsorption capacity is of crucial importance [1-4]. Recently, polyurethane has been used as the most common commercial absorbent in oil spill cleanup from synthetic organic polymers because of economical and feasible preparation process. Polyurethane (PU) sponge is a 3D porous compound with high absorption, low density, properly elasticity, cost effective and good electronic and mechanical properties, which can be employed in various industries including supercapacitors, sensors, and absorbents. However, commercial polyurethane has low selectivity towards aqueous and organic phases due to its hydrophilic nature; hence it cannot be used as an oil absorbent alone. As such its structure then requires to be modified and its hydrophilic properties have to be converted into super hydrophobic features [4].

Using magnetic nanoparticles (MNPs) to remove the dispersed oil from produced water is a promising way to overcome the difficulties faced by current treatment technologies [5]. The MNPs can be also regenerated and reused, minimizing the generation of hazardous waste since the MNPs-attached oil droplets can be quickly and efficiently separated with the application of an external magnetic field. The MNPs can be also regenerated and reused, minimizing the generation of hazardous waste [1,2,3].

The inert nature of most commercial polymers and nanomaterials limits their development for specific applications in various industries and, therefore, surface modification must be carried out to improve their adhesion, printing and wetting by bringing a variety of polar and other functional groups on surfaces of polymer and nanostructures [6-9]. Several surface functionalization methods have been established during the past decades that generally follow a common path: first the binding of primary reactive functional groups to the polymer chain ends at the surface, followed by modifying the reactive surface with active/bioactive agents, hydrophobic and hydrophilic monomers, oligomers or polymers to achieve specific surface characteristics matching the needs of the end use [6-9].

The immobilization of active/bioactive agents on a polymeric surface is generally performed by covalent bonds, electrostatic interactions and ligand-receptor pairing. Non-covalent physical adsorption is desirable for some applications such as certain drug delivery systems and re-generable antimicrobial textiles [10,11]. The covalent immobilizations offer some other advantages by providing the durability of active/bioactive agents, the extended half-life for biomolecules and preventing their quick metabolism as well as preventing the migration of bioactive agents to food from the active food packaging films. Grafting of poly-functional and anchoring compounds via a spacer molecule onto the surface of the solid substrate leads to an increase in the number of available active/bioactive agents per unit area and improves the efficiency of active/bioactive agents by reducing steric restrictions [12-14].

In general, oily wastewater refers to the wastewater that has mixed with oil with a broad range of concentrations [4]. The oil compounds found in oily wastewater may consist of fats and hydrocarbons as well as petroleum fractions. Many industries produce a huge amount of oily wastewater which have significant adverse impacts and threats to the surrounding environment and human

beings due to the presence of hazardous contents in the wastewater. For instance, high consumption of oil and gas in conventional petrochemical refinery industries poses critical environmental issues in the waste disposal management. Oily wastewater which collected from different industrial source may vary in term of its chemical composition, physical characteristics [4]. Hence different treatment designs have been reported based on the required specifications, wastewater's characteristics and pollution parameters. Produced water generated from oil well is known to be one of the most hazardous waste stream if the wastewater is disposed directly without treatment as it contains large quantity of oily pollutants such as dissolved oil, grease, suspended particles, gases and minerals, as well as some insoluble organic substances. The evaporation of these contents may cause air pollution and the penetration of produced water into under ground water resources. These pollutants also resulted in several problems in process equipment such as tubular corrosion and scaling formation in heat exchanger. Besides that, the discharge of these oily components also known to affect crop production and destructing the natural landscape[4].

An appropriate wastewater strategy is required to treat the produced water prior to their disposal or reuse for other purposes [4]. The appropriateness of an identified technology is normally dictated by the characteristics of the oil components in water. Particularly, it is known that the degree of dispersion and the oil droplet stability in water has strong influence in the readiness of separation. Different treatment methods have been utilized to remove the oil impurities. The treatment processes normally involved the removal of dispersal oil and grease; soluble organic; suspended solid removal, dissolved gas such as carbon dioxide; desalination for salt removal and disinfection of microorganisms. Currently, a wide selection of treatment methods has been established for the removal of the oil impurities in order to minimize or prevent the negative impacts of oily wastewater on our environments. Some of the prevailing technologies include membrane filtration, electrochemical treatment, adsorption, floatation and chemical coagulations as well as the hybrid technologies that integrate two or more approaches mentioned above. These technologies are known to serve different purposes in oily wastewater treatment. The primary treatment that consist of gravitational separation and sedimentation normally aims to remove oil and grease components in free oil form and the settlement of some unstable colloidal particles [4].

The emergence of a wide range of nanomaterials rendered with astonishing properties has promised innovative and novel way to treat wastewater hence minimizing the negative impact of the oily wastewater discharge into the water sources [15,16]. In term o nanomaterial selection, several kinds of surface wetting properties have been considered to delivery efficient oily wastewater treatment. These surface properties include hydrophobic and oleophilic, hydrophilic and oleophobic, superhydrophilic and superoleophobic, and responsive wetting properties. For example, the superoleophobic nanomaterials normally exhibit very high water affinity but extremely low underwater oil adhesion force. As a result, higher water permeation can be obtained and excellent oil repellent can be achieved under water. The surface properties of nanomaterials are known to be affected by their chemical composition and surface roughness. It is also known that superwetting surface can be created by choosing the suitable materials and

through various physical or/and chemical treatment [17]. Hence, various strategies have been developed to synthesize or modify the nanomaterial surfaces in order to obtain desired features like high permeability, self-cleaning ability, catalytic reactivity and ability to mitigate fouling. To date, many efforts have been paid to design and fabricate superwetting nanomaterials for adsorption and membrane-based oil/water separation[4].

Injection water is commonly used as an effective and economical method in recovery after primary recovery has been finished [18]. Produced water is an inextricable part of the organic and inorganic compounds, and the largest volume by-product associated with oil and gas recovery process [19,20]. Treated produced water can be recycled and used for water flooding [produced water reinjection (PWRI)] and other applications [21,15]. Oil and water mixture can be classified as free oil with oil droplets larger than 150 μm , dispersed oil, with oil droplets in the range of 20–150 μm and emulsified oil with oil droplets smaller than 20 μm . Several methods have been used for the removal of residual oil from produced water such as adsorption, flocculation, electrocoagulation and flotation [21].

Among them, adsorption is found to be cheap, effective and easy to adapt and has been confirmed as one of the most promising technologies for removing oil from wastewaters [22-24]. To date, many adsorbents have been used for oil removals, such as chitosan organic resins and mesoporous solid basis produced powdered activated carbon (PAC) from agricultural waste[23-31].

In this study, the physicochemical properties of the produced PVP-magnetite nanocomposite were investigated with fourier transform infrared spectrophotometer (FTIR), X-ray diffraction (XRD) and thermogravimetric analysis (TGA) analysis. The effects of increasing PVP -magnetite nanocomposite concentrations, the effects of separation time, effect of pH on the removal of oil were investigated. The removals of individual oil types with different carbon (C) ring numbers (from C 9 up to C 25) were investigated during oil removal.

Materials and Methods

Characterization of Oil Industry Wastewater

Table 1 shows characterization of oil industry wastewater.

Table 1: Characterization of oil industry wastewater

Parameters	Unit	Concentrations
COD	(mg/l)	7600
COD _{dis}	(mg/l)	3400
BOD5	(mg/l)	2900
TSS	(mg/l)	2300
VSS	(mg/l)	1900
Total oil	(mg/l)	450
TN	(mg/l)	34
TP	(mg/l)	13
pH		6.8
Total hydrocarbon	(mg/l)	789

Production of PVP -Magnetite Nanocomposite

$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (ferrous chloride) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (Ferric chloride) along with PVP, were used as precursors, and NH_4OH was used as a precipitation agent. First, PVP (Mw 10 kDa, 0.22 mmol) was added to 8.40 ml deionized water while the solution was stirred at 85°C. Then, 1.3 mmol $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and 5.2 mmol $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were added to the solution and stirred at 85°C. In the next step, 0.14 mmol PVP was dissolved in the solution. Then 6.25 ml NH_4OH with a percentage of 30% was added into the solution at 21°C temperature with stirring. After the addition of NH_4OH , the color of the mixture turned from yellow to black immediately and the black suspension was allowed to mix for 25 min at 90°C. The precipitates were washed once with deionized water and separated by magnetic decantation and redispersed in water again via sonication.

Characterization of PVP and Magnetite Coated PVP Nanocomposites

The PVP and magnetite coated PVP nanocomposites were characterized by FTIR, PerkinElmer. TGA was conducted on a TA Instruments Q5000 using a heating rate of 10°C/min under constant nitrogen flow. XRD was performed on a Rigaku D/max 2100 diffractometer (Cu $K\alpha$ radiation, $\lambda = 1.59876 \text{ \AA}$). The average crystal size was calculated according to the full width at the half-maximum height of the (201) plane using Scherrer

Equation (1):

$$\text{XRD} = K \lambda / \beta \cos \theta \quad (1)$$

Where L_{XRD} is the crystal size, K is a shape factor (0.89 for magnetite), λ is the X-ray wavelength (1.54088 \AA), β is the half-maximum height of the diffraction peak corresponding to 2θ after subtracting the instrumental broadening and θ is the Bragg's diffraction angle.

Analytical Procedures

COD, COD_{dis}, TP, TN, BOD5, total hydrocarbon, pH, TSS and VSS were measured according to the Standard Methods (2017) 5220 B, 5220 D, 4500-P, 4500-N, 5210-B, ASTM-D7675-15, 4500-H+, 2540-D, 2540-E, respectively [32]. Total-N, Total-P were measured with cell test spectroquant kits (Merck) in a spectroquant NOVA 60 (Merck) spectrophotometer (2003).

Gas chromatography–mass spectrometry (GC–MS) analysis was also performed to quantify the removal efficiency for individual alkanes. Methyl tertiary butyl ether (MTBE) was used to extract oil from the water and NPs. GC-MS analysis was performed on an Agilent gas chromatography (GC) system.

Oil concentration was measured using a UV–vis spectroscopy fluorescence spectroscopy and a GC–MS. UV–vis absorbance was measured on a UV–vis spectrophotometer and oil concentration was calculated using a calibration plot which was obtained with known oil concentration samples.

Statistical Analysis

ANOVA analysis of variance between experimental data was performed to detect F and P values, i.e. the ANOVA test was used to test the differences between dependent and independent groups [33]. Comparison between the actual variation of the experimen-

tal data averages and standard deviation is expressed in terms of F ratio. F is equal (found variation of the data averages/expected variation of the data averages). P reports the significance level, d.f indicates the number of degrees of freedom. Regression analysis was applied to the experimental data in order to determine the regression coefficient R^2 (STATGRAPHICS Centurion XV, software, (2005). The aforementioned test was performed using Microsoft Excel Program.

All experiments were carried out three times and the results are given as the means of triplicate samplings. The data relevant to the individual pollutant parameters are given as the mean with standard deviation (SD) values.

Results and Discussion

FTIR Analysis

Figure 1 shows FTIR spectra of the PVP and PVP-coated magnetite nanocomposite. For PVP, the absorbent peaks at 1002, and 3000 $1/\text{cm}$ belong to scissoring bending, asymmetric and symmetric stretching vibrations of methylene (CH_2), respectively. For the PVP-coated magnetite nanocomposite spectrum, peak at 2500 $1/\text{cm}$ can be attributed to the stretching vibration of C-N and C=O , respectively. Comparison between PVP and PVP-coated magnetite nanocomposite spectra show that peak at 2500 $1/\text{cm}$ for PVP suppressed in the PVP-coated magnetite spectrum. These results suggest that PVP is coated on nanoparticles through the PVP carbonyl group.

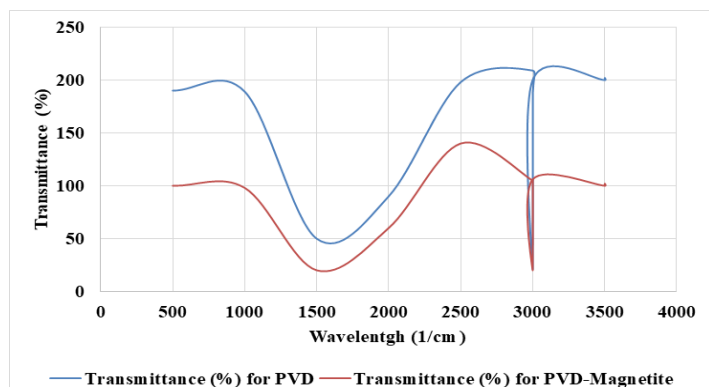


Figure 1: FTIR spectra of PVP and PVP-magnetite nanocomposite

The FT-IR spectrum of prepared ZFHA core-shell nanocomposite. The peak appears around 3600–3400 $1/\text{cm}$ is attributed to the O-H stretching vibration and around 1600–1500 $1/\text{cm}$ is attributed to the O-H bending of the surface adsorbed water [29]. In the present study, for PVP, the absorbent peaks at 1002, and 3000 $1/\text{cm}$ belong to scissoring bending, asymmetric and symmetric stretching vibrations of CH_2 , respectively. For the PVP-coated magnetite nanocomposite spectrum, peak at 2500 $1/\text{cm}$ can be attributed to the stretching vibration of C-N and C=O , respectively.

XRD Analysis

The XRD spectrum of the synthesized PVP-magnetite composite nanoparticle is shown in Figure 2 which shows that magne-

tite (Fe_3O_4) is the dominant phase of the composite nanoparticles (JCPDS No. 01-075-0449), although the presence of some magnetites cannot be found. By using Equation 1, the average crystal size of 14.3 nm and particle size of 16.8 nm were calculated.

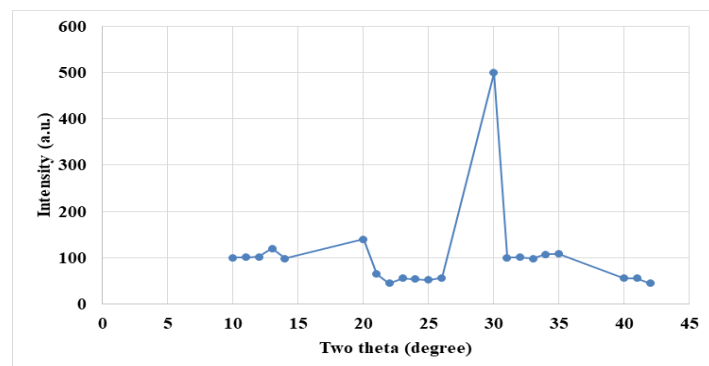


Figure 2: XRD spectrum of PVP-magnetite nanocomposite

The morphology, crystallinity and elemental composition of the ZFHA core-shell nanocomposite are observed by HR-TEM image, corresponding selected area electron diffraction (SAED) pattern and energy-dispersive X-ray (EDX), respectively [29]. The TEM image shows the core/shell structure of the nanoparticles formed; where the cores appear darker and the shells lighter. This is due to the difference in electron penetration efficiencies of the oxide particles (core) and of the hydroxyapatite (shell). The size of the nanoparticles is about 5 and 12 nm for cores and shells, respectively; which is in agreement with crystalline sizes estimated by Scherer's equation. The SAED pattern result indicates that the prepared ZFHA core-shell is polycrystalline. The rings are sharp and continuous, refers to the highly crystalline formation. The EDX pattern result gives chemical elements in ZFHA core-shell nanocomposite; from which the elements Zn, Fe, P, Ca and O were identified. The average Ca/P and Fe/Zn molar ratios are about 1.67 and 2, respectively which is agreed with the stoichiometry of HAp (1.67) and ZnFe_2O_4 in nature. From the ratios of their peaks, pure stoichiometric of $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ and ZnFe_2O_4 -could be performed [29]. In this study, the XRD spectrum of the synthesized PVP-magnetite composite nanoparticle which shows that magnetite (Fe_3O_4) is the dominant phase of the composite nanoparticles (JCPDS No. 01-075-0449), although the presence of some magnetites cannot be found. By using Equation 1, the average crystal size of 14.3 nm and particle size of 16.8 nm were calculated.

TGA Analysis

Figure 3 is the TGA analysis of the PVP-coated iron oxide nanoparticle. In the TGA curve, a high weight loss at 300°C (70%) is due to evaporation of physically absorbed water. About 69% weight loss was observed at 500°C and this is attributed to decomposition of PVP. This is in agreement with other studies, which show that PVP decomposition starts at 300°C, whereas PVP-coating magnetite nanocomposite start to decompose at lower temperature and have a slower decomposition rate. By using this proposed hydrothermal technique, sufficiently monodispersed nano magnetite with median size of 11 nm and coated with PVP were synthesized.

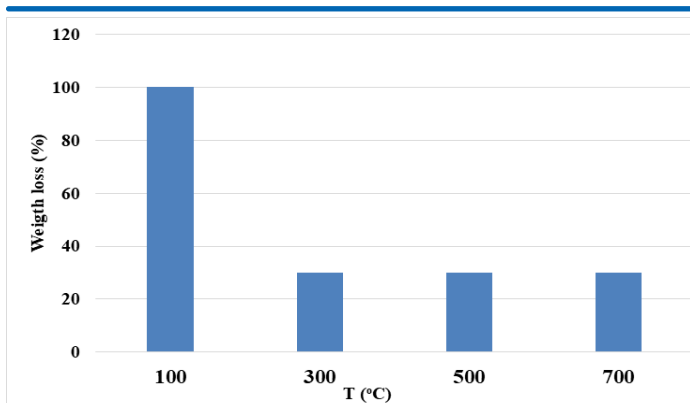


Figure 3: TGA analysis in the PVP-magnetite nanocomposite

Effects of PVP-magnetite Nanocomposite Concentration to Total Oil Removal

In order to determine the total oil removals the PVP-magnetite nanocomposite concentrations were increased from 1 mg/l up to 8 mg/l after 30 min contacting time. Based on these results, by increasing the nanocomposite concentration from 1 mg/l to 3mg/l the total oil removal yields increased from 56% to near 98%. Also, by increasing nanocomposite concentration, fluorescence intensity increased indicating low removal of total oil. However, when PVP-magnetite nanocomposite concentration was further increased to 5 mg/l. The yield of oil removal decreased remained the same (97%) (Table 2). The lower removal percentage at the 8 mg/l PVP-magnetite nanocomposite concentration is likely due to increased nanocomposite aggregation at this concentration, reducing surface area and absorption capacity of the nanocomposites.

Table 2: Effect of PVP-magnetite nanocomposite concentrations on the removals of total oil

Time (min)	PVP-magnetite nanocomposite concentrations (mg/l)	Total Oil removal efficiencies (%)
30	1	56
	2	76
	3	98
	5	97
	6	97
	8	67

Effect of Separation Time on the Removal of Total Oil at a Optimum PVP-magnetite Nanocomposite Concentration of 3 mg/l

To investigate the effect of separation time on the oil extraction capacity of nanocomposite, individual oil experiments using an optimized nanocomposite concentration (3 mg/l) at varying separation times were performed (Table 3). The maximum total oil removal efficiency was detected after 25 min separation time as 99.90%.

Table 3: Effect of separation time on the removal of total oil at a optimum PVP-magnetite nanocomposite concentration

Time (min)	PVP-magnetite nanocomposite concentration (mg/l)	Total Oil removal efficiencies (%)
5	3	56
10	3	76
15	3	79
20	3	83
25	3	99.90
30	3	98

patented a magnetic polymer nanocomposite for divalent metal ions removal from water[34]. The composite is a magnetic nanocomposite possessing a core of Fe_3O_4 in a shell of branched polyhydroxystyrene, entitled as $Fe_3O_4@BHPS$. The nanocomposite was prepared via co-precipitation in alkali solution. Results respectively depicted that the nanocomposite attained 93% adsorption of Pb(II) and 80% adsorption of Cd(II), in 30 min, reaching equilibrium in 120 minutes. The optimum adsorption capacities of Pb(II) and Cd(II) at 24.85°C were 186.2 and 125 mg/g, respectively. Finally, the nanocomposite with the heavy metal(s) adsorbed was easily removed from aqueous solution via the utilization of a magnetic field [34]. In this study, the maximum 99.90% total oil removal efficiency was observed at an optimized 3 mg/l PVP-magnetite nanocomposite concentration, at 25 min separation time, at an initial oil concentration of 450 mg/l, at between pH = 5.00 and 7.00, at 35°C, after 100 days of anaerobic fermentation, and this result is comparable higher than the yield observed by the mentioned above[34].

Removals of Individual Oil Types

In this study some oils with increasing C numbers were used to determine the effect of high and low molecular weights on the removals of individual oils. The removals of nonane, undecane elcosane with 9, 11 and 20 C ring numbers and ducosene and pentacosene with 22 and 25 C ring numbers were investigated after 25 min contacting time at 3 mg/l PVP-magnetite nanocomposite concentration. The analysis results showed that oil types with low C rings exhibited high removals (Table 4). Nonane and undecane with 9 and 11 C rings have high removal yields like 99.99% while the oils with high C rings (ducosene and pentacosane) such as 22 and 25 C rings exhibited low yields (80% and 72%, respectively). The oil types with high C ring (25 C) did not show high removal. The oil degradation depends to the C content of the oil.

Table 4: Removals of oil types containing different number of carbon ring

Time (min)	PVP-magnetite nanocomposite concentration (mg/l)	Individual oil removal efficiency (%)
25	3	
Name of oils		
Nonane (C 9)		99.99
Undecane (C 11)		99.99
Elcosane (C 20)		99
Ducosene (C 22)		80
Pentocosane (C 25)		72

Reusing of PVP-magnetite Nanocomposite

By using a magnetic separation allows PVP-magnetite nanocomposite reuse/recycle of which can further reduce the financial and environmental cost. Acetone and heating technique more than 90% of the initial oil absorption capacity of C soot sponge was recovered even after 40 cycles of oil absorption with a yield of 95%. Oily PVP-magnetite nanocomposite was cleaned/extracted with 3 ml acetone and 4 ml MTBE were mixed in a liter deionized water, then it was incubated at 45oC and finally the Fe₂O₃ particles were separated with magnet. Table 5 indicates the performed studies. The aforementioned nanoparticle can be used 29 times to remove the oil with a yield of 99.99%. After that the oil removal yield was detected as 98%. After 39 times of utilization the oil recovery yield was detected as 95%.

Table 5: Oil recovery with PVP-magnetite nanocomposite versus 40 cycles

Cycle	3 mg/l PVP-magnetite nanocomposite	Oil recovery (%)
1		99.99
2		99.99
3		99.99
4		99.99
5		99.99
6		99.99
7		99.99
8		99.99
9		99.99
10		99.99
11		99.99
12		99.99
13		99.99
14		99.99
15		99.99
.....	
30		98
31		98
32		98
33		98
34		98
35		98
36		98
37		98
.....	
40		95

also synthesized pH-sensitive and recyclable silica-coated Fe₃O₄ magnetic nanoparticles using dense liquid silica coating method [35]. The oil-water separation mechanism proposed by the authors pointed out that both electrostatic interaction and interfacial activity has significant roles in the oil-water separation. Under acidic condition, the magnetic nanoparticles adsorbed to the negatively charged oil droplets hence facilitate the flocculation of the oil droplets via electrostatic interaction thus can be easily separated through physical magnetic separation. On the other hand, under the neutral condition, the magnetic nanoparticles served as non-ionic surfactant and accumulated at the interface of oil-water whereas under alkaline condition, the silica coated nanoparticles were detached from each other due to the electrostatic repulsion [35]. These interesting characteristics of the magnetic nanoparticles have allowed the recycling of this material based on its pH sensitivity where it can be used as an effective adsorbent to remove emulsified oil droplets under acidic and neutral conditions, and can be recycled in alkaline solution through simple rinsing [35].

Furthermore, some technical hitches in separation and recycle together with the imaginable threat to surroundings and human health are instigated via the possible emission of nanoparticles into the surroundings [36]. However, a functional practice in curbing these technical hitches is to synthesize hybrid nanocomposite via the covering of fine particles over solid particles of larger size which will be effective for wastewater treatment and gas separation [36,37].

prepared Fe₃O₄ magnetic nanoparticles by a coprecipitation method and followed by surface coating with silica and 3-aminopropyltriethoxysilane (APTES) [38]. The resultant nanocomposite adsorbent was then supported onto quaternized chitosan (QC) for adsorption of oil. QC is known to demonstrate permanent cationic charges hence could establish electrostatic interaction with negatively charged oil droplets [38]. Owing to the excellent adsorptive properties, the adsorbent exhibited promising oil removal capability at various pH conditions where under both neutral and acidic conditions, the water transmittance of 98% was achieved at 34mg/l and under alkaline conditions, water transmittance of 98% was achieved with dosage of 38 mg/l. Importantly, the magnetic adsorbent shown good reusability for practical application where it still exhibited good performance of more than 90% water transmittance after 8 cycles of operations. In this study, the aforementioned nanoparticle can be used 29 times to remove the oil with a maximum yield of 99.99%, at an initial oil concentration of 450 mg/l, at between pH = 5.00 and 7.00, at 35°C, after 100 days of anaerobic fermentation, and this result is comparable higher than the yield observed by the after 8 cycles of operations mentioned above[38].

Effect of pH on the Removal of Oil

Experiments carried out in this study with pH = 5.00, 7.00 and 9.00 only allowed detecting some effect of pH on adsorption when the PVP -magnetite nanocomposite was used (Table 6). In this case, the pH required for 99.99 % oil removal from the oil with an initial oil concentration of 450 mg/l the were pH = 5.00 and 7.00, respectively, indicating that removal efficiency of oil was significantly

improved at pH between 5.00 and 7.00. This result is in agreement with those reported, who studied the adsorption of automobile fuels onto magnetite and, who evaluated the effect of pH on the adsorption of Pb(II) from wastewater by magnetic nanoadsorbents and concluded that adsorption efficiency increases at pH between 5.00 and 7.00. This behaviour of PVP magnetite nanocomposite could be explained by the fact that the theoretical value of the point of zero charge (pHPZC) of pure magnetite corresponds to a pH value of 6.00, and for commercial magnetite that point normally corresponds to pH value 5.00. It means that magnetite nanoparticles in a solution with a pH higher than that of the pHPZC are negatively charged. In other words, the anionic behaviour of silica nanoparticles became stronger for pH values between 5.00 and 7.00. However at pH = 9.00, the pHPZC was higher in the oil wastewater, therefore the oil removal yield decreased slightly to 80%. At pH 12.00 the oil removal decreased significantly.

Table 6: Effect of pH on the removal of oil in the oil industry wastewater

Parameter	pH values	Oil removal efficiencies (%)
Oil	5.00	99.99
	7.00	99.99
	9.00	80
	12.00	65

was investigated to the effect of pH on the adsorption of oil by Zn-Fe₂O₄-hydroxyapatite core-shell nanocomposites (ZFHA) for pH ranging between 2 and 10. The optimum pH of the medium was found to be [29]. The adsorption efficiency decreased with increasing pH of the adsorption medium. When the initial pH of the medium was adjusted to the higher values Cr(VI) precipitation was observed because of the existence of (OH) ions in the adsorption medium. At very low pH values, the surface of adsorbent would also be surrounded by the hydronium ions which enhance the interaction with binding sites of the sorbent by greater attractive forces. As the pH increased, however, the overall surface charge on the sorbents became negative and biosorption decreased. The maximum oil removal efficiency is reached within flow rate 3 ml/min and bed height 178.26 mm, regardless of the agitation type used. It is observed also that the highest oil removal percentage (78–100%) obtained at bed height 178 mm and at flow rate 3 ml/min; which is parallel to the results obtained at 5 ml/min [29]. In this study, 99.99% maximum oil removal efficiency was found at an initial oil concentration of 450 mg/l, at between pH = 5.00 and 7.00, at 35°C, after 100 days of anaerobic fermentation, and the similar result obtained by the mentioned above[29].

Treatment efficiency of all pollutants in the oil industry wastewater

Table 7 shows the pollutant removal efficiencies in the oil industry wastewater. As shown all the pollutant parameters were removed with yields as high as 96% and 99%.

Table 7: Treatment yields of all pollutants present in oil wastewater industry

Parameters	Removal efficiencies (%)
COD	99
CODdis	97
BOD5	96
TSS	99
VSS	99
Total oil	99.99
TN	99
TP	99
Total hydrocarbon	98

Conclusions

The analysis exhibited that oil from the oil industry wastewater was effectively removed by the PVP-magnetite nanocomposite produced under laboratory conditions. FTIR analysis results showed that in the spectrum of PVP-coated magnetite nanocomposite the peak at 2500 1/cm can be attributed to the stretching vibration of C–N and C=O. XRD spectrum of the synthesized PVP–magnetite composite nanoparticle exhibited that the dominant phase of the composite nanoparticle is magnetite with a particle size of 16.8 nm. TGA analysis showed that about 69% weight loss was observed at 500°C and this is attributed to decomposition of PVP.

Nonane and undecane with 9 and 11 carbon rings have high removal yields like 99.99% while the oils with high carbon rings (ducosene ana pentacosane) such as 22 and 25 C rings exhibited low yields (80% and 72%, respectively). The aforementioned nanoparticle can be used 29 times to remove the oil with a yield of 99.99%. The maximum CODdis, COD, TSS and oil removal efficiencies were 99%, 99.5%, 99% and 99.90% respectively via adsorption with 3 mg/l hydrophobic PVP-Fe3O4 / Polimer nanocomposite.

The utilization of nanotechnology in different environments has upgraded the presentday environmental engineering and science together with a fresh set of technology that emerged from nanotechnology. The emerged technology at nanoscale has stimulated the advanced utilization of innovative and low-cost techniques that are effective for filtration and adsorption processes for the removal of contaminants in environment. Polymer nanocomposites are materials that make use of advantages of the two materials (nanomaterials and polymers) that makes the composites. The utilization of these materials have resulted in the development of highly efficient materials for environmental utilizations, which have globally gotten the interest of academia and industry. In addition, the progresses in polymer nanocomposite materials properties have allowed numerous industrial utilizations. As an illustration, the integration of engineered nanoscale materials into a polymer membrane matrix has recently earned a substantial consideration for wastewater treatment utilizations.

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