Adsorptive removal of oil spill from sea water surface using magnetic wood sawdust as a novel nano-composite synthesized via microwave approach

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Abstract

Water pollution by oil is a serious environmental problem. Developing new generation of benign adsorbents satisfying several criteria required for real practical application is of great need. This work introduces an effort in this direction, by utilizing a facile synthesis of wood sawdust coated magnetite nanoparticles functionalized stearic acid (WSD@Fe₃O₄NPs/SA) as a novel nano composite along with its precursor WSD@Fe₃O₄NPs. SA was covalently bonded to the precursor by amide bond formation via the interaction with the silylating agent 3-aminopropyltrimethoxysilane (3-APTS). This mode of binding is more stronger than the conventional ester bond. Fourier transform infrared (FT-IR), X-ray powder diffraction (XRD), Scanning electron microscope (SEM) and Transmittance electron microscope (TEM) were employed for characterization and follow up the synthesis process. Application of the newly synthesized magnetic nano composite adsorbent under optimized parameters of contact time (min) and composite dosage (g) reveal high removal capacity values (g/g) evaluated to be 28.32 g/g, 5 min and 0.1 g for used motor oil removal and 41.22 g/g, 10 min and 0.1 g for crude oil. The high removal efficiency exhibited by WSD@Fe₃O₄NPs/SA was mainly argued to the long hydrocarbon chain of SA moiety and additional (CH₂)₃ groups incorporated 3-APTS. Moreover, Analysis of the oil adsorption experimental equilibrium data were well fitted with Freundlich model with correlation coefficients $r^2 = 0.9788$ and 0.9896 for used motor oil and crude oil, respectively. The kinetic data were correlated using two kinetic models and the results were in harmony with pseudo-second order.

Keywords Oil spill · Magnetic nano composite · Wood sawdust · Sea water · Stearic acid · Microwave synthesis

Introduction

Removal of oil spills from water surface is too important topic from both environmental protection and economy point of view. Huge amounts of the spilled oil around the world may be lost every year causing negative economic effects, in addition to great harm to marine environment and aquatic ecosystem [1]. The main oily contaminants in polluted water include lubricants,

petroleum products such as diesel, petrol, kerosene, etc. and spillage from oil tankers. In fact, different chemicals and techniques are reported for cleaning up water from oil spills. Examples of the techniques are: adsorption [2], ultra and microfiltration [3], reverse osmosis [4], gravity separation, coagulation, coalescence, skimmers and barriers [5, 6]. Materials like foam, highly porous synthetic organophilic sorbents [7], silica aerogels [8], zeolites [9], clays [10], exfoliated graphite [11], graphene frameworks [12], carbon nano tubes [13], cellulose fibre [14], collagen fibres, cellulose lignin polymers etc. have been also employed for treating oil contaminated water [15–17]. Moreover, there is a growing interest for developing other new adsorbing materials and composites for oil-water separation which should satisfy one or more of the criteria required for large scale environmental applications. These include high potential capacity, recyclability, cost effectiveness with non-complicated synthetic process and biocompatibility. Even though the removal of sorbent materials after oil adsorption from the aquatic system

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is tedious and time consuming [18]. To overcome this problem and achieving fast separation, magnetite nano particles ($\text{Fe}_3\text{O}_4\text{NPs}$) have attracted great attention as a core-shell in a variety of composites with wide spread applications in separation technology, especially as selective collectors for oils from water. Unfortunately, the synthesis of most of these composites require multiple steps and costly chemicals along with low yield which hinder bulk production for real application. Therefore, exploring facile preparation approach utilizing cheap and abundant materials with efficient and fast removal characteristics of oil spills from water surface is still an open area of research. In this context, we report herein, a simple, fast and solventless process for microwave preparation of a novel nano composite based on magnetite wood sawdust modified stearic acid. This composite collects together both the advantages of biocompatibility for all of its constituents and the highly abundant of wood sawdust as a ligno-cellulosic and hemicellulose material Fig. 1, but limited oil adsorption nature [19].

In this context, the aim of this manuscript is devoted to design and perform a solvent-less microwave synthesis for a wood sawdust coated magnetic nano particles modified stearic acid ($\text{WSD@Fe}_3\text{O}_4\text{MNPs/SA}$) as novel magnetic nano composite adsorbent. After characterization, its efficiency for oil spill removal from sea water surface is intended to be explored and optimized. Microwave technique adapted for the preparation of the precursor $\text{WSD@Fe}_3\text{O}_4$ NPs enables a fast and proper mixing of different mass ratios of both WSD and the pre-synthesized Fe_3O_4 NPs for determining the most suitable ratio realizing the highest oil removal. This is an advantage over the conventional co-precipitation method [20]. To maximize this initial efficiency, and increasing hydrophobicity, SA is chosen for this purpose. Its binding is achieved by amide

covalent formation using the silylating agent 3-aminopropyltrimethoxysilane. This mode of binding is stable and more strong [21] than usual ester bond [22].

On the other hand the newly synthesized nano composite assembles together both the advantages of biocompatibility of its constituents in addition to the high abundant of wood sawdust as natural lignocelluloses and hemicelluloses polymer Fig. 1.

Experimental

Reagents and materials

All reagents were A.G. and used without further purifications. Ferrous sulfate hepta hydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), ferric chloride hexa hydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), sodium hydroxide, stearic acid (SA), 3-aminopropyltrimethoxysilane (3-APTS) and *N,N'*-Dicyclohexyl carbodiimide (DCC) were purchased from Aldrich Chemical Company, USA.

Sea water sample was collected from Mediterranean Sea, (Alexandria Coast), El-Shatby beach, Egypt. The sample was clear and free from suspended matter after filtration and a pH evaluated to be 8.0. To prevent any contamination the sample container used for collecting was properly washed with doubly distilled water (DDW) in the laboratory and rinsed at least twice with sea water prior to the sample collection. The origin of the used wood saw dust (WSD) is scots pine. It is a typical and well-known softwood type. The scots pine (*Pinus sylvestris*) tree is a species of pine. WSD used was obtained from a local saw mill in Alexandria. It was first washed with DDW, oven dried at 60° for 6 h and kept in a tightly closed polyethylene bottle.

Two real samples of oils were testified, used motor oil ($d = 0.91 \text{ g/m}$) was obtained from auto oil change workshop and crude oil ($d = 0.83 \text{ g/m}$) was purchased from Alexandria Petroleum Company.

Instrumentation

A Microwave reactor (KOR-131G, Korea) with the following specifications: emitting 2.450 GHz microwave frequency, 200–240 V, 50 Hz, microwave input power: 1350 W, microwave energy output: 1000 W was used for the synthesis of the novel magnetic nano composite $\text{WSD@Fe}_3\text{O}_4\text{NPs/SA}$ and its precursor $\text{WSD@Fe}_3\text{O}_4\text{NPs}$. Their IR-spectra along with WSD and Fe_3O_4 were obtained from KBr pellets by using FT-IR Model 410 JASCO (Japan). X-ray diffraction (XRD) analysis was carried out by Philips X-ray diffractometer PW 1370; Co. with Ni filtered $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The surface morphology and particle size of the nano composite and precursor were examined by scanning electron microscopy (SEM) obtained using JSM-5400 LV JEOL (Japan) and transmission electron microscopy (TEM) Model Tecnai 12 (Philips, The Netherlands).

Fig. 1 Structure of the main chemical compositions of WSD (a) Cellulose (b) Lignin and Hemicellulose (c)

Scheme 1 Schematic representation for the microwave synthesis of wood sawdust coated magnetic nanoparticles ($\text{WSD@Fe}_3\text{O}_4\text{NPs}$) and its stearic acid (SA) functionalized form ($\text{WSD@Fe}_3\text{O}_4\text{NPs/SA}$), arose by amide covalent binding of SA via 3-APTS as linker

Preparation of Fe_3O_4 magnetic nanoparticles ($\text{Fe}_3\text{O}_4\text{NPs}$)

Magnetic nanoparticles were prepared using the co-precipitation method, via the slow addition of 5 M NaOH solution into a mixed solution of 0.25 M $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 0.5 M $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ till obtaining pH 11, at room temperature. The magnetite particles thus formed were left to settle, then magnetically separated from the supernatant where they thoroughly washed with DDW till reaching neutral medium [23, 24]. Finally, they collected and dried in oven at 60 °C. The $\text{Fe}_3\text{O}_4\text{NPs}$ thus produced using this method was dense, black and magnetic with a particle size in range 13.3–29.2 nm.

Fig. 2 The adsorption capacity of the magnetized WSD composites for removal of used motor oil and crude oil with different Fe_3O_4 : WSD mass ratios (a) 2:1, (b) 1:1, (c) 1:2 and (d) 1:3, respectively (adsorbent mass 0.1 mg, volume of oil 5 mL and contact time 20 min)

Microwave modification of wood sawdust

Synthesis of wood saw dust coated magnetite nano particles ($\text{WSD@Fe}_3\text{O}_4\text{NPs}$)

A novel method is adapted for this purpose, where a solid – solid interaction is performed under solvent less

Fig. 3 FT-IR spectra of (a) WSD, (b) $\text{Fe}_3\text{O}_4\text{NPs}$, (c) $\text{WSD@Fe}_3\text{O}_4\text{NPs}$, (d) SA and (e) $\text{WSD@Fe}_3\text{O}_4\text{NP}$

microwave condition. Thus, $\text{Fe}_3\text{O}_4\text{NPs}$ were mixed with WSD in different w/w ratios 2:1, 1:1, 1:2, 1:3, 1:5 and 1:10, respectively. These mixtures were thoroughly grinding using mortar of agate, wetted with drops of DDW and then microwaved at actual power 200 w for 5 min. The produced composites were dry and homogeneous with different degrees of brown color. Finally, they were tested for their oil spill removal efficiencies as a function of increasing WSD mass ratio, along with maintaining magnetic properties.

Synthesis of wood sawdust coated magnetite nano particles covalently functionalized stearic acid nano composite (WSD@ Fe_3O_4 NPs / SA)

The precursor WSD@ $\text{Fe}_3\text{O}_4\text{NPs}$ with 3:1 mass ratio of WSD: $\text{Fe}_3\text{O}_4\text{NPs}$ was chosen for modification by SA. It satisfies the conditions of highest oil adsorption capacity and keeping potential magnetic properties. Thus for covalent binding of SA, 2.0 g of WSD@ Fe_3O_4 NPs was first silylating by mixing with 4 ml of 3-APTS and microwave irradiated at power 200 w for 15 min. The silylated product WSD@ Fe_3O_4 NPs-3APTS was mixed with SA by 1:2 mass ratio and subjected to 200 microwave power for 10 min in presence of DCC (peptide synthesis reagent [24]). The final product showed pale brown color after thoroughly washing with hot distilled water and oven drying. The microwave synthetic approach was indicated in Scheme.1.

Results and discussion

Optimization of Fe_3O_4 : WSD mass ratio

Microwave technique adapted for the preparation of WSD@ $\text{Fe}_3\text{O}_4\text{NPs}$ enables proper mixing of selected mass of both WSD and the presynthesized $\text{Fe}_3\text{O}_4\text{NPs}$ for optimizing oil removal efficiency. In contrast, in the conventional coprecipitation method the iron species present in solution mixture is allowed to be precipitated over the solid substrate required to be magnetic. The adsorption capacity of the magnetized WSD composites with different $\text{Fe}_3\text{O}_4\text{NPs}$: WSD mass ratios were evaluated for removal of used motor oil and crude oil spill localized on sea water sample, (20 mL volume in 25 mL beaker) were determined and represented graphically as shown in Fig. 2.

It is clear that, as the mass of WSD increases, the adsorption capacity for oil removal increases according to the order 2:1 < 1:1 < 1:2 < 1:3 $\text{Fe}_3\text{O}_4\text{NPs}$:WSD mass ratio. These ratios meet WSD % and adsorption capacity in g/g (for used motor oil and crude oil) equal 33.3% (5.42, 5.52) < 50% (7.5, 7.9) < 66.7 (7.51, 8.73) < 75% (7.58, 8.94), respectively. On the other hand, both the mass ratios 1:5 and 1:10 were not suitable, where a decreasing in magnetic efficiency of the nano adsorbents was observed.

The results obtained were in consistent with decreasing hydrophilic nature of WSD surface by incorporating magnetite nano particles into large mass of wood sawdust [25, 26]. Consequently, the composite with 1:3 mass ratios was chosen as an optimum $\text{Fe}_3\text{O}_4\text{NPs}$: WSD ratio for further modification

Fig. 4 X-ray diffraction of (a) $\text{Fe}_3\text{O}_4\text{NPs}$, (b) WSD, (c) WSD@ $\text{Fe}_3\text{O}_4\text{NPs}$ and (d) WSD@ $\text{Fe}_3\text{O}_4\text{NPs/SA}$

Fig. 5 SEM images of (a) $\text{Fe}_3\text{O}_4\text{NPs}$, (b) WSD, (c) $\text{WSD@Fe}_3\text{O}_4\text{NPs}$ and (d) $\text{WSD@Fe}_3\text{O}_4\text{NPs/SA}$

and functionalization by stearic acid (SA) for increasing hydrophobicity.

Characterization of magnetic nano adsorbents

Ft-IR

FT-IR spectra for WSD as a main component forming the novel nano composite $\text{WSD@Fe}_3\text{O}_4\text{NPs/SA}$ and its precursor $\text{WSD@Fe}_3\text{O}_4\text{NPs}$ reflect its complex cellulose – hemi cellulose – lignin nature. Fig. 3a shows a verity of spectral FTIR bands of WSD. It was found a strong broad band located at 3381.57 cm^{-1} for at OH stretching, C–H stretching in methyl and methylene groups at 2920.06 cm^{-1} . Comparing the spectra of cellulose and lignin [27] reveals that the absorptions situated at 1509.99 cm^{-1} and 1659.45 cm^{-1} (aromatic skeletal vibrations) are caused by lignin and the absorption located at 1725.98 cm^{-1} is caused by the C=O stretch in non-conjugated ketones, carbonyls and ester groups. The vibrations at 1426.1 cm^{-1} can be due to aliphatic and aromatic C–H groups in the plane deformation vibrations of methyl, methylene and methoxy groups. A narrow band spectrum was observed at around 1381.75 cm^{-1} , this can be attributed to the aromatic CH and carboxyl–carbonate structures. In addition, the peaks at $1267.97\text{--}1030.77\text{ cm}^{-1}$ represented C–OH stretching vibration. On other hand, for the bare magnetite $\text{Fe}_3\text{O}_4\text{NPs}$, Fig. 3b showed the vibrational bands at 448.04 cm^{-1} and 584.91 cm^{-1} characteristic to the (Fe–O) [28]. Further two bands at 3419.88 cm^{-1} and 1628.34 cm^{-1} ascribed to stretching and bending vibrations of surface hydroxyl

groups, respectively. This is due to that magnetite is very sensitive to oxygen, and in the presence of air some might undergo oxidation to $\text{Fe}(\text{OH})_3$ [23]. To emphasize the formation of our novel composite, it was necessary to explain the spectra of stearic acid as shown in Fig. 3c. Two strong peaks located at 2925 cm^{-1} and 2855 cm^{-1} belonging to $-\text{CH}_2$ and $-\text{CH}_3$ stearic acid skeleton. Also, a characteristic C=O carboxylic acid was observed at 1769.29 cm^{-1} [20, 29].

$\text{WSD@Fe}_3\text{O}_4\text{NPs}$ spectra explained at Fig. 3d. The peaks of -OH stretching vibration, $-\text{CH}_3$ asymmetric and CO stretching vibration characterized to WSD peaks shifted to 3422 , 2927 , and 1430 cm^{-1} , respectively. In addition to peaks of magnetite ($\text{Fe}_3\text{O}_4\text{NPs}$) appeared at 560 , 634 cm^{-1} and 1631 cm^{-1} confirming the formation of the precursor $\text{WSD@Fe}_3\text{O}_4\text{NPs}$.

Finally, the modification of $\text{WSD@Fe}_3\text{O}_4\text{NPs}$ with stearic acid was confirmed by FTIR as shown in Fig. 3e. The bands at 2852.98 cm^{-1} were attributed to CH_2 of the alkylsilane. $\text{WSD@Fe}_3\text{O}_4\text{NPs}$ functionalized with stearic acid also showed remarkable spectral changes comparing to the previous spectra, especially the appearance of characteristic amide linkage at 3298.27 cm^{-1} , 1630.42 cm^{-1} and 1566.51 , 1452 cm^{-1} due to NH stretching, CO stretching and NH bending, respectively indicating that stearic acid was successfully grafted on the surface of $\text{WSD@Fe}_3\text{O}_4\text{NPs}$ [30].

X-ray diffraction (XRD)

For further clarifying the crystal structure and phase purity of the composite, the XRD patterns of the WSD, $\text{Fe}_3\text{O}_4\text{NPs}$, $\text{WSD@Fe}_3\text{O}_4\text{NPs}$, SA and $\text{WSD@Fe}_3\text{O}_4\text{NPs/SA}$ were

Fig. 6 TEM images of (a) Fe_3O_4 NPs, (b) $\text{WSD@Fe}_3\text{O}_4$ NPs and (c) $\text{WSD@Fe}_3\text{O}_4$ NPs/SA

Fig. 7 Adsorption capacity of $\text{WSD@Fe}_3\text{O}_4$ NPs/SA as a function of time for removal of used motor oil and crude oil

obtained in Fig. 4. The cellulose characteristic peaks could be seen at around 15.5° and 22.0° for the untreated sawdust [31]. The recorded XRD patterns show a good consistency with the standard data of magnetite crystal without any extra noticeable peaks. Characteristic peaks could be clearly identified correspondingly to Fe_3O_4 NPs ($2\theta = 30.1^\circ, 35.5^\circ, 43.3^\circ, 53.4^\circ, 57.2^\circ$ and 63.1°) [32, 33]. By studying the XRD pattern of stearic acid, it was shown that pure SA presented two intense diffraction peaks at $2\theta = 24.1^\circ$ and 21.5° . For $\text{WSD@Fe}_3\text{O}_4$ NPs, the intensity of the peaks decreases and becomes slightly wide, indicating the occurrence of coating of stearic acid shell onto the surface of the composite. The additional diffraction peaks of the composite at around $20.2^\circ, 35.6^\circ, 43.1^\circ, 53.4^\circ, 57.2^\circ$ and 62.7° revealed that SA particles were successfully attached to $\text{WSD@Fe}_3\text{O}_4$ NPs.

Fig. 8 Adsorption capacity of WSD@Fe₃O₄NPs/SA as a function of oil mass removal of used motor oil and crude oil

Scanning Electron microscope

The photography of Scanning Electron Microscope (SEM) of Fe₃O₄NPs revealed the presence of more dense and rough surface with clear crystal shape of particles, Fig. 5a. the parent WSD structure has soft surface with a fiber nature, Fig. 5b [24]. However, incorporation of magnetite nano particle (Fe₃O₄NPs) onto WSD surface resulted in a rough morphology surface with a regular shapes Fig. 5c [14]. Finally, Fig. 5d showed that the roughness increases because of SA functionalizing onto WSD@Fe₃O₄NPs surface. This behavior is well reflected in increasing oil removal capacity.

Transmission Electron microscope

The transmission electron microscopic analysis (TEM) was also performed for Fe₃O₄NPs, WSD@Fe₃O₄NPs and WSD@Fe₃O₄NPs/SA as represented in Fig. 6a, b, c,

respectively. The TEM image of Fe₃O₄NPs showed nano spherical particles in the range 13.3–29.2 nm Fig. 6a, WSD@Fe₃O₄NPs were recorded in the rang 14.6–18.8 nm Fig. 6b. However, TEM image of WSD@Fe₃O₄NPs/SA Fig. 6c exhibited more homogeneity with Fe₃O₄NPs being visible as dark spots inside the novel magnetic nano adsorbent and a final Nanometrical particles located in the range of 15.0–26.7 nm.

The collected results of characterization based on FT-IR, XRD, SEM and TEM analyses support the success of microwave synthesis for the magnetic WSD precursor (WSD@Fe₃O₄NPs) and its SA modified form (WSD@Fe₃O₄NPs/SA).

Application study for removal of used motor and crude oils from sea water samples by WSD@Fe₃O₄NPs/SA

Modification of WSD@Fe₃O₄NPs via covalent binding with SA using 3-aminopropyltrimethoxysilane as linker has led to increasing the length of SA hydrocarbon chain by additional three carbon members. This may play a part in increasing the potential removal efficiency of the newly designed nanocomposite.

Two types of oils were used for creating an artificial oil spillage, highly viscous black colored used motor oil ($d = 0.91$ g/m) which is due to the presence of fine carbon particles, and light crude oil ($d = 0.83$ g/m). The oil adsorption capacity of WSD@Fe₃O₄NPs/SA was determined by using weight measurements. For more accuracy, a known volume (5, 10, 15 and 20 mL) of the examined oil were taken, and their corresponding weights were calculated based on density values. For oil removal studies, a selected volume of oil was poured on 20 mL volume of sea water sample taken in 25 mL beaker to create an artificial oil spill. A weighed amount of the novel magnetic nano composite (100 mg) was spread over the oil spill and then waits for a period of time to allow contact

Fig. 9 Freundlich plot for adsorption capacity of (a) used motor oil and (b) crude oil using WSD@Fe₃O₄NPs/SA

Fig. 10 Langmuir plot for adsorption capacity of (a) used motor oil and (b) crude oil using WSD@Fe₃O₄NPs/SA

between oil spill and the magnetic nano composite surface. The composite after oil adsorption was separated by magnetic attraction using an external magnet. After sea water decantation, it was dried in an oven to constant weight. The oil retention capacity (q) was determined by using the following relation:

$$q = b - m/m \quad (1)$$

Where, ‘ m ’ is the mass (in grams) of the nano composite speared on top of the oil layer and ‘ b ’ is the mass (in grams) of the thoroughly dried nano composite collected after oil adsorption.

It is important to mention that all oil spill removal experiments were done at the real pH of sea water samples evaluated to be 8.0 and at ambient room temperature (25 °C).

Effect of contact time

The equilibrium adsorption capacity is important in the design of adsorption systems. Equilibrium studies in adsorption indicate the potential maximum capacity of the adsorbent during the treatment process. In order to find the optimum equilibrium and contact time for maximum uptake of oil spill under

studying from sea water sample by WSD@Fe₃O₄NPs/SA, experiments were conducted at different contact times ranging from 1 to 20 min. The two other parameters including adsorbent dosage (0.1 g) and initial oil concentration (5 mL) were kept constant. The results showed that, oil removal capacity increased with increasing contact time and reached maximum adsorption capacity of a value 28.32 g/g after 5 min for used motor oil and 37.36 g/g after 10 min for crude oil, Fig. 7. The fast removal rate at the beginning of contact time is due to the large number of vacant binding sites available for the adsorption of oil. The rapid uptake along with the high sorption capacity represents two of the most significant parameters for an efficient adsorbent. As the external surface of WSD@Fe₃O₄NPs/SA becomes saturated with oil spill, the rate of oil uptake starts to decrease till reaching equilibrium.

Effect of concentration of oil (mass of oil)

The effect of initial concentration on oil adsorption was investigated by varying the initial mass of used motor oil from 0.89 g (1 mL) up to 9.08 g (10 mL) and from 0.83 g (1 mL) up to 7.9 g (10 mL) of light crude oil, at fixed adsorbent dosage (0.1 g) and 5 and 10 min optimum contact time for used motor oil and crude oil, respectively. The results obtained based on equilibrium adsorption data indicated that the adsorption capacity of magnetic nano composite adsorbent WSD@Fe₃O₄NPs/SA initially increased with increasing mass of oil. At a mass of 0.89 and 0.83 g (1 mL) of used motor oil and crude oil the adsorption capacity determined to be 7.03 and 5.26 g/g, respectively. These values increase by increasing mass of oil to reach maximum values of 28.32 and 41.22 g/g at 4.5 and 4.75 g (5 and 6 mL) for used motor oil and crude, respectively, Fig. 8. This behavior implies indicates that the adsorption capacity is highly dependent on the initial concentration in solution. On the other hand, the higher oil uptake efficiency exhibited by WSD@Fe₃O₄NPs/SA comparing with its precursor WSD@Fe₃O₄NPs is mainly argued to

Table 1 Parameters of Freundlich and Langmuir isotherms constants for used motor oil and crude oil removal using WSD@Fe₃O₄NPs/SA

Isotherm	Type of oil adsorbent	
	Used motor oil	Crude oil
Freundlich:		
K_F	1.87965	1.706
n	0.74019	0.22
R^2	0.9788	0.9896
Langmuir:		
Q_O (g/g)	0.178	0.227
b (L/g)	5.62925	4.92
R^2	0.6381	0.6719

Fig. 11 Pseudo-second-order kinetic plot for the adsorption capacity of (a) used motor oil and (b) crude oil using WSD@Fe₃O₄NPs/SA

incorporation of SA with its own hydrocarbon chain and in part by an additional three methylene groups (CH₂)₃. These three carbon members were introduced via covalent binding of SA with WSD@Fe₃O₄NPs using 3-aminopropyltrimethoxysilane (3-APTS) as linker. Consequently, this will lead to increase the hydrocarbon chain length and hence increasing the hydrophobic nature of the newly magnetic nano composite for oil adsorption. In this context, it is important to indicate that this mode of modification is more better than modification of WSD by SA through esterification route [34, 35].

Adsorption isotherm

The adsorption isotherm is important from both theoretical and practical points of view. In order to optimize the design of an adsorption system to remove oil, it is important to establish the most appropriate correlations of the equilibrium data of each system. Equilibrium isotherm equations are used to describe the experimental sorption data. The parameters obtained from the different models provide important information on the sorption mechanisms and the surface properties and affinities of the adsorbent. In this study, the two most common isotherms, Freundlich and Langmuir models, were used to describe the experimental adsorption data.

Freundlich isotherm The most important multisite adsorption isotherm for heterogeneous surfaces is the Freundlich adsorption isotherm and the linear form of this isotherm is expressed as [36].

$$q_e = K_F \cdot C_e^{1/n} \quad (\text{non-linear form}) \quad (2)$$

Where, K_F and $1/n$ are Freundlich constants (indicators of sorption capacity and intensity, respectively) Fig. 9 Taking logs and rearranging of Eq. (1), it can give the linear form of Freundlich model which expressed as:

$$\log q_e = \log K_F + 1/n \log C_e \quad (\text{linear form}) \quad (3)$$

Here, the constants (K_F) and ($1/n$) can be calculated from the intercept and slope of this linear equation, respectively.

Langmuir isotherm The Langmuir equation is applicable to homogeneous adsorption where the adsorption of each adsorbate molecule on to the surface has equal sorption activation energy. The linear form of this isotherm is represented by the expression Fig. 10,

$$C_e/q_e = (1/q_{\max}) C_e + (1/q_{\max} K_L) \quad (\text{linear form}) \quad (4)$$

where, C_e and q_e are the equilibrium concentrations of adsorbate in the liquid and adsorption capacities in mmol mL⁻¹ and gg⁻¹, respectively. $q_{\max}$ and K_L are Langmuir constants, which are related to the maximum adsorption capacity. From these constants, it is clearly showed that the data is fitting very well to the Freundlich model (see Table 1).

Adsorption kinetic study

The kinetic adsorption data can be processed to understand the dynamics of the adsorption reaction in terms of the order of the rate constant. In this context, aqueous solutions (20 ml) with 100 mg of WSD@Fe₃O₄NPs/SA were agitated. In order to find the maximum oil uptake by WSD@Fe₃O₄NPs/SA and

Table 2 Kinetic parameters of fitted model to experimental data

Type of oil	q_e (exp.) g/g	Pseudo-second order		
		R^2	slope	Q_e (theoretical)(g/g)
Used motor oil	28.32	0.9508	0.031	32.26
Crude oil	41.22	0.9233	0.0214	46.72

to interpret the experimental data, two kinetic models, pseudo-first order and pseudo-second-order models were used in this study. The Lagergren pseudo-first-order model proposes that the rate of sorption is proportional to the number of sites unoccupied by the adsorbate [36]. The pseudo-first-order equation can be written in linearized form as follows:

$$\log (q_e - q_t) = \log q_e - (k_1/2.303) t \quad (5)$$

where, q_t is the adsorption capacity (g/g) at any preset time interval (t) and k_1 is the pseudo first-order rate constant (min^{-1}). A graph of $\log (q_e - q_t)$ versus time is plotted and the constant is found. From results, it can be seen that the data do not fit well to the first order model for two types of oil, as the R^2 values are less than 0.8 in most cases.

Additionally, the adsorption data were analyzed using the pseudo-second-order kinetic model. The pseudo-second order kinetic model can be written in linearized form as follows:

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (6)$$

where, k_2 is the second-order rate constant (g/g min). The plot of t/q_t vs time gives a straight line as shown in Fig. 11. The kinetic parameters such as adsorption capacity q_e and rate constant k_2 are computed from the slope and the intercept, respectively of the fitted curves and reported in Table 2. It was found that the theoretical adsorption capacity Q_e values, 32.26 and 46.72 g g⁻¹ were closed to the experimental q_e values, 28.32, 41.22 gg⁻¹ recorded

on using WSD@Fe₃O₄NPs/SA for used motor oil and crude oil removal, respectively.

Finally, these results along with R^2 values >0.9 seem to be in harmony with a pseudo-second-order kinetic model.

Sorption capacity comparison

The newly designed nano composite WSD@Fe₃O₄NPs/SA exhibits superior performance for removal of both used motor oil and crude oil spills from seawater surface in comparison with recently used adsorbents, Table 3.

Conclusion

A novel environmentally friendly green biocompatible nano composite (WSD@Fe₃O₄MNPs/SA) with superior oil sorption performance was successfully synthesized using solvent-less microwave approach. In addition to the well-known benefits (vis., safe, simple and time saving), of using this technique as a tool in surface modification [47], Its use for the preparation of the precursor WSD@Fe₃O₄MNPs enables fast and proper mixing of selected mass ratios of WSD and Fe₃O₄MNPs to attain the highest oil removal value. This represent an advantage over the conventional co-precipitation method, where the iron species present in solution mixture is allowed to be precipitated over the solid substrate required to be magnetized.

Table 3 Comparison of the oil removal efficiency of the newly synthesized magnetic nano composite and various adsorbents as a function of contact time and oil adsorption capacity

Adsorbent	Type of oil	Contact time (min)	Adsorption Capacity (g/g)	Reference
Magnetic sawdust	Lubrication oil		11.5	[37]
Horn shell residues	Crude oil	>10	0.61	[38]
Magnetic carbon nanotubes	Fatty acids		10.51	[39]
Oleic acid grafted sawdust	Vegetable oils	5 min	6.4	[20]
Castor oil grafted sawdust	Heavy crude oil	>5 min	5.79	[20]
Recycled wool-based nonwoven	Heavy crude oil	1–5 min	12.46	[40]
Sawdust	Crude oil	5 min	3.6	[41]
Acetylated rice husk	Crude oil	3–5 min	3.2	[42]
Raw rice husk	Crude oil	20 min	6.0–9.2	[42]
Acetylated rice husks	Diesel oil	>5 min	10.31	[42]
White rice husk ash	Crude oil	25 min	2.8	[43]
Magnetic exfoliated graphite	Crude oil	>5 min	2.98	[44]
Acetylated fibers	Crude oil	10 min	21.75	[45]
Carbon nanotube sponge	Diesel oil	30 s	110	[46]
WSD@Fe ₃ O ₄	Used motor oil	30 min	7.58	This study
WSD@Fe ₃ O ₄	Crude oil	30 min	8.94	This study
WSD@Fe ₃ O ₄ /SA	Used motor oil	5 min	28.321	This study
WSD@Fe ₃ O ₄ /SA	Crude oil	10 min	41.218	This study

Application of the nano composite (WSD@Fe₃O₄MNPs/SA) for magnetic separation of used motor oil and crude oil spills from sea water surface under external magnet revealed high oil removal capacity evaluated to be 41.22 g/g and 28.32 g/g, respectively. This high efficiency was argued mainly to the hydrocarbon chain incorporated SA, and in part by elongation of this chain by additional three carbon members leading to increasing its hydrophobic nature. This occurred as a result of using 3-aminopropyltrimethoxysilane as linker between WSD@Fe₃O₄MNPs and SA during functionalization and amide bond formation. The adsorption behavior of the prepared magnetic nano adsorbent was the best represented by the Freundlich isotherm. The kinetic data were correlated using two kinetic models and the results were in harmony with pseudo-second order with correlation coefficients $R^2 = 0.9508$ and 0.9233 for used motor oil and crude oil, respectively.

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