

Removal of Motor Oil Using Hydrophobic Nano-Silica

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Abstract: Because of its environmental and economic impact, oil contamination is a global concern, and the treatment of oily water leftovers a challenge to environmental scientists and technologists. Amid current techniques for oil treatment, sorption is popular since it is inexpensive, easy and effective. Non-toxicity and availability at a competitive price are important aspects in the selection of adsorbents. In the present investigation, the effectiveness of a commercially existing hydrophobic nano-silica (R 812) was examined for the removal of motor oil (HD 40) from oily water, with the effect of pH being analyzed for its removal efficiency. The highest removal of oil (up to 95%) was obtained for a pH value of 7. The results of the batch kinetic studies revealed a high level of correlation with first-order kinetics. The adsorption isotherm behavior was also studied for different adsorbent dosages at pH 7. The isotherm data were fitted with various models reported in the literature. The fit was mostly found to be poor. It is found here that nano-silica (R 812) with a surface area of 260 m²/g can effectively remove as much as 15g of motor oil per gram of the adsorbent at neutral pH.

Keywords: Hydrophobic; isotherms; motor oil; nano-silica; sorption.

1 Introduction

One of the utmost challenging environmental snags today, is the removal of oil from wastewater (Quevedo et al., 2009). The petroleum reserves are continuously being exploited leading to ongoing oil pollution in marine and terrestrial environment both. It is estimated that annually 1,300,000 tons of oil enter the sea (National Research Council, 2003), around 53% of which comes from human activities such as petroleum extraction, transportation and consumption (International Petroleum Industry Environmental Conservation Association, 2005). The catastrophic effects of the environmental event are evident when considering that the highest concentration of some petrochemicals in water e.g. benzene are 0.005 mg/L. Just one litre of benzene can make several million gallons of water unsafe for humans (Eweis et al., 1998).

As the oil mixes with water, it produces a form of emulsion that must be treated before it is discarded, as it is a toxic substance. Even small amounts of this oil can cause negative reactions, as it poses a hazard to the microorganisms involved in the biodegradation of sewage. Therefore, the effective separation of oil from the produced fluids prior to the disposal of effluents has long been a challenging technical task in the petroleum industry (He and Chen, 2003; Xia et al., 2003; Rajakovic and Skala, 2006; Sayed and Zayed, 2006).

There are various hydrophobic adsorbent used in current years, such as natural sorbents: Populus seed fibers, Silk-floss fiber, Hollow carbon fibers of natural cotton, Kapok fiber, Silkworm cocoon waste, Fir fibers, Low & high micronaire raw cotton, Kenaf core, Cattail fiber, Salviniasp, Low grade raw cotton fibers, Cotton grass, Sugar cane bagasse, Human hair, Sugi fiber, Milkweed, Rice husk, Corn stalk (agriculture residue), Wheat straw, Barely straw, Chrome shavings, Sisal leaves, Cellulosic fibers, Modified wheat straw, Sawdust, Coconut coir, Mixed sawdust, Wool fibers, Coir fiber, Sponge gourd, Reed canary grass, Leaves residues, Hemp fiber, Treated bark, Hydrophobic aquaphyte – Salviniasp, Bentonite, Peat moss, Chitin, Raw luffa fibers, Rubber powder, Walnut shell, Protein wastes (feather, goat hair), Green coconut shells, Garlic and onion peel, Corn cob, Wood chips, Coconut husk, Chitosan, *Mucorrouxii* and *Absidiacoerulea* (Syed , 2015).

Organic polymers (synthetic): Fabricated polystyrene (PS) fibers, Nano-porous polystyrene fibers, Composite of polypropylene fiber and waste tire powder, PBMA/SiO₂ coated kapok fiber, Coated kapok fiber, Polydimethylsiloxane treated mesoporous grapheme, Super hydrophobic kapok fiber,

Polypropylene fiber cut, Polyurethane sponge, Oil Superabsorbent Polymer (Oil-SAP), Macroporous rubber gels (organogels), Acetylated kapok fibers (PAKF), Polyester sponge, Cellulose aerogel of paper waste, Graphite/isobutylene-isoprene rubber (IIR), Butyl Rubber, Ternary polyacrylate copolymer resin, Hydrophobic cotton fibers, Butyl acrylate grafted polypropylene fiber, Polypropylene, Ethanol grafted polyacrylonitrile, Wool-based nonwoven material, Nano-porous polydivinylbenzene (PDVB), Polydimethylsiloxane coated (PDMS) silica nano-particles, Nonwoven polypropylene, Foams of polyurethane or polyether, Polyurethane foams, Organo-clays, Surface treated hydrophobic aerogel granules, Fatty acid grafted sawdust (oleic, stearic, decanoic), Vegetable oil grafted sawdust (mustard, castor), Cyclohexane-oligomers (CPDO) poly(dimethylsiloxane) (PDMS), Glycerol modified vermiculite, Organic/mineral powder, Amberlite XAD-4, Magnetic polymer nanocomposites, Hydrogel of chitosan (polyacrylamide), Waste tire powder, Hexadecyltrimethylammonium modified fly ash, Dodecyl benzene sulphonic treated $MgCO_3$, $CaCO_3$, Sodium oleate modified high calcium fly ash, Palm leaves (modified), X-type zeolite (propyl, esterification), Magnetically super hydrophobic bulk material, Polyester fiber, Surfactant modified barely straw, Polyethylene, Hybrid-modified resin, Bromide modified polystyrene resin, Dodecyl benzene sulphonic treated CaO , MgO and Yellow horn shell residues (Syed, 2015).

Mineral materials (inorganic): CNT sponge, Carbon nano-tube sponges, Exfoliated graphite, Carbonized fir fibers, Exfoliated vermiculite /carbon nanotube (EV/CNT-fluffy), Acetylated cellulose fibers (corn straw), Vertically aligned carbon nanotubes, Magnetic carbon nanotube sponges (Me-CNT sponge), Exfoliated vermiculite /carbon nanotube (EV/CNT-90), Carbonized pith bagasse, Nano-wire, Peat (PT-1), Hydrophobic silica aerogels, Expanded Perlite, Carbonized rice husks, Black rice husk ash, Amorphous silica, Silica xerogels, White rice husks ash, Hydrophobic aerogel, Chemically treated and untreated sludge of petroleum refineries, Loof ash skeleton, Sepiolite, Hydrophobized vermiculite (carnauba wax), Hard coal, Hydrophobic nano silica, Na-bentonite, Expanded vermiculite, Activated carbon, Talc, Fly ash, PTMA & ODTMA montmorillonite, Eggshell, Zeolites, Bentonite and Sand (Syed, 2015; Brandão, et al., 2010; Annunciato et al., 2005; Gammounet et al., 2007; Lim and Huang, 2007; Cambiella et al., 2006; Hussein et al., 2008; Viraraghavan and Moazed, 2003; Ahmad et al., 2005; Banerjee et al., 2006; Ahmad et al., 2005; Mysore et al., 2005; Radetic et al., 2003; Ceylan et al., 2009; Haussard et al., 2003; Linet et al., 2010; Bastani et al., 2006; Wei et al., 2003; Zunan et al., 1995; Eliset et al., 1995; Choiet et al., 1993; Viraraghavan and Mathavan, 1990; Brown, 1992; Webb, 1991; Barrer, 1989; Krasznai and Takats, 1982).

When developing an effective treatment method, it is necessary to choose an appropriate **absorbing** material to process the wastewater contaminated with oil. One of the most commonly used materials is activated carbon, an active, inorganic adsorbent, as it provides a large surface area, and has a large proportion of micro-pores. These particular factors make it particularly effective at adsorbing odours and vapours and breaking down or removing organic compounds such as oil. However, the high price, deprived mechanical strength, poor adsorption selectivity, and inefficient regeneration of activated carbon limit its usage in many applications (Reynolds and Richards, 1996; Zhou et al.). Moreover, the emulsified oil can blind pore spaces during operation, thereby seriously undermining its oil removal efficacy (Alther, 1995; Rajakovic-Ognjanovic et al., 2008).

Efforts worldwide are underway for developing various types of sorption material for the cost-effective removal of different kinds of oil contaminants from the oily water. Towards this end, the present study aims to examine the effectiveness of the hydrophobic nano-silica as a sorbent in treating the water contaminated with the motor oil. The strategy here is to employ commercially available nanosilica, which provides tremendous surface area owing to its nanometric dimension, for the physical adsorption of the motor oil. The selected nanomaterial (R 812) has an average primary particle size of 7-nm and a surface area of $260\text{-m}^2/\text{g}$. It is also important to consider the toxicity of sorbents when choosing one to apply. One compound with seemingly minimal or non-existent health implications is nano-silica (silicon dioxide), which is chemically inert.

2 Materials and Methods

2.1 Materials

The hydrophobic nano-silica (R812) used in this study was supplied by Evonik Degussa GmbH, Germany. Table 1 presents the characteristics of hydrophobic nano-silica as supplied by the manufacturer. Note that the adsorbent contains over 99.8% silicon dioxide, which poses no health hazards either to human or to marine life.

Table 1. Characteristics of hydrophobic nano-silica

Characteristics	Values
<i>Physical characteristics</i>	
pH	7-7.5
Moisture content	≥0.5 %
Tapped density	60 g/l
Form	Powder
Color	White
Odor	Odorless
Loss on ignition	≥1.0-2.5 %
Average primary particle size	7 nm
Surface area	260 m ² /g
<i>Amountwt%</i>	
SiO ₂	≥99.8
Carbon	2-3
Al ₂ O ₃	≥0.05
Fe ₂ O ₃	≥0.01
TiO ₂	≥0.03
HCl	≥0.025

Note: Bothe physical and chemical values were obtained from Evonik Degussa GmbH, Germany

The motor oil (HD 40) employed in this work was purchased from a local fuel station in Riyadh. The oil density and viscosity were measured using a digital density meter and dynamic viscosity meter, respectively. Three measurements were run at 25 °C, and the mean values were 0.879 g.ml⁻¹ and 5.85 cP. It is worth noting that all the chemicals were used as received, without further purification.

2.2 Methods

Studies were conducted at the room temperature (22 ±0.5 °C) in a 200 ml glass beaker by placing 100 ml of tap water, 5 g oil and 0.35 g of sorbent. The characteristic color of oil was disappeared when hydrophobic nano-silica was added to the oil dispersion and adequate contact time was given for the sorption (Fig. 1). The oil concentration progressively decreased from the initial value to the final value, which showed no change further, even after a long contact, this point was taken as the equilibrium value.



Figure 1. Digital images of (A) motor oil emulsion, (B) motor oil emulsion mixed with hydrophobic nano silica.

The medium with hydrophobic nano-silica and oil had an initial pH 7, which was maintained without adding any buffer. pH 4 was achieved and maintained by citric acid (2 ml). On the other hand, pH 8 and 9 were obtained by addition of 2 and 4 ml of sodium phosphate solution, respectively.

For the batch kinetic studies, samples were drawn at different time intervals up to the equilibrium time. Then the slurry was centrifuged for 10 min and filtered through a 1.5 mm glass micro-filter to separate hydrophobic nano-silica and oily water. The filtrate was used for measuring oil concentration using an OCMA Horiba-310 Oil Content Analyzer with an integrated extractor (Horiba Ltd., Kyoto, Japan). Inside this instrument oil is automatically extracted by the solvent (polychlorotrifluoroethylene) and then analyzed by infrared spectrophotometry to provide directly the reading in mg/L. Experiments were duplicated and the average values were used in the calculations.

Batch isotherm experiments, up to the equilibrium time, were conducted using the oil-in-water emulsions at the room temperature and pH of 7 (optimum pH). Six representative quantities (0.1, 0.15, 0.2, 0.25, 0.3, and 0.35 g) were selected. As mentioned before, these representative quantities were added to a 200 ml beaker containing 100 ml of tap water and 5 g of the motor oil. At the end of equilibrium time, all the samples were withdrawn, centrifuged for 15 min and filtered and analyzed for oil in water. Experiments were duplicated and the average values were used in the calculations.

3 Results and Discussion

3.1 The Effect of pH

An important aspect of the present study was to analyze the effect of pH on the oil removal efficiency of the nano-silica. The dependence on the percentage of oil removal on pH values is shown in Fig. 2. It is seen here that, at the pH of 4, 90% of the oil is removed from the sample. As the pH increases to 7, the percentage of the oil removed increases to 95%. Further increase in pH leads to a slightly lower oil removal, which again shows a small increase to 94% as the pH is increased to 9. Thus, it is clear here that 7 is the optimum pH for the motor oil adsorption. Therefore, all subsequent experiments are carried out at pH 7. The hydrophobic nano-silica is particularly good at treating water, as the chemicals released during oil removal are pH-neutral. Therefore, there is no requirement to alter the pH before disposal of the effluent produced during the process.

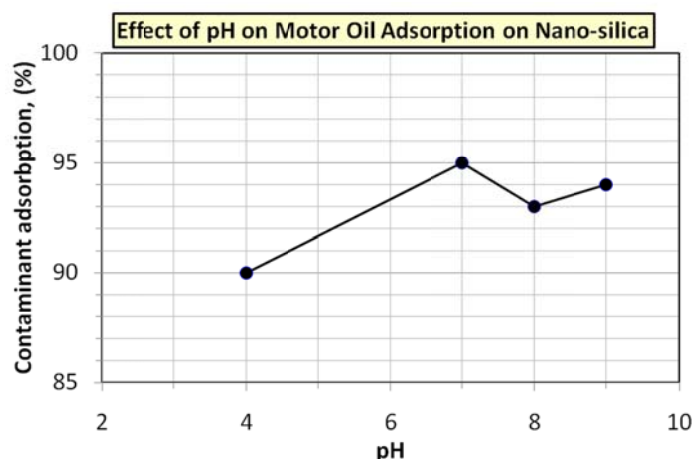


Figure 2. Effect of pH on the adsorption of the motor oil by nano-silica.

3.2 Effect of Contact Time and Adsorption Kinetics

When considering applying actions involving sorption separation, one must consider the kinetics of the adsorption. This is why batch kinetic studies were undertaken in this study. Figure 3 shows the results of these experiments. It is observed that up to 95% of the oil is removed after 29 min of contact. Moreover, the profile of the amount of the motor oil adsorbed versus time is almost linear. It is

worthwhile at this stage to analyze the batch kinetic data obtained to determine the relevant kinetic parameters. The rate equations for both the first and second-order adsorption kinetics are presented in the following along with their solutions as discussed in the literature (Syed et al., 2011). The parameter values are reported next.

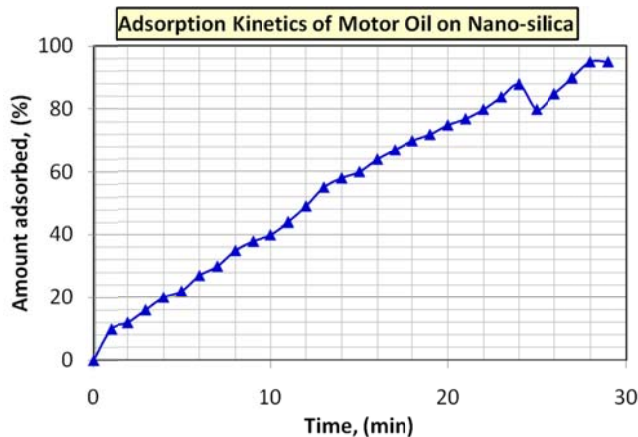


Figure 3. Batch kinetic data of motor oil adsorption on the nano-silica at pH 7 using 3.5 g of nano-silica in 100ml solution containing 5-g motor oil.

The first-order adsorption kinetics can be described as:

$$\frac{dq}{dt} = k_1 (q_e - q) \tag{1}$$

where q_e is the equilibrium amount of adsorbed contaminant (g) per unit mass (g) of the adsorbent, q is adsorbed amount at any time t , and k_1 is the first-order rate constant (1/min). Integrating the above equation with the limit $q = 0$ at time $t = 0$ gives:

$$\ln \left(\frac{q_e - q}{q_e} \right) = -k_1 t \tag{2}$$

Eq. (2) can also be rewritten as:

$$\ln(q_e - q) = -k_1 t + \ln(q_e) \tag{3}$$

Eq. (3) shows that a plot of $\ln(q_e - q)$ vs. time produces a straight line slope k_1 and the y-intercept as $\ln(q_e)$. The experimental data of first-order kinetic fit are shown in Fig. 4. It is seen here that the agreement is good with the slope of -0.09952 and the intercept of 2.8477.

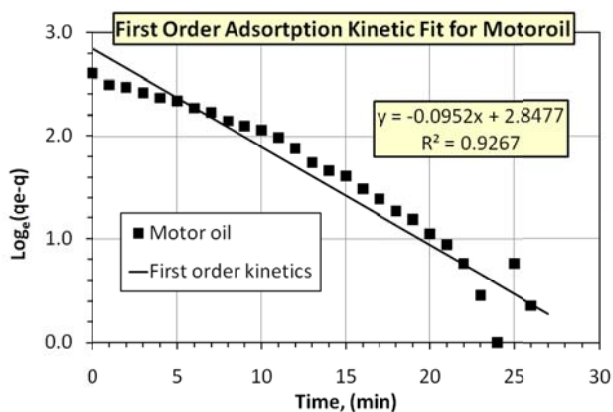


Figure 4. First-order kinetic fit for the experimental data of adsorption of motor oil on the nano-silica at pH 7 using 3.5 g of nano-silica in 100ml solution containing 5-g motor oil.

On the other hand, the second-order adsorption kinetics is represented as:

$$\frac{dq}{dt} = k_2 (q_e - q)^2 \tag{4}$$

Here, k_2 is the second-order rate constant (g adsorbent per g contaminant per min). The integration of Eq. (4) with the limit $q = 0$ at time $t = 0$ gives:

$$\left(\frac{1}{q_e - q}\right) - \left(\frac{1}{q_e}\right) = -k_2 t \tag{5}$$

Rearrangement of the above equation yields:

$$\left(\frac{t}{q}\right) = \left(\frac{t}{q_e}\right) + \left(\frac{1}{k_2 q_e^2}\right) \tag{6}$$

Therefore, a plot of (t/q) vs. time yields a straight line with the slope of $(1/q_e)$ and the y-intercept of $(k_2 q_e^2)^{-1}$. The second-order kinetic fit along with experimental data is shown in Fig. 5. In this case, the fit is not as good as in the case of the linear-kinetics. The slope obtained is now 0.033 and the intercept value is 1.2403. Parameter values obtained in both cases along with the goodness of fit, R^2 , are summarized in Table 2. Note that the value of the q_e obtained using the first-order fit is quite close to the actual experimental value.

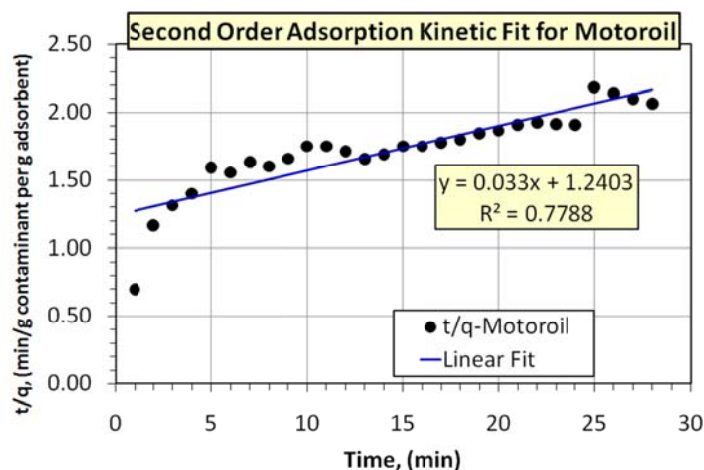


Figure 5. Second-order kinetic fit for the experimental data of adsorption of motor oil on the nano-silica at pH 7 using 3.5 g of nano-silica in 100ml solution containing 5-g motor oil.

Table 2. Summary of kinetic parameters for the motor oil sorption on the nano-silica

Kinetics	Slope	Intercept	R ²	q _e	Rate constant
First order	-0.0952	2.8477	0.9267	17.24807	0.0952
Second order	0.033	1.2403	0.7788	30.30303	0.000878

3.3 Effect of Adsorbent Dosage and Adsorption Isotherms

Since the pH 7 provides the highest removal efficiency, an isotherm study was therefore carried out at this pH by varying the amount of the adsorbent in the 100 ml solution containing 5 g of motor oil. Figure 6 represents the uptake levels of motor oil in relation to the amount of adsorbent stored at room temperature. The results show that as more adsorbent is applied, motor oil is removed in greater amounts. These results correlate with findings in relevant literature (Syed et al., 2011). However, there is a linear dependence between the percentage of oil removed and the dosage amounts. Around 0.35g of nano-silica is required to reach the highest level (95%) of removal.

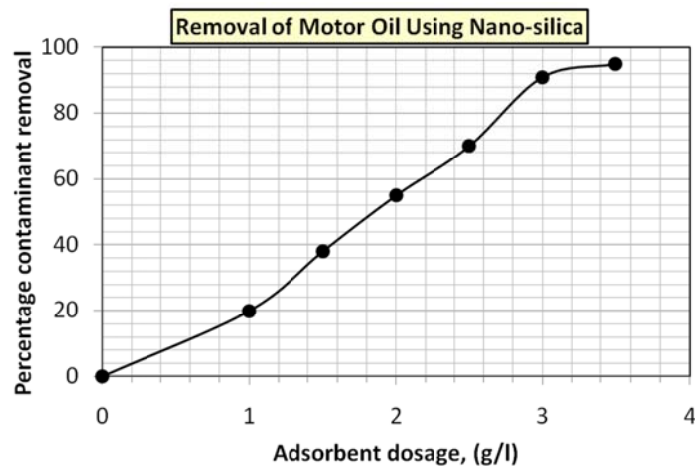


Figure 6. Dependence of the motor oil removal on dosage of nano-silica.

The next section considers the experiment results in relation to various isotherm models applied in recent scholarship [39]. The Freundlich adsorption isotherm is often represented as:

$$q_e = KC_e^{1/n} \tag{7}$$

Here, K and n are isotherm parameters, which can be conveniently determined by rearranging the above equation as:

$$\ln(q_e) = \frac{1}{n} \ln(C_e) + \ln(K) \tag{8}$$

Obviously, a plot of $\ln(q_e)$ vs. $\ln(C_e)$ yields a straight line of slope $\frac{1}{n}$ and the y-intercept as $\ln(K)$. This is shown in Fig. 7. The isotherm fit along with the parameter values and the R2 is also presented together.

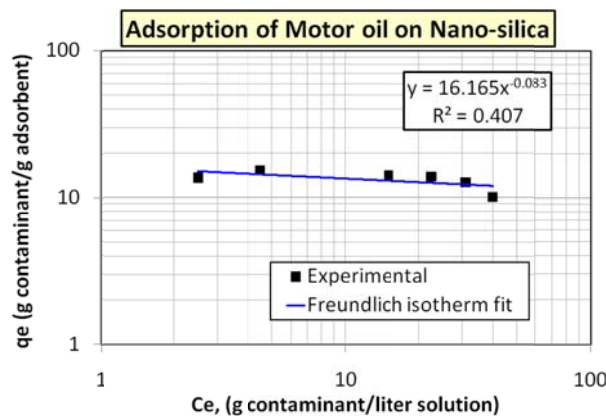


Figure 7. Freundlich isotherm fit for the adsorption of the motor oil using nano-silica.

On the other hand, the Langmuir isotherm is generally given as:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \tag{9}$$

Here, q_m and b are Langmuir isotherm parameters, which can be estimated by plotting $\left(\frac{1}{q_e}\right)$ vs. $\left(\frac{1}{C_e}\right)$. This will result in a straight line of slope $\frac{1}{q_m b}$ and the y-intercept as $\frac{1}{q_m}$.

The experimental data and the Langmuir isotherm fit are shown in Figure 8 along with parameter values. It is clear here that the fit is markedly poor when it comes to representation of the experimental data of motor oil adsorption on the nano-silica.

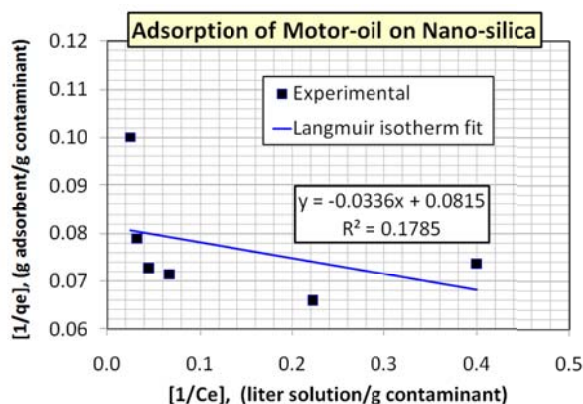


Figure 8. Langmuir isotherm fit for the adsorption of the motor oil of nano-silica.

Similarly, the Temkin isotherm is represented as:

$$q_e = A + B \ln(C_e) \tag{10}$$

The fit of the Temkin isotherm with the experimental data is presented in Fig. 9. The parameter B is found to be -1.026 while parameter A is estimated to 15.82 with the value of R2 being 0.6205 as seen in the figure. The parameters of all the three isotherms are summarized in Table 3. It is clear from the table that the fit is mostly poor.

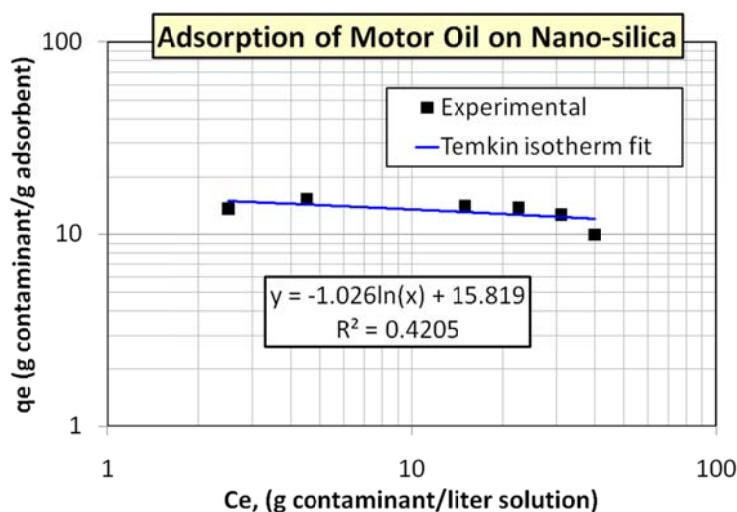


Figure 9. Temkin isotherm fit for the adsorption of the motor oil of nano-silica.

Table 3. Summary of isotherm parameters for the adsorption of motor oil with nano-silica

Adsorption isotherm	Slope	Intercept	R ²
Freundlich isotherm	16.16	-0.083	0.407
Langmuir isotherm	-0.00336	0.0815	0.1785
Temkin isotherm	15.819	-1.026	0.4205

At this point, it is important to consider the sorption capacity and removal efficiency of the nano-silica compound. Figure 10 reveals the sorption capacity of nano-silica in different dosage amounts. One relevant feature of the graph is that sorption capacity remains roughly constant with the uptake of around 14g motor oil per gram. This adsorbent has a superior removal rate than most commercial adsorbents considered in previous studies. Their performance is presented in the Table 4 for the pH value of 7, in view of the fact that effluent at this pH requires no further treatment before its disposal. It can be seen from the table that the removal efficiency of nano-silica is substantially higher than that of other reported inorganic material, and moreover it outperforms organic materials as well. It should, however, be noted that the reported sorption capacity of some organic material could be higher, but their performance is only effective either in acidic or alkaline medium.

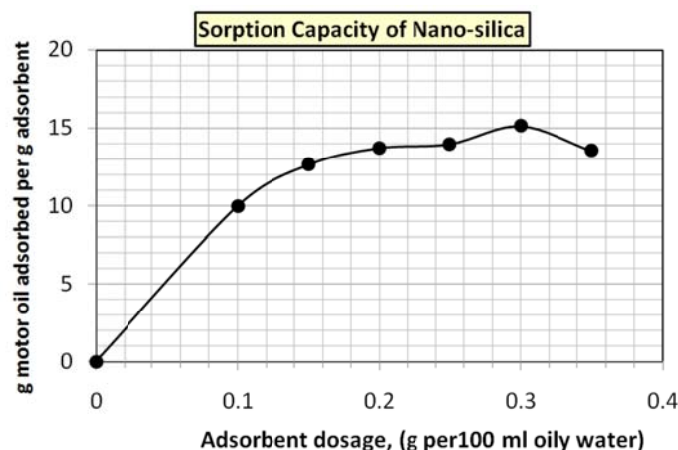


Figure 10. Motor oil sorption efficiency of nano-silica at room temperature for pH =7.

Table 4. Motor oil removal efficiency of various adsorbent at pH 7

Material	Removal (%)	Reference
Nano-silica	95	Present work
Natural wool fibers	82.4	(Alther,1995)
Recycled wool-based nonwoven material	31.3	(Alther,1995)
Sepiolite	20.7	(Alther,1995)
Zeolite	18.8	(Alther,1995)
Bentonite	16.8	(Alther,1995)

4 Conclusions

In this study, hydrophobic nano-silica has been used to remove motor oil from contaminated water at room temperature, and result in a neutral pH level. The results reveal that first-order adsorption kinetics correlate to the batch-kinetic data. No existing adsorption isotherm models could accurately describe the isotherm of motor oil when this non-silica was applied. It was however noted that the levels of polluting material removed did alter depending on the amount of adsorbent applied. When considered against the available data from scholarship, it is clear that nano-silica is more efficient at removing unwanted products than other organic or inorganic adsorbents with a neutral pH.

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References

1. Ahmad, A.L., Bhatia, S., Ibrahim, N., Sumathi, S., (2005). Adsorption of residual oil from palm oil mill effluent using rubber powder. *Brazilian J Chem Eng.*, 22; 371 – 379.
2. Ahmad, A.L., Sumathi, S., Hameed, B.H., (2005). Residual oil and suspended solid removal using natural adsorbents chitosan, bentonite and activated carbon: a comparative study. *J Chem Eng.*, 108: 179–185.
3. Alther, G.R., (1995). Organically modified clay removes oil from water, *Waste Manag.*, 15: 623–628.
4. Annunciado, T.R., Sydenstricker, T.H.D., Amico, S.C., (2005). Experimental investigation of various vegetable fibers as sorbent materials for oil spills. *J Hazard Mater.*, 50: 1340–1346.
5. Banerjee, S. S., Joshi, M. V., Radha Jayaram, V., (2006). Treatment of oil spills using organo-fly ash. *Desalination*, 195: 32–39.
6. Banerjee, S. S., Joshi, M. V., Radha Jayaram, V., (2006). Treatment of oil spills using organo-fly ash. *Desalination*, 195: 32–39.
7. Bastani, D., Safekordi, A.A., Alihosseini, A., Taghikhani, V., (2006). Study of oil sorption by expanded perlite at 298.15K, *Sep Purif Technol.*, 52: 295–300
8. Brandão, P. C., Souza, T. C., Ferreira, C. A., Hori, C. E., Romanielo, L. L., (2010). Removal of petroleum hydrocarbons from aqueous solution using sugarcane bagasse as adsorbent. *J. Hazard Mater.*, 175: 1106–1112.
9. Brown, A., Method for removing oil spills using a natural recyclable absorbent. International Patent No WO 92/22501 of 23 December 1992. 13pp.
10. Cambiella, A., Ortea, E., Ríos, G., Benito, J.M., Pazos, C., Coca, J., (2006). Treatment of oil-in-water emulsions: Performance of a sawdust bed filter. *J. Hazard Mater.*, 131: 195–199.
11. Ceylan, D., Dogu, S., Karacik, B., Yakan, S.D., Okayo, O. S., Okayo, O., (2009) Evaluation of Butyl Rubber as Sorbent Material for the Removal of Oil and Polycyclic Aromatic Hydrocarbons from Seawater. *Environ Sci Technol.*, 43: 3846–3852.
12. Choi, H.M., Kwon, H., Moreau, J.P., (1993). Cotton nonwovens as oil spill cleanup sorbents. *Tex Res J.*, 63: 211–218.
13. Ellis, J., Korth, J., Peng, L., (1995). Treatment of retort waters from Stuart oil shale using high-silica zeolites. *Fuel*, 74, 860–864.
14. Eweis, J. B., Ergas, S. J., Chang, D. P. Y., Schroeder, E. D., (1998). *Bioremediation Principle*, McGraw Hill, New York, USA, p. 83.
15. Gammoun, A., Tahiri, S., Albizane, A., Aziz, M., Moros, J., Garrigues, S., de la Guardia, M., (2007). Separation of motor oils, oily wastes and hydrocarbons from contaminated water by sorption on chrome shavings. *J Hazard Mater.*, 145, 148–153.
16. Haussard, M., Gaballah, I., Kanari, N., Donato, P. D., Barres, O., Villieras, F., (2003). Separation of hydrocarbons and lipid from water using treated bark. *Water Resear.*, 37, 362–374.
17. He, G., Chen, G., (2003). Separation of water and oil from water-in-oil emulsion by freeze/thaw method, *Sep Purif Technol.*, 31, 83–89.
18. Hussein, M., Amer, A.A., Sawsan, I.I., (2008). Oil spill sorption using carbonized pith bagasse. *J Anal Appl Pyrolysis.*, 82, 205–211.
19. International Petroleum Industry Environmental Conservation Association (IPIECA), 2005. Action against oil pollution, IPIECA Report, London, U K, 2005 p. 20
20. Krasznai, M., Takats, A., 1982. Removal of organic contaminants from wastewaters, Hungarian Patent No. HU 2993 A850828, 8pp
21. Lim, T.T., Huang, X. (2007). Evaluation of kapok (*Ceibapentandra*(L.) Gaertn.) as a natural hollow hydrophobic-oleophilic fibrous sorbent for oil spill cleanup. *Chemosphere*, 66, 955–963.
22. Lin, C., Hong, Y., Hu, A. H., (2010). Using a composite material containing waste tire powder and polypropylene fiber cut end to recover spilled oil. *Waste Manag.*, 30, 263–267.
23. Mysore, D., Viraraghavan, T., Jin, Y., (2005). Treatment of oily waters using vermiculite. *Water Resear.*, 39, 2643–2653.
24. National Research Council (NRC), 2003. Executive Summary of Oil in the Sea III: Inputs, Fates, and Effects. National Research Council, Committee on Oil in the Sea: Inputs, Fates, and Effects, 1–4.

25. Quevedo, J. A., Patel, G., Pfeffer, R., (2009). Removal of oil from water by inverse fluidization of aerogel, *Indian Eng Chem Res.*, 48, 191–201.
26. Radetic, M.M., Jovic, D.M., Jovancic, P.M., Petrovic, Z.L., Thomas, H.F., (2003). Recycled wool-based nonwoven material as an oil sorbent. *Environ Sci Technol.*, 37, 1008–1012.
27. Rajakovic, V., Skala, D., (2006). Separation of water-in-oil emulsions by freeze/thaw method and microwave radiation, *Sep Purif Technol.*, 49, 192–196.
28. Rajakovic-Ognjanovic V., Aleksic G., Lj. Rajakovic, (2008). Governing factors for motor oil removal from water with different sorption materials, *J Hazard Mater.*, 154, 1558–563.
29. Reynolds, T.D., Richards, P.A., 1996. *Unit Operations and Processes in Environmental Engineering*, PWS Publications Co., Boston, USA, p. 110
30. Sayed, S.A., Zayed, A.M., (2006). Investigation of the effectiveness of some adsorbent materials in oil spill clean-ups. *Desalination*, 194, 90–100.
31. Syed, S., (2015), Approach of cost-effective adsorbents for oil removal from oily water, *Critical Reviews in Environmental Science and Technology* 45, (17)1916-1945.
32. Syed, S., Alhazzaa, M.I., Asif M., (2011). Treatment of oily water using hydrophobic nano-silica, *Chem Eng J.*, 167, 99-103
33. Viraraghavan, T., Mathavan, G.N., (1990). Treatment of oily waters using peat. *Water Pollut Res J Canada*, 25, 73–90.
34. Viraraghavan, T., Moazed, H., (2003). Removal of oil from water by bentonite. *Fresenius Environ Bull.*, 12, 1092–1097.
35. Webb, J., Method for cleaning up liquids, adsorbent pellets for use in such method, and method for making such pellets, International Patent No. WO 91/01356 of 7 February 1991. 12pp.
36. Wei, Q. F., Mather, R. R., Fotheringham, A. F., Yang, R. D., (2003). Evaluation of nonwoven polypropylene oil sorbents in marine oil spill recovery. *Bulletin*, 46: 780-783.
37. Xia, L., Lu, S., Cao, G., (2003). Demulsification of emulsions exploited by enhanced oil recovery system, *Sep Purif Technol.*, 38: 4079–4094.
38. Zhou, Y., Tang, X., Hu, X., Fritsch, S., Lu, J., (2008). Emulsified oily wastewater treatment using a hybrid-modified resin and activated carbon system, *Sep Purif Technol.*, 63: 400–406.
39. Zunan, Q., Yi, Z., Yuqiao, F., (1995). Removal of oil from concentrated wastewater by Attapulgitic and coagulant. *Water Quality Res J Canada*, 30: 89–99