Application of synthesized acetylated silica in the remediation of oily wastewater

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ABSTRACT
Acetylated materials have been applied successfully in oily water remediation with some degree of success. Many of these materials which have been acetylated are, however, from seasonal fruits and other plant parts. This work reports the successful acetylation of silica extracted from diatomaceous earth by refluxing silica and acetic anhydride using 1% N-bromosuccinimide as a catalyst. The functionalization was confirmed by the presence of absorption bands at 1406 cm⁻¹ (C–O) and 1568 cm⁻¹ (C = O) on an IR spectrum and the presence of C, Si, and increased amount of O on the EDX spectrum. The synthesized materials were applied in the optimization of the removal of oil from synthetic oily wastewater using response surface methodology giving a percentage oil removal of 99.7%. The optimum conditions for oil removal were as follows; 7867 mg/L oil concentration, with adsorbent dosage of 0.001 g and a duration of 21.6 h, and the adsorption capacity under these conditions was found to be 1039 mg/g. The outcomes proved that acetylated silica is an excellent material for oil adsorption and can therefore be used in oil spill clean-ups.

1. Introduction
Many economies of the world are becoming increasingly dependent on oil. As a result, there is increased exploration, transportation and consumption of oil with an associated risk of oil spills at each stage. These spills lead to stress on the environment, causing death to marine organisms, leading to shortage of water and giving it a top spot on the environmental issues list [1–3]. Research in recent years has been geared towards finding the best method to reverse the impacts of pollution arising from oil exploration and use especially in the area of oily water remediation. Methods which have been employed include mechanical methods such as skimming and in situ burning [4], the use of oil dispersants [5], bioremediation methods [6] and the use of oil sorbents [7].

However, the use of adsorbent materials is becoming increasingly popular because of the ease of use, affordability and effectiveness of these materials [7–9]. Adsorbent materials can either be synthetic organic polymers, inorganic materials or organic natural polymers [4]. Synthetic organic polymers like polyurethane usually have high adsorption potential but are non-biodegradable [4]. Inorganic materials like organoclays are biodegradable but have low adsorption capacities [10,11]. Organic adsorbents, on the other hand, are relatively cheap, easily accessible and have been shown to have high adsorption capacities [12,7].

Silica, a major component of the ubiquitous diatomaceous earth [13], can also be mined from ores and has been extracted from agricultural wastes like rice husk [14–17], sugarcane bagasse [18,19], palm ash [20] and corn cob [21,22]. It has found application in several areas such as solar energy systems and water filtration. Silica has proven to be an excellent adsorbent and has been applied in the treatment of water contaminated with gasoline and diesel [23–28]. There have also been studies using silica functionalized with petroleum vacuum residues in the treatment of oily water and oily brines at different pH values [29]. Two major drawbacks of these studies however were pH adjustments and the use of mechanical shakers to aid adsorption which are not achievable in actual oil spills. The search for a cost-effective and practicable adsorbent is still on with many researchers coming up with different materials.

In a bid to find the perfect adsorbent, this study looks at the modification of silica with acetyl groups, the optimization of oil removal from synthetic oily wastewater using the central composite design of the response surface methodology software without the application of mechanical shakers/ stirrers or pH adjustment so as to make it applicable in actual field treatments.
2. Materials and methods

2.1. Chemicals and reagents

Silica previously extracted from diatomaceous earth [30] was used after drying to a constant weight. Acetic anhydride, acetone, ethanol and ethyl acetate were of analytical grade and obtained from Rochelle Chemicals (Johannesburg, South Africa). N-bromosuccinimide was also of analytical grade and obtained from Sigma–Aldrich (St Louis, USA). Sodium dodecyl sulphate was obtained from Telstar technologies (Barcelona, Spain). Milli-Q water from Millipore S. A.S (Molsheim, France) (18.2 µS/cm at 25°C) was also used in all dilutions. Telstar Lyoquest-55 freeze dryer (Shanghai, China) was also used in all dilutions. Telstar Lyoquest-55 freeze dryer (Shangai, China) was used to freeze dry all samples, spectroquant UV spectrophotometer from Merk Group (Germiston, South Africa) was used for total organic carbon testing. Tea bags were obtained from retail outlets in Thohoyandou, South Africa and ALPHA FT-IR spectrophotometer from Bruker Pty (Sandton, South Africa) was used in functional group analysis.

2.2. Acetylation of silica

Acetylation was done by modifying the methods of Nwadiogbu et al. [31] and Nwadiogbu et al. [32]. To 1 mmol of the pre-prepared silica, 5 mmol of acetic anhydride was added. This mixture was refluxed over an oil bath at 100°C for 30 h using 1% N- bromosuccinimide as catalyst. After which, the resulting solution was decanted while still hot. The solute was then washed with 2 mL each of acetone, ethanol and water and freeze-dried.

2.3. Characterization

The resulting residue from acetylation was characterized using a Bruker Alpha IR spectrophotometer (Randburg, South Africa). Scanning electron microscope and energy dispersion X-ray spectroscopy (EDX) FEI Nova NanoSEM 230 with field emission gun, (Eindhoven, Netherlands) was used to examine the morphology and elemental composition of the prepared adsorbent and silica before modification. An FEI T20 absorption electron microscope (TEM )with a CCD camera embedded (2048X2048) was used for further morphological evaluation.

2.4. Preparation of synthetic oily wastewater

Synthetic oily wastewater (SOWW) was prepared using the method described by Shoba et al. [33]. Vacuum pump oil was mixed with sodium dodecyl sulphate (90:1, v/v) in 1 L of water, sonicated for 5 min at an amplitude of 75% and cycle of 0.5 to obtain a homogenous solution. This oily wastewater was used in the optimization experiments.

2.4.1. Response surface optimization of oil removal

Optimization was done by placing variable amount of adsorbent (0.001–0.004 g) in a tea bag, whose tea leaves had previously been emptied out (Figure 1). The bag was then sealed using a plastic sealer and placed in the SOWW (192–9250 mg/L), it was allowed to stand undisturbed for a pre-set time (16–60.5 h) which was also varied. After this, the solution was filtered and the total organic carbon was measured for the initial SOWW and adsorbent treated SOWW using a spectroquant UV spectrophotometer. The equilibrium adsorption was calculated from Equation (1) and percentage removal from Equation (2).

\[
Q_e = \frac{(C_i - C_f)}{m} \times V, \quad (1)
\]

\[
\% \text{ Removal} = \left(1 - \frac{C_f}{C_i}\right) \times 100, \quad (2)
\]

where \(C_i\) and \(C_f\) are the oil concentrations (mg/L) before and after treatment with adsorbent respectively; \(V\) (L) is the volume of the solution, \(m\) (g) is the mass of the adsorbent and \(Q_e\) is the equilibrium adsorption capacity per milligram dry weight of the adsorbent.

2.5. Experimental design

Experiments for optimization of oil removal without shaking were done by varying the weight of the adsorbent, oil concentration and contact time using the central composite design in the response surface methodology (RSM) software. The range of optimized parameters are listed in Table 1.
Table 1. Range of optimized parameters.

| Parameter               | Minimum | Maximum |
|-------------------------|---------|---------|
| Oil concentration (mg/L)| 192     | 9250    |
| Sorbent dosage (g)      | 0.0011  | 0.004   |
| Contact time (h)        | 16.0    | 60.5    |

3. Results and discussion

3.1. Characterization of synthesized adsorbent

Figure 2 represents the infra-red spectra for silica and acetylated silica. The absorption band at 1406.18 cm\(^{-1}\) was due to C–O, the absorption band at 1568.37 cm\(^{-1}\) was due to C=O and the band at 1042 cm\(^{-1}\) was most likely due to Si–O. The absence of peak at 1715 cm\(^{-1}\) showed that there were no unreacted acetic anhydride and the absence of peaks around 1840–1760 cm\(^{-1}\) indicated that the acetylated products are free from acetic acid by-products. These results are in line with what was observed by Nwadiogbu et al. [34] who illustrated that the presence of the carbonyl bands are key to successful acetylation when they reported the acetylation of corn cobs. El Boustani et al. [35] also observed same peaks when they studied the effect of acetylation on the fibres of flax and wood pulp using sulphuric acid as catalyst. Onwuka et al. [36] had similar findings as well during the acetylation of cocoa pods, pride of Barbados pods and empty oil palm fruit bunch.

Figure 3 is the XRD spectra of silica and the modified silica. The plots for both the raw silica and acetylated silica had identical diffraction patterns with no new peaks formed. As can be seen from the plots, sharp peaks present at 2\(\theta\) = 26 indicated that the material was crystalline. It is also worthy of note, that acetylation did not change the crystalline nature of silica suggesting that acetylation occurred on the surface of silica. This is contrary to observations made by Nwadiogbu et al. [32] who discovered that acetylation led to the conversion of crystalline phases into amorphous phases. This disparity can however be explained by the fact that their material was mainly cellulose and as they correctly opined, acetylation of cellulose materials leads to a decrease in crystallinity [37]. Dong et al. [38], however reported

![Figure 2. FT-IR spectra of raw silica and acetylated silica.](image)

![Figure 3. XRD plots of raw and acetylated silica.](image)
similar findings to those obtained in this study when they prepared acetylated cellulose nanocrystals using phosphoric acid as solvent.

Figure 4(a) shows the TEM, SEM and EDX pictographs of the unmodified silica and the corresponding acetylated silica (Figure 4(b)). It was evident that the external pores visible on the surface SEM images of the former were no longer present on the surface of the acetylated silica but have been replaced with a bit of wrinkles and grooves most likely because of the conversion of hydroxyl groups on the surface of silica to more bulky acetyl groups leading to a closure of most of the external pores indicating successful functionalization [39]. The EDX indicated that the unmodified silica had silicon, oxygen and carbon which most likely came from the coating material and the acetylated silica has increased intensity of oxygen and carbon as a result of the introduction of acetyl groups. TEM images shows that the acetylated silica particles were aggregated. This same trend has been observed by other researchers [40,41].

3.2. RSM experiments and model fitting

Quadratic model of the central composite design of the response surface methodology (RSM), a statistical software that allows for estimation of interactions including quadratic effects, was used for modelling experiments. Three reaction parameters were varied as indicated in Table 1: namely, initial oil concentration (mg/L), adsorbent dosage (g) and contact time (h). The actual percentage removal as calculated using Equation (2) are presented in Table 2 which had 20 runs and pictorial representation of the optimization experiments presented Figure 5. It was seen that changes in the optimized parameters were reflected as changes in colour intensity of the SOWW in Figure 5.

The model predictions for percentage removal of oil from SOWW was compared with the values obtained from experiments and plotted in Figure 6 to obtain a straight line with most of the points close to the line. The coefficient of determination R2 was 0.99 indicating that predicted and actual values were in good agreement and that the quadratic polynomial model chosen was sufficient to represent the design space, and was able to explain the relationship between the responses and significant variables [18,42,43].

3.3. Regression model and analysis of variance (ANOVA)

In order to investigate the significance of the model and the model terms, analysis of variance (ANOVA), an essential test used to determine the adequacy and significance of a model was carried out (Table 3). ANOVA
Table 2. RSM design and the actual values of responses.

| Run | Oil concentration (mg/L) | Sorbent dosage (g) | Contact time (h) | Percentage adsorption |
|-----|--------------------------|--------------------|-----------------|-----------------------|
| 1   | 6650                     | 0.004              | 16.0            | 15.6                  |
| 2   | 9250                     | 0.003              | 38.2            | 97.6                  |
| 3   | 9250                     | 0.003              | 38.2            | 97.3                  |
| 4   | 9250                     | 0.003              | 0.85            | 98.3                  |
| 5   | 9250                     | 0.001              | 16.0            | 95.2                  |
| 6   | 704                      | 0.005              | 38.2            | 97.5                  |
| 7   | 704                      | 0.004              | 16.0            | 62.6                  |
| 8   | 192                      | 0.003              | 38.2            | 19.3                  |
| 9   | 704                      | 0.004              | 60.5            | 57.4                  |
| 10  | 6650                     | 0.001              | 60.5            | 95.5                  |
| 11  | 9250                     | 0.003              | 38.2            | 97.6                  |
| 12  | 9250                     | 0.003              | 38.2            | 97.6                  |
| 13  | 9250                     | 0.002              | 38.2            | 97.6                  |
| 14  | 9250                     | 0.001              | 38.2            | 99.0                  |
| 15  | 7250                     | 0.003              | 58.2            | 95.9                  |
| 16  | 704                      | 0.001              | 60.5            | 68.0                  |
| 17  | 6650                     | 0.004              | 60.5            | 96.3                  |
| 18  | 6650                     | 0.001              | 16.0            | 96.4                  |

Table 3. ANOVA for model and model terms.

| Source                  | % Removal | F-value | p-Value |
|-------------------------|-----------|---------|---------|
| Model                   |           | 23.64   | <.0001  |
| A-Oil concentration     |           | 140.65  | <.0001  |
| B-sorbent dosage        |           | 22.26   | .0015   |
| C-contact time          |           | 8.52    | .0193   |
| AB                      |           | 20.77   | .0019   |
| AC                      |           | 12.33   | .0080   |
| BC                      |           | 6.54    | .0338   |
| A²                      |           | 5.15    | .0530   |
| B²                      |           | 0.0251  | .8781   |
| C²                      |           | 0.0686  | .8001   |
| Lack of fit             |           | 5.02    | .0572   |

Determines the significance or otherwise of a model by dividing the variation of the results into two sources, distinguishing model variations from experimental error. It is then able to determine and show if variation from the model is significant when compared to the variation due to residual error with the aid of the Fisher’s F-test value also known as F-value (ratio between the mean square of the model and the residual error) [44,45].

P-value, the more significant the factor is. Generally the smaller the p-value, the less likely the observed trends occurred by chance [46].

It was discovered that the quadratic polynomial model used to represent percentage adsorption was significant (p-value <0.05 and high F-value). The lack of fit p-value was found to be greater than 0.05 indicating that the model fits and further confirmed that the model chosen was adequate to show how concentration, adsorbent dosage, and contact time affected the percentage removal of oil. Only initial oil concentration, adsorbent dosage and contact time and their interaction influenced the percentage oil removed Figure 6.

3.4. Effect of oil concentration and sorbent dosage

As seen from the response surface plot in Figure 7, percentage adsorption increased steadily up to 99%, which was the maximum with an increase in initial
oil concentration and then decreased to 93% with a further increase in initial oil concentration. When initial oil concentration was increased, the oil droplets increased and passed into the pores of the adsorbent easily, hence the initial increase in percentage adsorption [47,48,49]. A point was reached however, when the size of the oil droplets equalled the size of the adsorbent pores. At this point, there was maximum or effective adsorption but as the size of the oil droplets became greater than the size of the adsorbent pores, less oil was adsorbed and there was a subsequent decrease in percentage adsorption. Also, as adsorbent dosage was increased, percentage adsorption increased slightly. The reason for this observed trend was as a result of the introduction of new binding sites on the adsorbents [50,51].
3.5. **Effect of oil concentration and time**

As can be seen from the response surface plots in Figure 8, percentage oil removal increased with time, this was because there was an increased chance of positive interaction between the adsorbent and oil as the adsorbent stayed longer in contact with the solution [50]. The effect of oil concentration is as discussed in section 3.4.

3.6. **Effect of adsorbent dosage and time**

The response surface plot for effect of adsorbent dose and time on percentage adsorption in Figure 9 shows an increase in percentage adsorption with time. With adsorbent dosage, percentage adsorption increased, a maximum was reached, and it decreased. As the dosage was increased, more binding sites were made available and as time was increased, there was more time for the oil molecules to interact with the binding sites. Therefore, at higher dosages, more oil was adsorbed since there are more empty binding sites [51].

4. **Conclusion**

Acetylated silica has been synthesized by use of acetic anhydride producing a material with a wrinkled, groove-like surface. Response surface optimization revealed that oil adsorption using this material depended largely on initial oil concentration, adsorbent dosage and contact time. The optimum conditions for the removal of oil from SOWW using acetylated silica were as follows: 7867 mg/L oil concentration, with adsorbent dosage of 0.001 g and a duration of 21.6 h with a desirability of 1.00. The percentage oil adsorption was found to be 99.3%, meaning that 99% of oil contained in an oily wastewater sample was adsorbed by the acetylated silica under these conditions and the adsorption capacity under these conditions was found to be 1039 mg/g. On-going studies also show that mechanical pressure applied on the adsorbent followed by oven drying at 60°C released the adsorbed oil giving the adsorbent a potential for reuse. Oil adsorption using acetylated silica was carried out without pH adjustments or stirring/shaking making the material applicable in the treatment of field wastewater.

**Disclosure statement**

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