Original Article

Development of amino-functionalized silica nanoparticles for efficient and rapid removal of COD from pre-treated palm oil effluent

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\keywords{Adsorption, Palm oil mill effluent, Silica nanoparticles, Chemical oxygen demand, Sol–gel synthesis}

\ABSTRACT

In this study, low cost synthesis of three-dimensional mesoporous amino-functionalized silica nanoparticles (AFS-NPs) were synthesized by sol–gel method with the addition of two different silica modifiers, 3-aminopropyltrimethoxysilane (APTMS) and 3-aminopropytriethoxysilane (APTES) to two different silica sources, tetramethoxysilicate (TMOS) and tetraethoxyxosilicate (TEOS) separately. The presence of amino group on synthesized nanoparticles from the four different combinations was confirmed by Fourier transform infrared (FTIR) spectroscopy. The synthesized AFS-NPs were of narrow particle size within the range of 500–600 nm and having high specific surface area (148 m\textsuperscript{2} g\textsuperscript{−1}). The AFS-NPs were then utilized to investigate the adsorptive removal of COD from palm oil mill effluent (POME). The maximum removal efficiency (>90\%) of AFS-NPs was found at pH 7, adsorbent dose 0.25 g and temperature 30 °C. At equilibrium the maximum adsorption capacity was found to be 271.11 mg g\textsuperscript{−1}. The Langmuir adsorption isotherm gave the best fit to the experimental data signifying the presence of adsorption monolayer on the surface of the adsorbent. The results have positively qualified grafted silica nanoparticles as one of the adsorptive media for removal of COD from POME.

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1. **Introduction**

Hybrid and composite materials have been extensively studied over a long period of time due to their diverse properties [1–7]. Their properties combine the advantages of the inorganic material (i.e., rigidity, thermal stability) and of the organic substances (i.e., flexibility, ductility, and process ability). In this respect, organically modified silica nanoparticles are a typical class of hybrid materials [8]. Modified silica nanoparticles have been studied in the past few decades due to their unique characteristics and widely studied synthesis techniques [9]. One of the main methods utilized to synthesize silica nanoparticles is the sol–gel method [10,11]. Silica nanoparticles with high specific surface area and silanol concentration compared to their bulk counterpart are expected to drastically alter the properties of composite material. However, the silica surface is hydrophilic in nature and thus has limited affinity for hydrophobic matrix [12]. The surface modification of silica with selected functional groups increases covalent bonding with the hydrophobic matrix, improves affinity between the two phases and thus avoids phase separation [13]. These organically modified silica nanoparticles find their applications in a number of fields [14–19].

Palm oil mill effluent (POME) has been treated with different methods such as coagulation–floculation, biological anaerobic processes, evaporation, membrane technology and photocatalysis [20,21]. Among all these methods, biological and membrane technology are the most common while photocatalytic technology is still at developmental stage. However, all these methods though effective but have various setbacks in terms of their sustainability in the long run [21,22]. For example membrane technology is equally effective as it enhances quality treated water but is very expensive to maintain due to fouling of the membrane that need to be replaced overtime [23]. In contrast, adsorption provides an attractive, reliable and versatile alternative treatment [24,25] and adsorption of COD over activated carbon (AC), zeolite, kaolin has been previously studied to evaluate the overall adsorption behavior in wastewaters. The application of AC has been proved an effective absorber in the removal of both organic as well as inorganic pollutants from wastewater. However, the high cost of commercially available AC limits their industrial applications and therefore great attention has been focused on the production of low-cost alternative adsorbents.

Thus, the development of cheaper, eco-friendly and more efficient adsorbent capable of removing various pollutants including COD from wastewater is a subject of intensive research [26–28]. Silica molecules have high density of hydroxyl groups and can be modified with specific functional groups, such as carboxyl, amino and chloro for their various applications. Several studies have explored the utilization of organically modified silica in wastewater treatment [17,29,30]. Despite the uniqueness of modified silica nanoparticles as adsorbents the syntheses of reported modified silica involves expensive raw materials, multistep synthetic approaches and tangible workup processes.

In this study, syntheses of three-dimensional mesoporous silica nanoparticles modified with amino (–NH₂) group for removing the COD from POME was carried out. This synthesis involves the inexpensive raw materials and simple work up processes. The main objective of this work is to investigate the simultaneous removal of both organic and inorganic oxidizable moieties from POME. The different developed adsorption parameters such as pH, AFS-NPs dose, temperature, initial concentration of COD and contact time were optimized for COD.

2. **Materials and methods**

2.1. **Chemicals**

3-Aminopropyltriethoxysilane (C₂H₅O)₃Si(CH₂)₃NH₂ (APTES) containing one amino group was purchased from Aldrich. 3-Aminopropyltrimethoxysilane (CH₃O)₃Si(CH₂)₃NH₂ (APTM), hexadecyltrimethylammonium chloride (CTAC) a surfactant, tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS) were purchased from Merck. All the chemicals were used as received. Distilled and deionized water was used to prepare the solutions, which was collected from the Bio Process Laboratory of Department of Chemical Engineering and Energy Sustainability, University Malaysia Sarawak.

2.2. **Synthesis of AFS-NPs**

Amino-functionalized silica nanoparticles (AFS-NPs) were synthesized using sol–gel method [31]. Hexadecyltrimethylammonium chloride (CTAC) as template and 1 M sodium hydroxide solution as catalyst were added in 800 g of a methanol/water (50% w/w) solution. Further a mixture of 8.24 mmol of tetraalkoxysilane (TAOS) and 0.43 mmol of 3-aminopropytriethoxysilane (APTS) were added with vigorous stirring at 298 K. Herein, a ratio of TAOS 95% and APTS 5% was selected to produce nanoparticles with higher degree of monodispersity. The solution was allowed to stir for 8 h and afterwards the mixture was aged overnight. The white nanoparticles, which settled down during overnight were filtered, washed three times with distilled water and dried at 318 K for 72 h. To remove the templates, the AFS-NPs were treated with 1 mL of 0.6 M hydrochloric acid at 333 K for 3 h followed by filtration, washing with ethanol and dried at 318 K. The AFS-NPs were then treated with 1 mL of ammonia solution (28%) to remove residual Cl⁻ ions and the solid was recovered by filtration, washed with ethanol, and finally dried in vacuum at 423 K for 12 h.

Using the method mention above, four combinations of gelator silica and modified silica were used to get the optimum yield of AFS-NPs. All the four combinations of silica source and silica modifier are represented in Scheme 1. In the first two combinations (i, ii), TMOS was treated with APTMS and APTES separately and in the next two combinations (iii, iv), TEOS was treated with APTMS and APTES separately to get the AFS-NPs. The product in all these cases has the same molecular structure as the methoxy (–OCH₃) and ethoxy (–OCH₂) side chains present the silica source (TMOS/TEOS) and silica modifier (APTMS/APTES) are hydrolyzed. The presence of methoxy (–OCH₃) and ethoxy (–OCH₂) side chains in the reactants has a remarkable effect on the reaction rates and morphology of
the products. The effect of side chains on reaction kinetics and morphology of the product is explained in detail in Section 3.2
\[(i) \text{TMOS} + \text{APTMS}; (ii) \text{TMOS} + \text{APTES}; (iii) \text{TEOS} + \text{APTMS};
(iv) \text{TEOS} + \text{APTES}\]

2.3. Characterization

AFS-NPs were isolated and characterized. Infrared spectra (IR) were recorded on a Perkin Elmer FTIR (spectrum RXI) spectrometer. IR spectrographs helped to study the changes in the functional groups of reactant and product. Morphology and particle size of nanoparticles were studied using SEM (Jeol JSM-6390LA). The surfaces of the samples were coated with gold before the measurements. The average particle diameter was calculated from the diameters of 100 particles in an SEM picture. The nitrogen adsorption isotherm was measured using a Belsorp-mini II (BEL Japan) at 50 °C. The sample was evacuated at 100 °C under 10−3 mm Hg before measurement. The pore diameter was calculated by using the Barrett–Joyner–Halenda (BJH) method and the specific surface area was calculated using adsorption data in the P/P0 plot, considering the linearity of a Brunauer–Emmett–Teller (BET) plot. Thermal stability of the modified silica nanoparticles was studied using TGA Universal Analyzer 2000 with Universal V4.7 A software.

2.4. POME Collection

The pre-treated POME was collected from aerobic treatment pond of Salcra palm oil mill in Bau, State of Sarawak, Malaysia. The collected POME was stored in a refrigerator at 4 °C to avoid its decomposition by air. The standard method for examination of water and waste water was followed for sample collection and storage [32]. The initial characteristics of the pre-treated POME were measured and presented in Table S1.

2.5. Adsorption study of POME by AFS-NPs

For adsorption experiment, 0.1 g of AFS-NPs was added into 100 mL of POME at pH 5.0 and the beaker was then stirred on a magnetic stirrer for 30 min. The amount of COD after adsorption was determined using COD digester (Rocker COD reactor CR25, USA) with subsequent chemical titration analysis as described in APHA standard methods for the examination of water and wastewater [32]. The % values of COD were obtained from Eq. (1) and at equilibrium, the amount of COD adsorbed by AFS-NPs (Qe) was calculated by Eq. (2).

\[
\% \text{COD} = \left( \frac{C_i - C_e}{C_i} \right) \times 100
\]

\[
Q_e = \left( C_i - C_e \right) \frac{V}{m}
\]

where \(C_i\) (mg L−1) is the initial concentration of the COD before adsorption, while \(C_e\) (mg L−1) is final concentration of COD after adsorption, \(Q_e\) (mg g−1) is the adsorption capacity, \(V\) (L) is the volume of the solution and \(m\) (g) is the mass of AFS-NPs.

To study the effect of initial pH on the adsorption of POME onto AFS-NPs, the experiment was performed at initial pH of 1.0, 3.0, 5.0, 7.0, 9.0, 11.0 and 13.0 using 0.1 g adsorbent at temperature 25 °C and stirred for 30 min. To optimize the AFS-NPs dose, the experiment was performed for 0.10, 0.15, 0.20, 0.25, 0.30, 0.35, 0.40, and 0.45 g of AFS-NPs at optimized pH, temperature 25 °C and stirred for 30 min. The effect of temperature was studied by varying the temperature at 10, 20, 30, 40, 50, 60 and 70 °C.

3. Results and discussion

3.1. Characterization of AFS-NPs

The morphology of the AFS-NPs was observed using SEM analysis and SEM images are shown in Fig. 1, which reveals that silica nanospheres were obtained in all the four combinations. From detailed images analysis, it was observed that the particle diameters were between 500 and 600 nm for TMOS/APTMS combination (Fig. 1a), 150–650 nm for TEOS/APTES combination (Fig. 1b), 200–650 nm for TMOS/APTMS combination (Fig. 1c) and 100–700 nm for TEOS + APTMS combination (Fig. 1d). Further the histograms of the particle size distribution of AFS-NPs from all four combinations were shown in Figure S1. General observation of the images revealed that the percentage of monodispersity was more close to monodispersity in case of product obtained from combination of TMOS/APTMS (Fig. 1a). This behavior of morphology of obtained AFS-NPs is
The presence of amino groups on silica surface was confirmed using FTIR and spectra of AFS-NPs obtained from all four combinations are shown in Fig. 2. A sharp and strong stretching peak at ~1050 cm\(^{-1}\) was observed for all samples that indicated Si–O–Si stretching frequency. Two peaks observed at ~1630 cm\(^{-1}\) and at ~780 cm\(^{-1}\) correspond to free water adsorbed on silica surface through hydrogen bonding. The shoulder observed at ~1525 cm\(^{-1}\) (N–H bending) indicated the presence of –NH\(_2\) groups. The peak corresponding to N–H stretching is expected to overlap with the stretching vibrations of O–H groups at ~3500 cm\(^{-1}\). A shoulder at ~950 cm\(^{-1}\) corresponds to the presence of silanol groups on the silica surface. This shoulder was available in the products of three combinations viz. TEOS/APTES, TMOS/APTMS and TMOS/APTES (Fig. 2B, C and D) representing the availability of –OH group on silica surface. This shoulder was not observed for the product of TMOS/APTMS (Fig. 2A). The absence of shoulder at ~950 cm\(^{-1}\) in Fig. 2A is a confirmation toward the completion of condensation reactions between the silica surface (silanol groups–OH) and APTMS (–NH\(_2\) groups). The product of TMOS/APTMS was denoted as product A. The FTIR spectra of all the samples showed absorption peak at ~2950 cm\(^{-1}\) (C–H stretching), which indicated the presence of –CH\(_2\) groups but the spectrum 2A showed two peaks in this region (2975 cm\(^{-1}\) and 2922 cm\(^{-1}\)) corresponding to intense and clear existence of CH\(_2\) groups in product A as compared to other three combinations, possibly owing to the higher loading of propylamine groups onto Silica surface [12,14,33,34]. It could be concluded from the FTIR results that synthesized product from all the combinations is AFS-NPs, but the best product was obtained in the case of TMOS/APTMS. For further reactions and characterization, the product A was selected. Reaction efficiency between TMOS and APTMS is in accordance with the theoretical concept behind the reaction chemistry.

In order to determine the thermal stability of amino (–NH\(_2\)) group onto silica surface, the AFS-NPs (product A) was
calcined up to 450 °C. Figure S2 shows the FTIR spectra for the aminofunctionalized silica before and after heat treatment. The non-calcined aminofunctionalized silica was used for adsorption purposes. The calcined silica was used only for assessment and to ascertain the presence of amino group in modified silica. Characteristic peak of silica in spectra (Figure S2) at 1035 cm⁻¹ corresponding to Si–O–Si bond of the siloxane backbone has been observed in all the spectra and this indicates that main backbone of silica remains the same before and after calcination [18]. Disappearance of peaks from 2975 cm⁻¹ and 2930 cm⁻¹ is evidence that propyl group along with amino group has been removed from silica surface. Appearance of a peak at 958 cm⁻¹ is due to retention of hydroxyl group (OH), which was retained because of decomposition of Schiff base group. FTIR results further revealed that calcination removes the aminopropyl group and the remaining product is mere silica (SiO₂).

TGA has been used to determine thermal stability of AFS-NPs and both the TGA curve (black line) as well as the first derivatives curve (blue line) of the AFS-NPs is shown in Fig. 3A. There are three decomposition steps exhibited by AFS-NPs, the first step occurs within temperature range of 30–125 °C (8 wt%) representing the elimination of adsorbed water and gases, followed by decomposition of aminopropyl groups which occurred slowly between 125 and 380 °C (4 wt%) and this led to rapid degradation above 380 °C (3 wt%). In addition, this step also produced water, ammonia and ethylene groups. The final step produced ethylene, ammonia, methane and hydrazine.

### 3.2 BET

The adsorption capacity and behavior of AFS-NPs can be predicted from the information about surface area and porosity. The adsorption isotherms of AFS-NPs have been presented in Fig. 3B, which indicates that all those samples having adsorption isotherm have shown much longer straight-line portion of the curve. The starting point of the straight line has been named as point “B” due to Bruauer and Emmett [35] and this shows that the adsorption at point “B” has been due to the capacity of the monolayer. However, formation of multi-layers of adsorbate occurs on the surface of the adsorbent by increasing pressure gradually. Moreover, no appreciable differences in the shape and the amount adsorbed on the adsorbent surface have been noticed in the isotherm plot before capillary condensation has commenced.

The threshold capillary condensation causes a rapid increase in the volume of the adsorbed amount, which has been noticed at relative pressure (P/P₀) of 0.61. Similarly, there is saturation pressure (P/P₀ = 1) very close to the horizontal branch where all the pores have been filled with adsorbed liquid. These assertions are in agreement with the results earlier obtained from the SEM analysis because it equally shows that small particles have higher adsorption capacity. Surface area analysis indicates that the specific surface area of the grafted silica (AFS-NPs) as determined by Bruauer–Emmett–Teller (BET) method is much higher (148 m² g⁻¹) and the pore volume and the diameter are 0.97 cm³ g⁻¹ and 21 nm respectively. Based upon the above-mentioned studies and characterization, the AFS-NPs (product A from TMOS/APTMS combination) were selected to study the adsorptive behavior of POME.

### 3.3 Effect of pH on adsorptive behavior of COD onto AFS-NPs

The effect of pH is regarded as one of the important parameters affecting the adsorption technique. Adsorption removal of COD onto AFS-NPs was carried out in the pH range of 1.0–13.0 using 0.1 g adsorbent for 30 min at 25 °C with shaking speed of 300 rpm as shown in Fig. 4A. The results indicated that the % COD removal increased at low pH from 1.0 to 7.0 and with further increase in pH, the % COD removal was decreased. The higher values of removal efficiency of COD at pH < 8 may be due to the positive charge on the surface of the adsorbent increases, resulted in significantly high electrostatic interactions between positively charged AFS-NPs and organic compounds (COD) [36]. This is not surprising as the point of zero charge (pHₚzc) of AFS-NPs is around 8.5. Therefore, at a pH higher than pHₚzc, the nanoparticle surface is negatively charged attracting cations, whereas at a lower pH, the surface is positively charged attracting anions. The results also showed that the adsorption is not favored in alkaline medium, this is indicated by a decline in % COD removal at pH > 8 and this could be attributed to increasing hindrance to the diffusion of organic compounds due to abundance of OH⁻ ions or could be due to the increase of solubility of the pollutant at high pH.

![Figure 3](image-url)

**Fig. 4** – Effect of adsorption parameters on COD removal over AFS-NPs (A) pH, using 0.1 g AFS-NPs for 30 min at 25 °C with shaking speed of 300 rpm. (B) Adsorbent dose, at pH 7 for 30 min at 25 °C with shaking speed of 300 rpm. (C) Temperature, at pH 7, 0.3 g AFS-NPs for 30 min with shaking speed of 300 rpm. (D) Contact time, at pH 7, 0.3 g AFS-NPs for 30 min at 30 °C with shaking speed of 300 rpm.

**Scheme 2** – Schematic representation of general synthesis of AFS-NPs and application in removal of COD.
values [37]. It is expected that adsorption of COD on AFS-NPs can take place through physical adsorption, chemical adsorption or ion exchange. However, it is rather difficult to predict the exact mechanism of adsorption and ion exchange could be ruled out as with increasing pH most functional groups become dissociated. Results for pH were similar to some previous reports where neutral pH was described for maximum COD removal [38,39]. The synthesis of AFS-NPs and application to remove COD from POME is illustrated in Scheme 2.

3.4 Effect of AFS-NPs dose on adsorptive behavior of COD

The effect of AFS-NPs dosage on percentage COD removal was studied at pH 7 for 30 min at 25 °C with shaking speed of 300 rpm and the results were represented in Fig. 4B. The amount of AFS-NPs was increased from 0.1 to 0.4 g and it was observed that the removal percentage of COD increased with increasing in the AFS-NPs dose and this may be attributed to the increase in the total surface area of the prepared AFS-NPs, and therefore more active sites were available for the adsorption of COD [40]. Equilibrium was reached at 0.3 g of AFS-NPs dose and further increase in the adsorbent dose had a little effect on COD removal, which may be linked to saturation of adsorption sites due to particle interaction and this decreases the total surface area of the adsorbent available to COD [41]. The results of the present study also showed an agreement with a previously reported work where cow-dung ash was used to remove COD [38].

3.5 Effect of temperature on adsorptive behavior of COD onto AFS-NPs

Adsorption of organic molecules on the surface of silica nanoparticles has been found to be relatively dependent on thermodynamic properties such as temperature rise as reported by Schreiber et al. [42]. The effect of temperature on the removal of COD was carried out in the temperature range of 10–40 °C at pH 7, AFS-NPs dose 0.3 g for 30 min with shaking speed of 300 rpm. The results showed in Fig. 4C revealed that the gradual rise in temperature increases the adsorptive removal of COD from POME. The highest percentage removal is attained at 30 °C. However, as the temperature is increased there is gradual drop in the adsorption of COD, leading to a little decrease in the percentage of COD removed. This anomalous increase in adsorption as a result of temperature rise is due to increased penetration of POME inside micropores at higher temperatures which might have led to the creation of new active sites for adsorption of COD [43].

3.6 Effect of contact time on adsorptive behavior of COD onto AFS-NPs

The effect of contact time is an important adsorption parameter and therefore the effect of time on COD removal by AFS-NPs was studied at pH 7, ASF-NPs dose 0.3 g, temperature 30 °C with shaking speed of 300 rpm. The time interval was from 10 to 70 min and the results were shown in Fig. 4D, which indicated that the removal of COD was very rapid during first 25–30 min to reach about 94% due to a large number of available surface sites, representing the fast phase. The COD removal then continues to rise slowly until it reaches an equilibrium value at 50 min where most of the adsorption sites were saturated to maximum removal efficiency, representing the slower phase [44]. After 50 min (regarded as equilibrium time), the amount of COD removed remained constant, which might be attributed to saturation of the adsorption sites as contact time increased. The smooth and independent nature of curve, as in Fig. 4D, indicates the formation of monolayer of COD cover on the outer surface of AFS-NPs.

3.7 Adsorption isotherms

The adsorption phenomenon was studied with respect to the effect of initial COD concentration. The % removal and adsorption capacities of the COD were investigated by changing the initial COD concentration (C0) from 50 to 90 mg L−1 as shown in Fig. 5A. With an increase in the initial COD concentration, the % removal of COD changed from 91.66% to 75.31% and this decrease may be due to the fact that a large number of free active sites of adsorbent were available for the COD molecules at the lower initial concentration and as the COD concentration increased, the saturated sites made it difficult to adsorb COD molecules. On the other hand as the COD concentration increased, the adsorption capacity increased until 271.12 mg g−1. This sorption characteristic represented that surface saturation was dependent on the initial COD concentrations. The binding sites are limited keeping biomass loadings as constant.

In the present work, the relationship between COD adsorption capacities of AFS-NPs and the initial concentrations of COD at equilibrium was analyzed with different isotherm models. The experimental data were fitted to the Langmuir, Freundlich and Temkin isotherm models using origin linear regression. Values for the determined parameters of each isotherm and respective R² value for each regression are shown in Table 1 and the equations for the adsorption isotherm models are represented in Eqs. (3)–(5) [45–47].

Langmuir model

\[
\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{bQ_m}
\]

(3)

where \( Q_m \) and \( b \) are Langmuir constants indicating, respectively, the adsorption capacity (mg g−1) and energy of adsorption (L mg−1). Values of \( Q_m \) and \( b \) are determined from the linear regression plot of \( (C_e/Q_e) \) versus \( C_e \) (Fig. 5B).

Freundlich model

\[
\log Q_e = \frac{1}{n} \log C_e + \log K_F
\]

(4)

where \( K_F \) is the Freundlich constant and \( 1/n \) is a measure of adsorption intensity. The values of \( K_F \) and \( n \) can be measured from linear regression plot between \( \log C_e \) and \( \log Q_e \) (Fig. 5C).

Temkin model

\[
Q_e = B \ln C_e + B \ln A_T
\]

(5)

where \( B \) is a constant equal to RT/\( b_T \). \( A_T \) (L/mg) and \( b_T \) (j/mol) are the Temkin constants. \( b_T \) is related to heat of adsorption and \( A_T \) is the equilibrium binding constant corresponding to the maximum binding energy. \( R \) (8.314 J mol−1 K−1) is the universal
Fig. 5 – Effect of initial COD concentration on the % removal and adsorption capacity of COD onto AFS-NPs (A), Langmuir isotherm model (B), Freundlich isotherm model (C) and Temkin isotherm model (D).

Table 1 – Langmuir, Freundlich and Temkin isotherms parameters for COD adsorption.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Exp. adsorption capacity</th>
<th>Langmuir</th>
<th>Freundlich</th>
<th>Temkin</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFS-NPs</td>
<td>Qe (mg g⁻¹) 271.1</td>
<td>Parameters</td>
<td>Qm (mg g⁻¹)</td>
<td>b (L g⁻¹)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Values</td>
<td>307.7</td>
<td>0.274</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Parameters</td>
<td>Kf (mg g⁻¹)</td>
<td>n</td>
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<td></td>
<td></td>
<td>Values</td>
<td>128.4</td>
<td>4.25</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Parameters</td>
<td>Af (L mg⁻¹)</td>
<td>b_T (g mol⁻¹)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Values</td>
<td>91.22</td>
<td>49.76</td>
</tr>
</tbody>
</table>

gas constant and T (K) is the absolute temperature. The values of A_T and b_T are calculated from the linear regression plot of Q_e versus ln C_e (Fig. 5D).

The results presented in Table 1 showed that the higher values of R² (>0.9) obtained for isotherms models showed that the adsorption process of COD from treated POME by prepared AFS-NPs in this work could be well explained by Langmuir, Freundlich and Temkin models and R² values for all three models are adsorbent specific. The values of Langmuir constant b in the range of 0–1, indicates that the AFS-NPs are favorable for adsorption of COD. The value of n from the Freundlich model for AFS-NPs falls within the range 1–10, which indicates favorable adsorption. The higher value of b_T from the Temkin isotherm model demonstrates a strong interaction force between adsorbates and absorbents.

But by comparing the three models with respect to R² values, it can be concluded that the sorption equilibrium data of COD removal from POME onto the AFS-NPs predominantly can be described by Langmuir model than other two models. This is because of the R² value of >0.99 and also the experimental Q_e is close to theoretical Q_m calculated from Langmuir model suggesting formation of monolayer coverage of COD molecules over outer surface of AFS-NPs. The similar behavior of COD removal was also reported in another study by Ligaray et al. recently [28].

Table 2 lists the comparison of the adsorption capacity and % COD removal by various adsorbents. The AFS-NPs prepared in this work showed comparable and relatively better efficiency to remove COD as compared to some previous works reported in the literature.
Table 2 – Comparison of COD removal by various adsorbents.

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Qe (mg g⁻¹)</th>
<th>% COD removal</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nano-CaO@clinoptilolite</td>
<td>50.4</td>
<td>[26]</td>
<td></td>
</tr>
<tr>
<td>Coffee-waste based AC</td>
<td>68.5</td>
<td>[48]</td>
<td></td>
</tr>
<tr>
<td>Sugarcane bagasse derived AC</td>
<td>77.8</td>
<td>[49]</td>
<td></td>
</tr>
<tr>
<td>Activated carbon fiber (ACF)</td>
<td>85.0</td>
<td>[50]</td>
<td></td>
</tr>
<tr>
<td>Activated carbon cloth (ACC)</td>
<td>500</td>
<td>[51]</td>
<td></td>
</tr>
<tr>
<td>Periwinkle shell-based granular activated carbon (PSC)</td>
<td>77.5</td>
<td>[52]</td>
<td></td>
</tr>
<tr>
<td>Date-pit activated carbon (DP-AC)</td>
<td>241.4</td>
<td>[53]</td>
<td></td>
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<tr>
<td>Commercially available BDH activated carbon (BDH-AC)</td>
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<td>[53]</td>
<td></td>
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<tr>
<td>Γ-Fe₂O₃ NPs</td>
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<td>[54]</td>
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<tr>
<td>Activated carbon prepared from date palm shell</td>
<td>95.5</td>
<td>[27]</td>
<td></td>
</tr>
<tr>
<td>Charcoal ash</td>
<td>68.3</td>
<td>[55]</td>
<td></td>
</tr>
<tr>
<td>Amino polyethylene glycol (PEG) functionalized CNTs</td>
<td>99.7</td>
<td>[41]</td>
<td></td>
</tr>
<tr>
<td>Chiston-coated bentonite</td>
<td>73.34</td>
<td>[28]</td>
<td></td>
</tr>
<tr>
<td>AFS-NPs</td>
<td>271.1</td>
<td>91.7</td>
<td>Present study</td>
</tr>
</tbody>
</table>

4. Conclusions

The AFS-NPs were designed and synthesized and the results showed that the modification could effectively increase its amino content, leading to an increase in adsorption capacity. The adsorbent showed a hybrid mesoporous structure and narrowly dispersed nanoparticles size distribution. The appearance of FTIR peak at 1050 cm⁻¹ corresponds to (Si–O–Si) of the siloxane backbone and (Si–O–Si) deformation confirmed that the modification process was successful. The experimental results of AFS-NPs fit well to Langmuir isotherm model and maximum theoretical adsorption capacity was 307.7 mg g⁻¹. Due to high surface area (148 m² g⁻¹) and hydrophilic and hydrophobic functionalities, AFS-NPs can adsorb both hydrophilic and hydrophobic species present in POME showing favorable adsorptive removal of COD from pre-treated POME. From the view of environmental impact, AFS-NPs could be regarded as cost-effective adsorbent in future water treatment.

Conflict of interest

The authors declare that there is no conflict of interest.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jmrt.2018.03.002.

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