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# Cellulose modified diatomite for toluene removal from aqueous solution

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## ABSTRACT

The presence/existence of harmful aromatic compounds, such as toluene in water poses a significant environmental hazard. Thus, their elimination from water is required. In this regard, here we found an efficient methodology for the removal of toluene using diatomite-cellulose (modified diatomite). The chemical treatments were used to obtain cellulose from sisal fibres and to modify the diatomite. All the adsorbents were characterised via X-ray florescence (XRF), Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), Thermogravimetry (TGA) and Brauner-Emmett-Teller (BET) techniques. The impact of adsorption parameters, such as pH, contact time and initial toluene concentration on the adsorption (%) of toluene was evaluated. The maximum percentage removal of toluene on the natural diatomite was observed to be 79.33% (142.30 mg/g) at pH 6, temperature 22°C, an agitation speed of 150 rpm, adsorbent dosage of 0.1 g and initial concentration of $3\times10^{-3}$ mol/L toluene. Furthermore, under the same conditions, the percentage increase to 97.45% (161.43 mg/g) was observed for the modified diatomite. The kinetic data was conforming to the pseudo-second order model with good correlation. The results showed that the adsorption of toluene could be described by Freundlich isotherm model on the natural and modified diatomite. Thus, our work revealed that the diatomite-cellulose could be used as an effective adsorbent to remove toluene from water.

*Keywords:* Diatomite; Sisal fibers; Cellulose; Kinetics; Toluene; Adsorption

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## 1. Introduction

Despite, the huge efforts of the scientific community, environmental pollution still causes the major problems of health and environment, especially through water contamination [1]. One of the principal water polluting agents is volatile organic compounds, such as toluene. It is one of volatile organic compounds that are frequently used in the manufacturing process and chemical production [2]. Its complex aromatic molecular structural and xenobiotic proprieties make it difficult to degrade spontaneously [3]. Therefore, its removal is critical to ensure the safety of water supplies and to protect the human health. Different types of technologies were proposed to remove the aromatic compounds from water. However, adsorption is the most used method in the industry. For this purpose, various adsorbents were applied to adsorb the aromatic compounds. Recently, an extensive attention was paid to the biological adsorbents with high capacity of adsorption, for easy regeneration and low price. Currently, silicas, zeolites, metals oxides, polymeric resins, cellulose, diatomite and modified clays, as cost-effective and green materials, were investigated widely. For example, acid-activated palygorskite has

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exhibited an excellent toluene adsorption and can be utilised as an effective adsorbent [4]. In another study, ammonia treated activated carbon was a sustainable and renewable adsorbent for the treatment of volatile organic compounds in polluted waters [5]. In addition, Yu et al., [6] reported that magnetic $Fe_3O_4$-SN-diatomite had a good adsorption performance for phenols. The diatomaceous earth ($SiO_2.nH_2O$) is a pale sedimentary rock of biogenetic origin [7]. It has numerous advantages as an adsorbent, for organic and inorganic chemicals having low cost, commercial availability, high permeability and porosity (80%–90% pore space), small particle size (10–200 μM) and large surface area [8,9]. The reactivity of diatomaceous earth was linked to the reactivity of the hydroxyl groups and the acid sites on the surface of the amorphous silica [10]. The literature provides few works for combined natural diatomite with natural polymers for the adsorption application [11].

The cellulose is known as the most abundant biopolymer in the nature. It contains about 1,500 β-glucose units and its chains are held together by intermolecular hydrogen bonding [12]. Due to the exceptional properties of cellulose nano-fibres (big surface area, high aspect ratio, low coefficient of thermal expansion, inexpensive feature), its individualisation from renewable sources has been evolved. The cellulose is considered as an efficient natural adsorbent. Several reports demonstrated its ability to adsorb aromatic compounds, such as toluene, dyes and heavy metal ions [13–15]. The hydroxyl groups, in cellulose, are very reactive and can be easily modified by various reactions, such as oxidation, halogenation, esterification and etherification [16]. Furthermore, the characteristics of cellulose are not constant and vary depending on its origin and preliminary treatments. The sisal fibres are cheap natural fibres with high cellulose content, which make them suitable for the adsorption application. It is from one of the agave families and is composed mainly of 64% of cellulose, 19% of hemicelluloses and has 10–11% of moisture content. The extraction of cellulose from sisal fibres can be carried out by using chemical and mechanical treatment [17]. Despite the excellent adsorbent activity of diatomite and cellulose, very few reports have showed the efficacy of the combined natural diatomite with cellulose fibres for toluene adsorption.

In this study, the diatomite-cellulose was selected as an adsorbent for the removal of toluene in aqueous solution. The raw diatomite was treated using the acid solution to remove fines and other impurities, and to achieve the neutralisation and enhance its adsorption capacity. Various textural XRF, FT-IR, XRD, TGA and BET techniques were used to characterise the samples. The adsorption performances of the treated diatomite, before and after the combination with cellulose, were examined. The effect of several factors, such as contact time, initial concentration and pH on the adsorption capacity was investigated. Thereafter, the use of pseudo-first and pseudo-second order model for analysing the adsorption systems were evaluated and the applicability of the isotherm models—Langmuir and Freundlich models were studied.

## 2. Materials and methods

### 2.1. Materials

The used raw diatomite sample was collected from Gafsa, Tunisia. The cellulose and modified diatomite were prepared using hydrochloric acid (HCl) (Panreac, ACS reagent, 37%), sodium hydroxide (NaOH) (Panreac, 98%), sodium chlorite ($NaClO_2$) (Panreac, ≥99.0%), hydrogen peroxide ($H_2O_2$) (Sigma Aldrich, ≥30%), magnesium sulphate heptahydrate ($MgSO_4$. $7H_2O$) (Sigma Aldrich, >99.5), urea (Scharlau, 99%), calcium carbonate ($CaCO_3$) (Fluka, >99.0%) and acetone (Sharlau, 93%). The chemical tested was toluene (Fisher scientific UK, >99.0%). All the chemical components were used in the laboratory directly without any purification.

### 2.2. Methods

#### 2.2.1. Treatment of diatomite

The raw diatomite was completely crushed with hammers to obtain powder sample. An acid solution was used (HCl 2M) to remove fines and other adhered impurities. Specifically, the crushed powder was mixed with HCl at a 10% ratio of solid (g)/liquid (mL), at the room temperature for 3 h. Then, the resulting material was filtered and rinsed with HCl and distilled water for a couple of times, and then dried in a vacuum oven at 100°C for 24 h.

#### 2.2.2. Preparation of cellulose

The cellulose used in this work was prepared as following: the sisal fibres were stirred in 1.5 M NaOH solution (1:20 w/v ratio) at 120°C for 2 h. Then the pulp was filtered and rinsed with distilled water and submerged in 1.8 M NaOH (1:20 w/v ratio) at 120ºC for 90 min. The bleaching was carried out by treating the fibres in 0.2 M $NaClO_2$ solution (1:30 w/v ratio) at 75°C. After 2 h, the fibres were submerged in 3M $H_2O_2$ solution (1:10 ratio and pH 11) using magnesium sulphate (0.2 wt%) and pentetic acid (0.5 wt%). After bleaching, the cellulose was rinsed many times until neutral pH. Lastly, drying process was carried out at 50°C for 24 h.

#### 2.2.3. Diatomite-cellulose preparation

The synthesis of diatomite/cellulose was done via physical reaction. The diatomite didn't undergo any changes in its chemical structure. Thus, the cellulose served to transform diatomite from its powder state to the beads form, creating reactivity on its surface because of the presence of OH group. In addition, the proposed mechanism between diatomite and cellulose is illustrated in Fig. 1.

The diatomite-cellulose was processed by using the following methodology (Fig. 2): 20 g of cellulose was dissolved into a mixture of NaOH (7 wt%)/urea (12 wt%) at –15°C. Then 10 g of treated diatomite and 3 g of $CaCO_3$ were included. After, the sample was dropped in the acidic solution (2M HCl). The diatomite-cellulose was then immersed in distilled water to dissolve $CaCl_2$ and transferred into acetone. After 24 h, the modified diatomite was washed with distilled water and acetone for several times and finally was put in the vacuum at 50°C for 10 h.

#### 2.2.4. Adsorption procedures

The adsorption was studied by mixing 100 mg of adsorbent with 100 ml of water with various initial concentrations

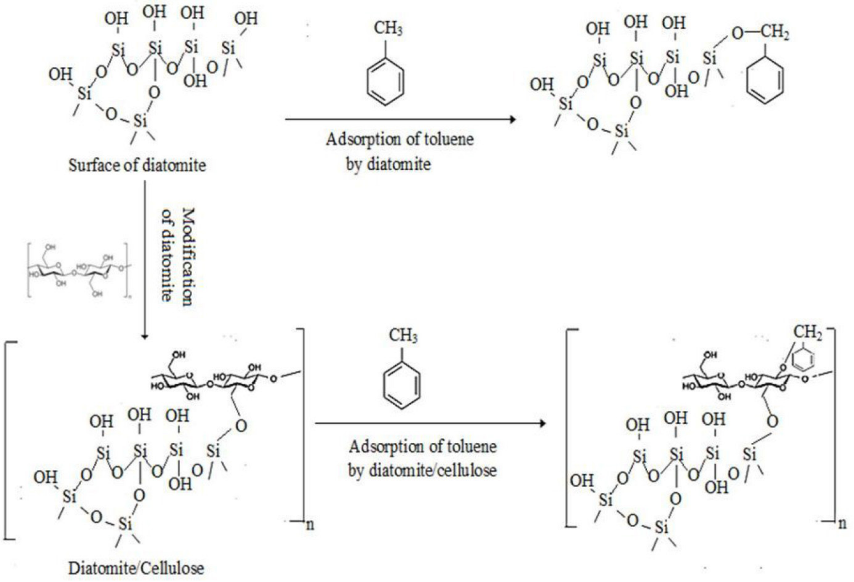

Fig. 1. Proposed mechanism between diatomite and cellulose.

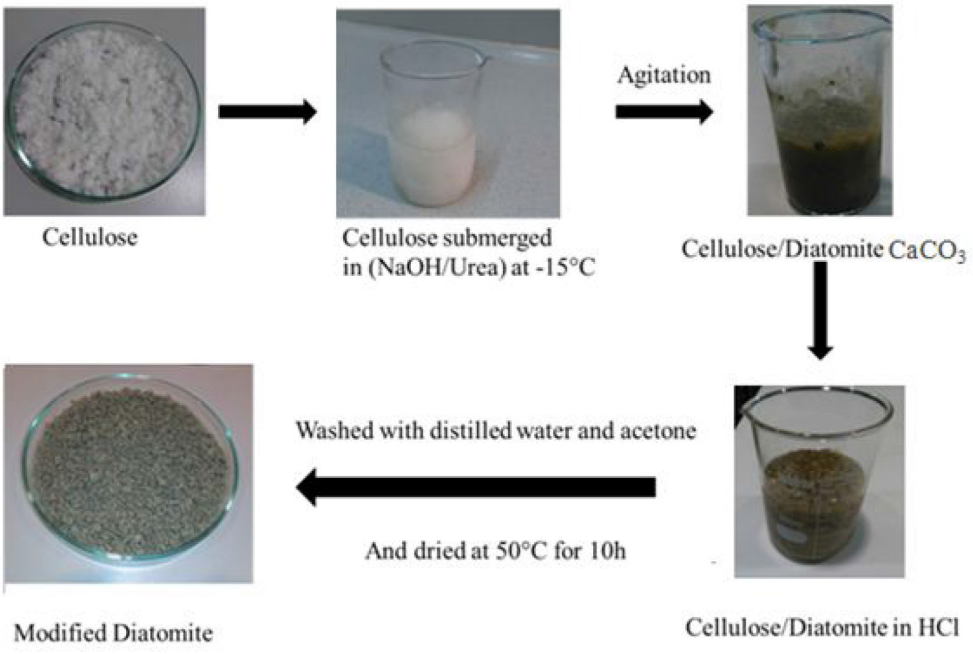

Fig. 2. Preparation of diatomite-cellulose.

of toluene (0.5 x $10^{-3}$, 1 x $10^{-3}$ and 3 x $10^{-3}$ mol/L). The mixture was kept under agitation (150 rpm) at room temperature for 24 h to attain the equilibrium conditions. The absorbance change was determined at different time intervals. The comparison between the adsorption capacity of the natural and modified diatomite was studied. The solution was filtered through a 0.22 μm membrane filter. The analysis was immediately made using a spectrophotometer Jasco V-630 instrument at the $\lambda_{max}$ of toluene, which is 261 nm [18].

The amount of adsorbed toluene ($Q_t$)( (mg/g), at time $t$ (min), obtained is as follows:

$$Q_t = \left(C_o - C_t\right) \times \frac{V}{m} \tag{1}$$

where$C_o$ and$C_t$ are the initial concentration (mg/g) and the concentration (mg/g) at time $t$ respectively, $m$ is the mass of adsorbent and $V$ is the volume of the solution.

### 2.2.5. *Adsorption kinetics models*

The pseudo-first and second-order models were employed to study the adsorption, determining the toluene adsorption onto the surface of all adsorbents. The two kinetics models used are as follows:

$$\frac{dq_t}{dt} = k_1\left(q_e - q_t\right) \tag{2}$$

The following equation is obtained after integration of Eq. (2), as given by Lagergren [19]:

$$\log\left(q_e - q_t\right) = -k_1 t + \log q_e \tag{3}$$

where $q_t$: amount of solute adsorption at different time, $k_1$: constant of pseudo-first order model, $q_e$: equilibrium adsorption capacity.

The pseudo-second order equation is expressed as follows [20]:

$$\frac{t}{q_t} = \frac{1}{k_2.q_e^{\,2}} + \frac{1}{q_e}.t \tag{4}$$

where $q_t$: amount of solute adsorption at different time, $q_e$: equilibrium adsorption capacity, $k_2$ (g/mg min): rate constant of pseudo-second order adsorption.

The pseudo-second-order kinetics model was used to check the adsorption dynamics in this work.

### 2.2.6. Adsorption isotherms

The equilibrium isotherms have a key function in the adsorption process. The adsorption was determined using two isotherm models: Langmuir's and Freundlich's. They represent the best models to describe the reversible adsorption. The Langmuir model is available for monolayer adsorption onto a surface, which has identical sites. The linear expression for this isotherm is as follows:

$$\frac{1}{q_e} = \left(\frac{1}{q_m}\right) + (1 / K_l \cdot C_e \cdot q_m) \tag{5}$$

where $q_e$: quantity adsorbed at equilibrium, $C_e$: concentration of toluene adsorbed at equilibrium, $q_m$: constant related to the area occupied by a monolayer of adsorbate, reflecting the adsorption capacity (mg/g), $K_l$: Langmuir constant

The Freundlich adsorption isotherm was applied for the removal of toluene on diatomite and modified diatomite. This model can be applied for multiplayer adsorption without uniform distribution of adsorption energies and affinities onto the heterogeneous surface. The equation of this empirical model is given as follows:

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \tag{6}$$

where $q_e$: quantity adsorbed at equilibrium, $C_e$: concentration at equilibrium, $K_f$: Freundlich constant

### 2.2.7. Analysis

The natural diatomite was analysed by powder XRD with $\lambda\text{Cu}_{K\alpha}$ ($\lambda\text{Cu}_{K\alpha\text{media}}$ = 1,5418Å, $\lambda\text{Cu}_{K\alpha1}$ = 1,54060Å and $\lambda_{\text{CuK}\alpha2}$ = 1,54439Å) on PanalyticalCubiX$^3$ diffractometer. The chemical composition of the diatomite sample (before and after the treatment) was measured by XRF technique.

The natural and modified diatomite were characterised by attenuated total reflectance, FT-IR spectroscopy (ATR-FTIR, PerkinElmer Spectrum) by the range from 400 to 4,000 cm$^{-1}$ and the resolution of 8 cm$^{-1}$.

The TGA/SDTA 851 Mettler Toledo instrument was used for determining the thermal properties of the obtained materials. About 5 mg from each sample was subjected from room temperature to 900°C, under nitrogen atmosphere (20 mL min$^{-1}$), with a scanning rate of 10ºC min$^{-1}$.

## 3. Results and discussion

### 3.1. Surface properties

The quantitative analysis of raw and treated diatomite was achieved via X-ray florescence (XRF). As given in Table 1, the major constituent of diatomite was $SiO_2$ (29.60%). The raw material is not pure hydrous silica. However, it contains other elements, such as calcium, potassium, sodium, metals and alkaline earth metals. After the treatment with HCL, the amount of silica in diatomite sample increased to 78.83%; the high amount of $SiO_2$ in diatomite gives its structure the capacity to be a good adsorbent. Moreover, these results are in agreement with those of Xu and colleagues [21], although the predominant mineralogical component of their diatomite was $SiO_2$ (72%).

The XRD analysis results of the treated diatomite are shown in Fig. 3. It showed that the treated diatomite mainly consists of $SiO_2$ (quartz, tridymite and cristobalite), with some quantities of $Fe_2O_3$ and $Al_2O_3$ and other mineral components. The small peaks at low 2-theta values suggest the presence of clay minerals (palygorskite, sepiolite, smectite). The characteristic peaks of diatomite are 21.76° and 26.66°, corresponding to the amorphous silica and the quartz, respectively, and

Table 1
Composition of diatomite (before and after treatment).

| | Composition of diatomite before treatment (%) | Composition of diatomite after treatment (%) |
|---|---|---|
| $SiO_2$ | 29.60 | 78.83 |
| $AL_2O_3$ | 2.57 | 6.53 |
| $Fe_2O_3$ | 1.08 | 2.52 |
| MN | 0.00 | 0.00 |
| MgO | 5.78 | 2.01 |
| CaO | 0.20 | 0.59 |
| $Na_2O$ | 26.89 | 0.00 |
| $K_2O$ | 0.39 | 0.96 |
| $TiO_2$ | 0.16 | 0.38 |
| $P_2O_5$ | 4.12 | 0.05 |
| LOI | 28.11 | 8.10 |

the peak at 35.96° 2-theta is related to the mineral component. Similar XRD analysis of Turkish diatomite was investigated. The XRD patterns show the presence of amorphous silica between 20° and 26° 2-theta; quartz was also identified at 27° 2-theta [22].

The FT-IR spectra of the natural and modified diatomite are presented in Fig. 4. The analysis was achieved between 400 and 4,000 cm$^{-1}$ to describe the surface characteristics of the adsorbents. The adsorption peak at 3,328 cm$^{-1}$, that is related to the O-H vibration of the physically absorbed $H_2O$, and the structural hydroxyl groups were recorded. The presence of $H_2O$ in diatomite is confirmed by the peak at 1,658 cm$^{-1}$. In addition, the strong amount of $SiO_2$ on the natural diatomite is confirmed by two vibrations, at around 1,023cm$^{-1}$ and 671 cm$^{-1}$, which are related to the asymmetric stretching vibration mode of siloxane (Si-O-Si). Moreover, the diatomite contains some impurities of various kind of clay, which explains the fact that the presence of the peak at 786 cm$^{-1}$ is attributed to Al-O-Si stretching vibration, according to the clay impurities in diatomite. Same results were found on the previous works; a commercial diatomite was used to remove aniline, the raw material was characterised by FT-IR analysis and the main peaks of this diatomite were 3,370, 1,471, 1,100, 800 and 468 cm$^{-1}$, which represented the specific peaks of it [23]. In addition, Yucheng Du and co-authors [24] confirmed the presence of those peaks on the spectrum of their commercial diatomite, using for the adsorption and photo reduction of Cr(VI); the peaks were at 3,430, 1,633, 468, 1,098, 798 and 532 cm$^{-1}$.The presence of those specific peaks on the natural diatomite used in this study, compared with the other commercial ones, proves the good quality of our diatomite.

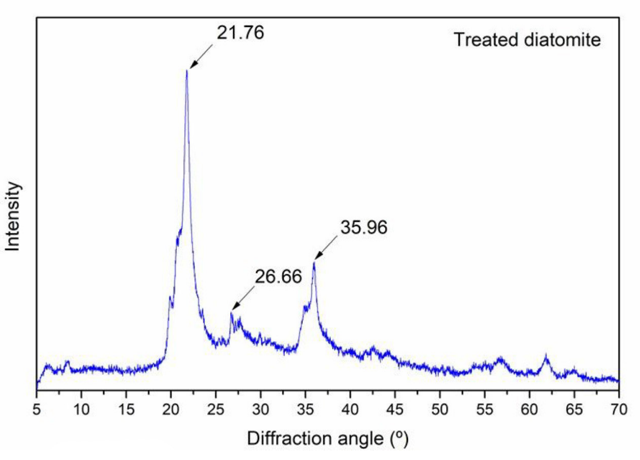

Fig. 3. Analyse of XRD for diatomite.

On the other hand, the specific peaks of cellulose are at 3,328, 1,716 and 2,894 cm$^{-1}$. The combination between diatomite-cellulose is confirmed by the FT-IR analysis. The most changes resulting is the appearance of the band are at 1,716 cm$^{-1}$, which corresponds to the carboxyl groups (C=O). The band at 3,328 cm$^{-1}$ will be larger and stronger, which can be ascribed to the O-H stretching, whereas that at 2,894 cm$^{-1}$ is attributed to the C-H stretching in cellulose.

To identify the thermal stability of the adsorbents and to ensure that the reaction was successful, the natural and modified diatomite were characterised by TGA technique. Fig. 5 represents the TGA curves; it is clear that the mass of diatomite remains stable from 25°C to 900°C. For the modified diatomite, the total mass loss of 50%, between 290°C and 350°C, corresponds to the thermal degradation of cellulose. The TGA analysis was also used by Xiaowei to characterise raw and modified diatomite. It was demonstrated that the mass of diatomite was stable between 25°C and 600°C, and there are no thermal degradation stages in this temperature. However, the degradation of lauric acid (LA) in the modified diatomite composite starts at 157°C and ends at 203°C, which indicates that the thermal stability increases after LA is impregnated into the pores of diatomite [25].

The specific surface was calculated by BET equation for diatomite and diatomite-cellulose; the calculated surfaces were 117.2594 m$^2$/g and 3.2965m$^2$/g, respectively. The reduction of the specific surface can be explained by the fact that the grafted cellulose fills up some pores of diatomite. Therefore, the increase of the adsorption capacity of the modified diatomite was related to the improved surface reactivity towards the adsorption.

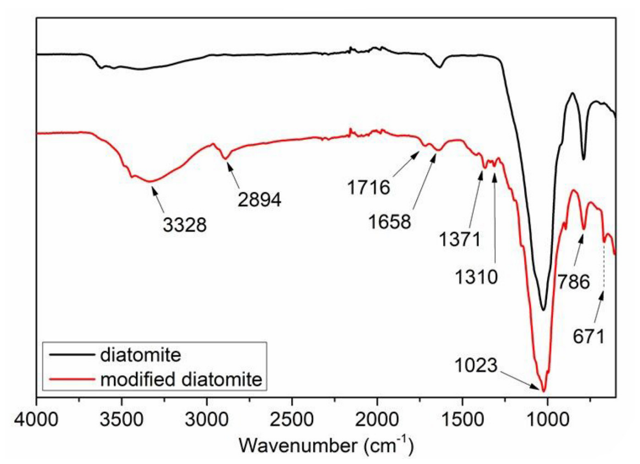

Fig. 4. FTIR of natural and modified diatomite.

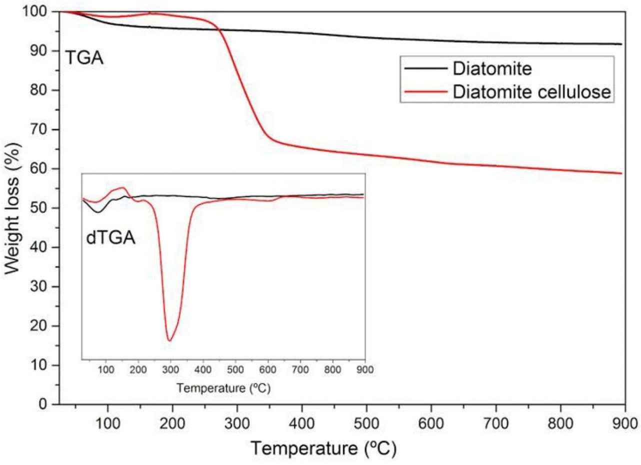

Fig. 5. TGA curves of the natural and modified diatomite.

### 3.2. *Contact time effect*

In this work, the adsorption of toluene onto diatomite and diatomite-cellulose was investigated as a function of contact time. Figs. 6(a), (b) illustrate the effect of contact time on the adsorption capacity of the toluene for natural and modified diatomite. As shown in Fig. 6(a), the adsorption of toluene was occurring very fast, for different concentrations, in the first 20 min. After 20 min of adsorption, the percentage removal of toluene on the natural diatomite was observed to be 57.97%, 65.89% and 72.58%, for the initial concentrations 0.5 x $10^{-3}$, 1 x $10^{-3}$ and 3 x $10^{-3}$ mol/L, respectively. Fig. 6(b) shows that the adsorption of toluene on diatomite-cellulose is also fast in the first stage. About 59.23%, 70.06% and 73.35% of toluene present in the solution, with the initial concentrations of 0.5 x $10^{-3}$, 1 x $10^{-3}$ and 3 x$10^{-3}$ mol/L, respectively, were adsorbed and the adsorption took place at the 20 min of contact and thereafter it remained constant. This percentage remained constant after 180 min, giving the maximum toluene adsorption capacity for the natural and modified diatomite. This observation is related to the available adsorbent surface area in the first step; however, after 180 min most of the sites were occupied leading to a linear curve. Furthermore, the most molecules of toluene were adsorbed on the external surface of natural and/or modified diatomite.

### 3.3. *Initial concentration effect*

The initial toluene concentration was varied from 0.5 x $10^{-3}$ to 3 x $10^{-3}$ mol/L to evaluate the effect of concentration on the adsorption process. The results indicate that the toluene removal rate was dependent on its initial concetration (Fig. 7). Thus, the removal increased with an increase of the initial concentration of toluene and a faster equilibrium was achieved at lower concentration. Despite the sufficient vacant active sites, the adsorption capacity at low concentration was low. This observation is related to the few number of molecules attaching with the adsorbent. Similar results were reported in the literature for the adsorption of toluene, benzene, xylene and ethylbenzene by montmorillonite modified with non-ionic surfactant [26], and for the adsorption of toluene and benzene—on coconut shell activated carbon [27].

### 3.4. *Comaparative experiment*

The toluene removal was carried out at various initial concentrations (0.5 x $10^{-3}$ mol/L, 1 x $10^{-3}$ mol/L and 3 x $10^{-3}$ mol/L). The highest adsorption of toluene was observed at the initial concentration of 3 x $10^{-3}$ mol/L, at the temperature of 22°C and at pH 6. As shown in Fig. 8, the removal rate of the treated diatomite was 79.33% (142.30 mg/g) and that of the cellulose extracted from sisal fibres was 85.45% (153.31 mg/g). However, the combination of diatomite-cellulose increased the adsorption capacity to

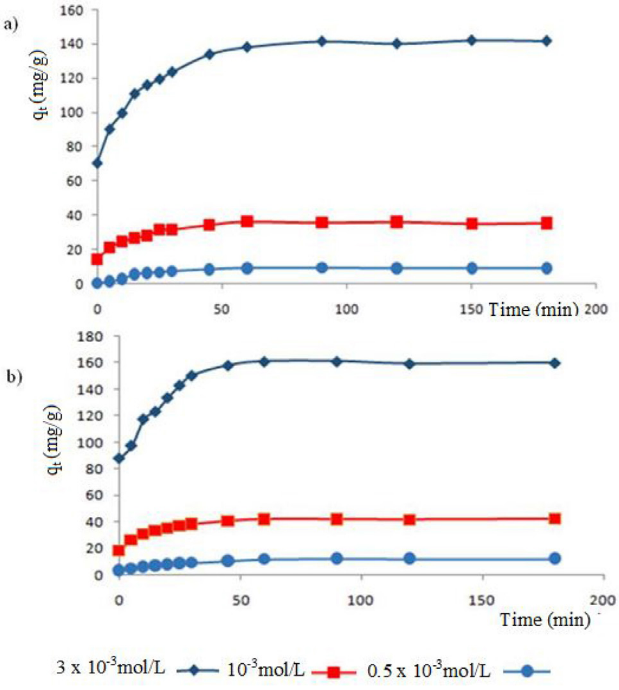

Fig. 6. Effect of contact time on adsorption of toluene on (a) natural and (b) modified diatomite (Equilirium time = 180 min, pH = 6, T = 22°C, agitation speed = 150 rpm, adsorbent dosage = 0.1 g).

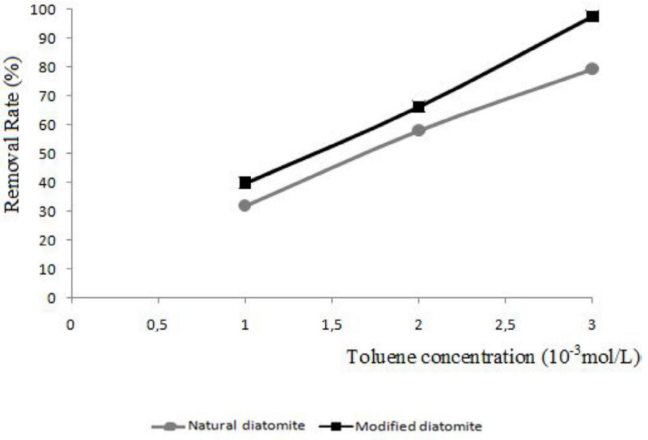

Fig. 7. Effect of initial toluene concentration of toluene on the adsorption on natural and modified diatomite (Equilibrium time=180 min, pH=6, T=22°C, agitation speed= 150 rpm, adsorbent dosage=0.1 g).

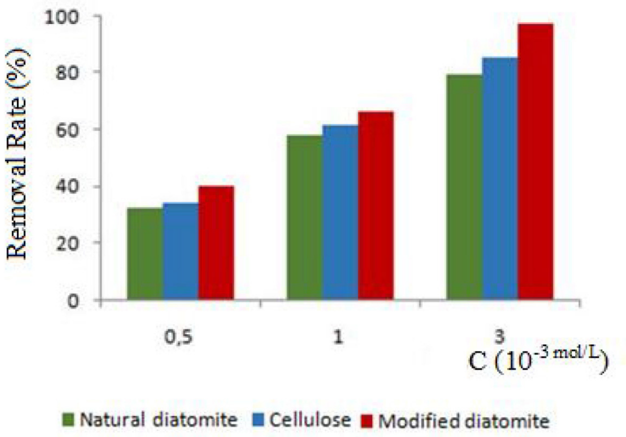

Fig. 8. Percentage of removal of toluene by natural and modified diatomite.

97.45% (161.43 mg/g). After modification, the cellulose filled up the pores of diatomite, which decreased the surface area of diatomite (from 117.2594 $m^2$/g to 3.2965 $m^2$/g); however, its adsorption capacity increased. This observation is related to the fact that both the components, interact with the hydroxyl groups on the surface of adsorbent created from the cellulose.

Despite the difference in the experimental conditions (initial concentration, temperature, pH), the comparison between the present observations and previous studies on the adsorption capacities of other materials is important. These results show that the natural and modified diatomite have greater adsorption capacity compared with the natural Iranian diatomite used in a previous study, which removed 71.45% and 96.91% of toluene, after modification with nickel oxide nanoparticles. Thus, the main composition of natural Iranian diatomite is quartz, anorthite and muscovite, and the surface area was just 7.5 $m^2$/g, which affected the adsorption capacity of the diatomite [28]. In another study, the maximum adsorption uptake of the modified cellulose for the removal of toluene was 82% after 180 min [29]. The modified activated carbon was used by Liu HB to remove toluene. The activated carbon was modified by the acidic and basic solution; the results showed that the acidic treatment reduced the adsorption capacity by 9.6%–20%, however the capacity increased by 29.2%–39.2% by using the basic treatment, compared with the adsorption capacity of its original form [30]. Abas and colleagues used multiwall carbon nanotubes and iron oxide impregnated carbon for toluene and p-xylene removal from the aqueous solution [31]. Their experiments showed that the adsorbent removed 70% of toluene, for soaking time of 2 h, with pollutant initial concentration of 100 ppm, at pH 6 and shaking speed of 200 rpm at 25°C [31].

### 3.5. pH effect

The effect of the solution pH (pH = 1–13) on toluene removal for natural and modified diatomite is provided in Fig. 9. The results showed a sharp increase in the adsorption capacity of toluene at pH 6. In high acidic condition (pH < 6), the main binding sites of the adsorbent, hydroxyl groups, were protonated because of the existence of high concentration of $H_3O^+$. Thus, the number of available binding sites was decreased, resulting in the low removal rate of toluene. However, when the pH increased to basic solution (pH > 6), the protonated functional groups were deprotonated and the electrostatic repulsion between the negatively charged ions increased, which reduced the adsorption efficiency [32]. Overall, the optimum pH values for toluene removal was 6.

### 3.6. Adsorption kinetic model

The kinetic of toluene adsorption on diatomite was performed using the pseudo first order model (Eq. (3)) and the pseudo second order model (Eq. (4)). The calculated kinetic parameters of natural and modified diatomite are given in Table 2. The results show that the correlation coefficient ($R^2$)

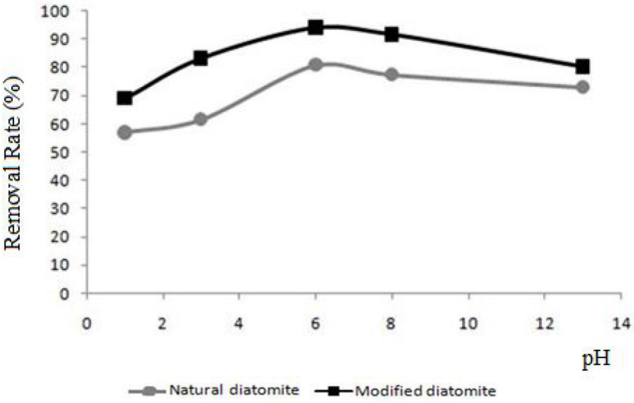

Fig. 9. Effects of pH on adsorption of toluene onto natural diatomite and modified diatomite.

Table 2
Parameters of Kinetics model for the adsorption of Toluene onto raw and modified diatomite.

| Material | Kinetic Models | Parameters | $0.510^{-3}$ mol/L | $10^{-3}$ mol/L | $310^{-3}$ mol/L |
|---|---|---|---|---|---|
| Raw diatomite | Pseudo-First order | $q_{ecal}$(mg/g) | 7.18 | 11.46 | 53.95 |
| | | $q_{eexp}$(mg/g) | 9.18 | 35.53 | 141 |
| | | $K_1$($min^{-1}$) | 0.015 | 0.011 | 0.016 |
| | | $R^2$ | 0.925 | 0.898 | 0.954 |
| | Pseudo-second order | $q_{ecal}$(mg/g) | 10.10 | 37.037 | 166.67 |
| | | $q_{eexp}$(mg/g) | 9.18 | 35.53 | 141 |
| | | $K_2$(g/mg.min) | 0.0079 | 0.0081 | 0.144 |
| | | $R^2$ | 0.983 | 0.998 | 0.999 |
| Modified diatomite | Pseudo-first order | $q_{ecal}$(mg/g) | 6.934 | 15.21 | 33.81 |
| | | $q_{eexp}$(mg/g) | 12.11 | 41.78 | 160.036 |
| | | $K_1$($min^{-1}$) | 0.013 | 0.016 | 0.008 |
| | | $R^2$ | 0.923 | 0.878 | 0.591 |
| | Pseudo-second order | $q_{ecal}$(mg/g) | 12.99 | 43.48 | 166.67 |
| | | $q_{eexp}$(mg/g) | 12.11 | 41.78 | 160.036 |
| | | $K_2$(g/mg.min) | 0.0086 | 0.0022 | 0.0076 |
| | | $R^2$ | 0.994 | 0.999 | 0.999 |

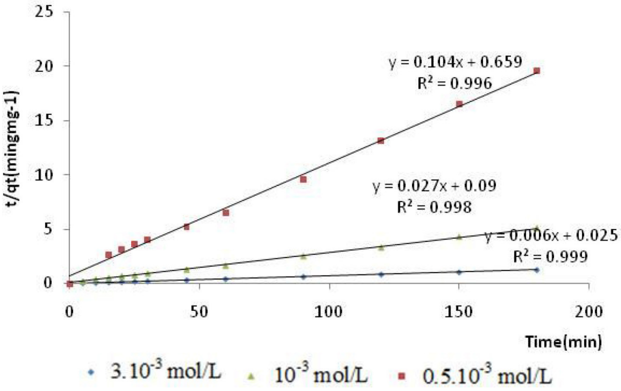

Fig. 10. Pseudo-second-order adsorption kinetics on raw diatomite.

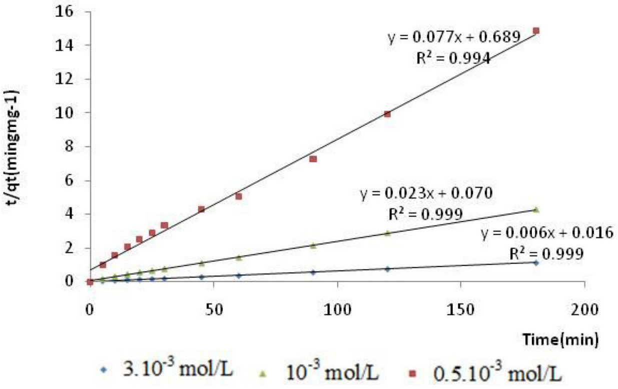

Fig. 11. Pseudo-second-order adsorption kinetics on modified diatomite.

of the pseudo first order is far from unity and the values of calculated $q_e$ and exprimental $q_e$ are not close, indicating that this kinetic model is not valid. However, the linear form of the pseudo-second-order model can better describe the adsorption kinetics, according to their correlation coefficient, which is close to 1 (Figs. 10 and 11). Furthemore, calculated $q_e$ and exprimental $q_e$ are nearly coincident [33].

### 3.7. Adsorption isotherm

The surface morphology and the affinity of the diatomite are highly related with the isotherm models. Thus, the adsorption isotherms were stimulated by Langmuir and Freundlich equations. The optimal parametres from the fitting of Langmuir and Freundlich equations are summarised in Table 3.The experimental data fitted well with the Freundlich model (Table 3), according to its high values of the coefficient of determination ($R^2$), 0.973 for natural and 0.949 for modified diatomite. In addition, the constant $1/n$ was higher than 1 and the values of $K_f$ were observed to be 2 x $10^{-4}$ for the natural diatomite and 8.69 x $10^{-9}$ for the modified diatomite. Furthermore, the adsorption behaviour of toluene does not follow the assumption, in which the Langmuir approach is considered, giving negative values of $q_m$ ($q_m$ = –12.99 mg/g (natural diatomite), $q_m$= -0.150 mg/g (modified diatomite) and $K_l$=–0.015L/mg (natural diatomite), $K_l$=–0.023 L/mg (modified diatomite), at low concentrations.The same approach were observed in the previous works, with $q_m$ = –0.710, –0.024 and –0.040 mg/kg and $K_l$ = –0.006, –0.032 and –0.040 L/mg, for the adsorption of toluene on the raw and thermal diatomite, at 550°C and 750°C, respectively [34].

Table 3
Langmuir and Freundlich isotherm parameters for toluene onto natural and modified diatomite.

| | Langmuir Isotherm | | | Freundlich Isotherm | | |
|---|---|---|---|---|---|---|
| | $Q_m$ (mg/g) | $K_l$ (L/mg) | $R^2$ | $K_f$ | $1/n$ | $R^2$ |
| Natural Diatomite | –12.99 | –0.015 | 0.973 | 2 × $10^{-4}$ | 3.216 | 0.997 |
| Modified Diatomite | –0.150 | –0.023 | 0.949 | 8.69 × $10^{-9}$ | 6.235 | 0.998 |

## 4. Conlusions

In this study, the natural and modified diatomite was used as adsorbents to remove toluene from aqueous solution. The chemical treatments were used to obtain cellulose from sisal fibres and to modify diatomite. The characterisation of purified diatomite indicates that the latter contains a very important quantity of $SiO_2$ with a higher surface area, favouring the adsorption process. In addition, the effects of exeprimental conditions, adsorption kinetic and isotherm were sudied in detail. The cellulose extracted from the sisal fibre significantly enhanced the adsorption capacity of diatomite, thus the maximum toluene removal percentage on the natural diatomite was 79.33%, and the maximum adsorption of diatomite-cellulose was recorded as 97.45% in the same conditions. Hence, the pH has a crucial role for the adsorption capacity. The results revealed the effect of pH; the maximum adsorption capacities for natural and modified diatomite were achieved at pH 6. In relation to the fitted models to the kinetic data, the adsorption kinetic was well described by the pseudo-second order model. Furthermore, the Freundlich model appeared to fit the data better than the Langmuir model. Considering the obtained results, it can be concluded that the combinantion of diatomite-cellulose is an excelent adsorbent for tolune removal.

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