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# Mesoporous silica synthesised from natural local kaolins an effective adsorbant for removing of acid Red 337 and its application in the treatment of real industrial textile effluents

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## Abstract

This paper presents a synthesis of mesoporous silica (MS) from natural clay as silica source using L35 pluronic (EO11PO16EO11) as structure directing agent. The prepared material was characterised by XRD, FRX, TGA, SEM, MET and N<sub>2</sub> adsorption-desorption analyses. Then, mesoporous material was used for the removal of Acid Red 337 (AR337) from aqueous solution, and the treatment of real textile effluent. The effect of pH, contact time, weight of adsorbent and initial concentration was studied in batch adsorption. The synthesized mesoporous material showed good discoloration efficiency with a 62% percentage. Experiment with real textile wastewater showed that 39%, 40% and 31.2% of the color, TOC and COD respectively were eliminated by using 1g of MS per litre of wastewater.

## Keywords

mesoporous silica (MS), clay, Acid Red 337, real textile wastewater.

## 1. Introduction

In recent years, research on ordered mesoporous silica-based materials has become a major area of interest [1],[2] and [3], due to their high specific surface area, and uniform pore size distribution and the important potential applications of mesoporous materials in catalysis [4], adsorption [5], [6] and [2], and wastewater treatment [7].

Typically, the mesoporous silica is prepared with tetramethylorthosilicate (TMOS) or tetraethylorthosilicate (TEOS) as silica sources [5,8] using a cooperative surfactant templating. Many minerals rich in  $\text{SiO}_2$  or  $\text{Al}_2\text{O}_3$  have been used as an alternative to silica source. Several studies refer to the use of raw silica sources in ordered mesoporous materials synthesis [9], such as SBA-15 from natural clay [10], MCM-41 from Kaolin [11,12], mesoporous silica materials from natural sands [2], natural halloysite [9] and Kaolin [13].

For several years, great effort has been made to study textile effluent treatment and dye removal, in particular. Textile dyeing industry is one of the most chemically intensive industries in the world and known to be one of the main sources of environmental pollution. It uses a variety of chemicals: dyes, surfactants, solvents, oxidizing agents, reducing agents, synthetic resins and many other chemical auxiliaries. In addition, a large quantity of water is consumed during production process. Approximately 200 L of water is required to produce 1 kg of textile [14]. Subsequently, large quantities of effluents are generated, which are rich in colour, (chemical oxygen demand) (COD) complex chemicals, inorganic salts, total dissolved solids (TDS), pH, temperature, turbidity and salinity [15].

Direct discharge of textile wastewater into freshwater gives an undesirable color that reduces sunlight penetration and resist photochemical and biological attacks to aquatic life. Traditional textile wastewater treatment technologies include various combinations of biological, physical, and chemical methods [14]. However, the adsorption method is a very promising technique because of its simplicity and economy, and the availability of a wide range of adsorbents [16-18].

Over the past few years, several experiments have been carried out using low-cost natural materials as silica source such as sawdust [18], active carbon [19-21] and clay soil [22,23]. They were successfully used to remove toxic dyes from aqueous solutions. A large compilation of potentially effective

adsorbents in dye removal can be found in a review of Yagub et al. (2014)[24]. Nevertheless, studies on the adsorption of real textile wastewater remain relatively scarce[25].

This study aims to present a novel synthesized mesoporous silica material using clay from northeastern Algeria and to investigate the ability of this material to remove Acid Red 337 and treat real textile wastewaters by adsorption.

## 1. Materials and methods

### 2.1. Materials

Natural Kaolin clay (DD3) was used as a silica source for synthesis of mesoporous silica material.

It was extracted from Djbal Dbagh mountains, located in Guelma province, Algeria, and is composed of halloysite and kaolinite (weight ratio halloysite/kaolinite of 1.23)[26][27]. Acid Red 337 was purchased from Alfa Kimya (Textile Chemical Company in Istanbul, Turkey) with commercial name Telon Red FRL (Table 1). Pluronic L35 (EO11-PO08-EO11, MW=1900) and sodium hydroxide (NaOH 97%) were purchased from Sigma–Aldrich, and hydrochloric acid (HCl 37%) was obtained from Riedel-deHaën.

The real textile wastewaters were supplied by COTITEX (a factory specialised in the manufacture of military fabrics in Algeria). During the manufacturing and dyeing processes, two types of dyes (vat and disperse) and different types of chemical substances were used, such as peroxide, caustic soda and auxiliaries products.

**Table 1:** Main properties of Acid Red 337 dye

### 2.2. Synthesis

Raw natural Kaolin (DD3) was calcined at 500°C for 4h at a rate of 2°C/min. Then, 10g of calcined clay mixed with 200mL of 6M HCl and stirred for 4h at 80°C after the solution was filtered, washed with deionized water and dried in ambient temperature. Mesoporous material was synthesised according to the literature procedure [3], using Pluronic L35 and natural Kaolin (DD3) as a silica source, 4g of Pluronic L35 dissolved in 6.67g of deionized water and

0.24gHCl, while stirring at 40°C. Then,8.54g of treated Kaolin (DD3)was added to the stirring solution.

These mixtures were stirred continuously for 24h.The white gel was observed and was transferred to a Teflon-coated autoclave and heated to100°C for 48h.The solid product was separated by filtration andwashed several times with deionized water, then dried at room temperature and calcined for 4h at 500°C at a rate of 2°C/minto remove the template L35 and obtain the synthetic mesoporous silica(MS).

### **2.3.Material characterisation**

The chemical composition of materials wasdetermined by Bruker-Axs: SRS 3400 and S8 TIGER X-ray fluorescence (FRX) spectrometer. MS was structurally characterised by the X-ray powderdiffraction (XRD) methodusingBruker D8 Advanceddiffractometerunder Copper K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) at 40 kV/30mA, with a scanning rate of 0.08°min<sup>-1</sup> over 2 $\theta$ -range between1°and10°.

Morphological and microstructure analyses were carried out using aQuanta 650 Scanning electron microscope (SEM) and JEOL 2100F transmission electron microscopy (TEM) operatingat 200kV and equipped witha probe aberration corrector, an EELS (GatanTridiem) spectrometer and an EDXSDDdetector.

Nitrogen adsorption-desorption experiments were measured at -196°C on a MicromeriticsQuantachrome NOVA 1000. The sample was outgassed for 1h at 100°C. The surface area was measured according to the Brunauer– Emmett–Teller (BET) method. The average pore size was determined from the N<sub>2</sub> adsorption branch of nitrogen isotherms using the Barrett–Joyner–Halenda (BJH) method.

TG analysis of the sample was performed on a DTG-60 instrument in an alumina pan at a 10°C/min heating rate from 20°C to 1000°C under an N<sub>2</sub> flow.

Effluents conductivity and pHwere determined by Thermo Scientific Orion Star A215 pH/ Conductivity Benchtop Meter.pH measurement is in accordance with ISO 10523.2008[28].Chemical oxygen demand (CODmg O<sub>2</sub>/L)was measured using the closed reflux colorimetric method[29].

Total organic carbon (TOC) was measured by a Lotix TOC Combustion analyzer.

Effluent's colorwas measured by UV-vis spectrophotometer (DR6000, HACH) according to the NCASI method[30].

## 2.4. Dye adsorption experiments

Firstly, the Acid Red 337 stock dye solution at 200 mg/L was prepared. Then, pH effect on the ability of mesoporous silica (MS) to adsorb Acid Red (AR 337) dye was examined in the range of 2-10. pH was adjusted to the desired value with NaOH or HCl 1 M before adding the quantity of adsorbent.

Batch adsorption was performed with 200 mL of dye solution at a concentration of ( $C_0 = 100$  mg/L) and, a weighed quantity ( $m = 0.4$  g) of MS. The mixture was stirred at room temperature at a speed of ( $r = 300$  rpm) for 24 h until it reached equilibrium. The solution was then separated from the adsorbent by centrifugation for 15 min at 5000 rpm.

Non-adsorbed dye in the final liquid phase was determined by a UV-vis spectrophotometer at a maximum absorbance wavelength of 500 nm. The quantity (mg) of dye adsorbed per gram of adsorbent was assessed ( $Q_t$ ) and the highest equilibrium values were used to define the maximum adsorption capacity ( $Q_{max}$ ) and at equilibrium ( $Q_e$ ).  $Q_t$  and  $Q_e$  (mg/g), were calculated using equations (1) and (2):

$$Q_t = \frac{(C_0 - C_t)V}{m} \quad (1)$$

$$Q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

Where,  $C_0$ ,  $C_t$ , and  $C_e$  (mg/L) are the liquid-phase concentrations of the adsorbate at initial time ( $t$ ) and at equilibrium, respectively;  $V$  (L) is the solution volume and  $m$  (g) is the adsorbent mass. To calculate the decolorization efficiency, equation (3) was used:

$$\%R = \left( \frac{C_0 - C_t}{C_0} \right) \times 100 \quad (3)$$

## 2. Results and discussion

### 2.1 Chemical analysis

The chemical composition of natural Kaolin (DD3) and synthesized mesoporous silica (MS) obtained by XRF are shown in Table 2. Results showed that after treatment of DD3 and synthesis of mesoporous silica, the content of all elements decreased except for  $\text{SiO}_2$ . Which increased from 41.74% to 89.3%.

**Table 2:** Chemical composition of natural Kaolin DD3 and synthesized mesoporous silica (wt %)

## 2.2 XRD and TEM analysis

The mesoporous silica structure was characterised by small angle X-ray diffraction (SAXRD), as shown in Figure 1. The pattern shows a small single diffraction peak at  $2\theta=2^\circ$  with smaller intensity. It indicates a formation of disordered mesoporous structure [30,31] which is similar to that of mesoporous silica synthesized by sodium silicate as a precursor [33]. TEM analysis results showed no obvious order in pore arrangement and confirmed the disordered structure of mesoporous material, as shown in Figure 2.

**Figure 1:** SAXRD pattern of as-synthesized mesoporous silica

**Figure 2:** TEM images of as-synthesized mesoporous silica

## 2.3 SEM analysis

SEM microphotographs of as-synthesized mesoporous material showed a platy particle shape (Figure 3). A similar morphology was found by Madhusoodana et al. (2006) and Li et al. (2015) [33,34].

**Figure 3:** SEM microphotographs of as-synthesized mesoporous silica

## 2.4 Porosity measurement

Figure 4 illustrates the  $N_2$  adsorption/desorption isotherm of as-synthesized MS. Based on IUPAC classification [36], MS isotherm exhibits a typical type IV class with an H3-type hysteresis loop due to capillary condensation processes, which is a characteristic of mesoporous material. Similar results have been found by Auta et al. (2012) [37]. Therefore, the size distribution and pore shape of as-synthesized MS are irregular. The BET specific surface area, pore width and total pore volume of as-synthesized MS and natural Kaolin (DD3) are presented in Table 3. An increase in the specific surface area of natural Kaolin DD3 was observed, suggesting an increase in their available adsorption sites.

**Figure 4:**  $N_2$  adsorption–desorption isotherms of as-synthesized mesoporous silica

**Table 3:** BET surface area, BJH surface area, total pore volume and pore size of natural kaolin DD3 and as-synthesized mesoporous silica (MS)

## 2.5 Thermal analysis

The evaluation of the product thermal stability by thermogravimetric analysis (TGA) weight curve and differential thermal analysis (DTA) of natural Kaolin (DD3) and synthesized MS, are presented in Figures 5A and 5B.

It can be noted that natural Kaolin DD3 has a mass loss of 8.1% at a temperature of 56.2°C (Figure 5A), which implies a loss of moisture. DTA result also shows an endothermic peak at approximately 479°C corresponding to the second weight loss (13.7%) and is attributed to the external halloysite hydroxylation [38].

For synthesized MS (Figure 5B), it can be observed that a very small weight loss (3.19%) at less than 80°C accompanied by an endothermic DTA peak corresponds to the loss of free water and a second weight loss of 1.4% between 600 and 1000°C is attributed to a loss of water due to silanol condensation [39]. It can therefore be deduced that the synthesized MS has good thermal stability.

**Figure 5:** TGA and DTA curves of (A) natural Kaolin (DD3), (B) as-synthesized mesoporous silica

## 3. Adsorption experiments

### 3.1 Effect of initial solution pH

The solution pH is an important parameter that dominates the adsorption of dyes on adsorbents [40]. pH can affect the surface charge of the adsorbent and the ionization degree of adsorbate functional groups [41].

Figure 6 shows the equilibrium capacities of Acid Red 337 over MS with different pH values, ranging from 2 to 10, for  $C_0 = 100$  mg/L and an adsorbent dose = 2.0 g/L.

**Figure 6:** Effect of pH on Acid Red 337 (A) adsorption capacity ( $Q_t$ ) and (B) % R over synthesized mesoporous silica ( $C_0 = 100$  mg/L,  $V = 200$  mL,  $T = 20$  °C,  $r = 300$  rpm,  $m = 0.4$  g)

In addition, it has been found that by increasing the initial pH from 2 to 10 the %R decreases from 62.61 to 0% (Figure 6B). This result can be explained by a low pH leading to an increase in  $H^+$  molecule concentration in the system. Moreover, the surface of MS exhibits positive charges by adsorbing  $H^+$ , and an electrostatic attraction is created between the positive charge of the surface of the synthesized MS and anionic dye molecules enhancing adsorption of color at pH 2, which was used for all further



adsorption studies. The expansion of the adsorption limit at pH 2 can also be attributed to the isoelectric point ( $pI$ ) of mesoporous silica adsorbents that is around 2.5-3 [42]. Indeed, the surface area of the adsorbent was positively charged at pH values below ( $pI$ ) and there were attractive forces between the positive charges of the surface and anionic dye molecules. When pH values were above ( $pI$ ), the surface area of the adsorbent was negatively charged and it did not allow the adsorption of anionic particles of dye, because of the electrostatic repulsion.

### 3.2 Effect of contact time ( $t$ )

Figure 7 illustrates the impact of contact time on AR337 adsorption over synthesized MS.

**Figure 7:** Effect of contact time ( $t$ ) on the Acid Red 337 adsorption capacity ( $Q_t$ ) and % R over the synthesized mesoporous silica ( $C_0 = 100 \text{ mg/L}$ ,  $V = 200 \text{ mL}$ ,  $T = 25^\circ\text{C}$ ,  $r = 300 \text{ rpm}$ ,  $pH = 2$ ,  $m = 0.4 \text{ g}$ )

Figure 7 also shows that dye adsorption is quick. It reached %R = 56 after 20 min and increased with an additional contact time. Equilibrium was achieved at ( $t = 60 \text{ min}$ ,  $Q_e = 31.3 \text{ mg/g}$ ) since no change in adsorption capacity was observed (the study was extended for 1440 min). The optimal contact time was 60 minutes.

### 3.3 Dye concentration effect

To examine the impact of anionic dye fixation on the limit of adsorption onto MS, several tests were performed by modifying the initial concentration of the dye between 10 and 200 mg/L (Figure 8).

**Figure 8:** Effect of initial dye concentration ( $C_0$ ) on: (A) adsorption capacity ( $Q_t$ ) and (B) % R over the as-synthesized mesoporous silica ( $m = 0.4 \text{ g}$ ,  $V = 200 \text{ mL}$ ,  $T = 20^\circ\text{C}$ ,  $r = 300 \text{ rpm}$ ,  $pH = 2$ )

Figure 8 shows that the increase in the initial Acid Red concentration leads to an increase in adsorption capacities. Furthermore, the rate of adsorption is fast and the equilibrium is reached in 10 min for all concentrations and 30 min for  $C_0 = 200 \text{ mg/L}$ . Thus, it indicates the availability for AR337 of accessible active sites on synthesized mesoporous silica [43]. The continuous curves showed the monolayer coverage on adsorbent surface [18].

### 3.4 Adsorbent concentration effect

To optimise the amount of the adsorbent, experiments were performed using different quantities of synthesized mesoporous silica (0.2, 0.4 and 1g/200mL). Figure 9 illustrates that an increase in the amount of MS from 0.2 to 0.4 g leads to a decrease in  $Q_{\max}$  values from 36 to 16.34 mg/g. This can be related to particle interactions, such as aggregation which would result in a decrease in the total surface area of the adsorbent [43]. Particle interactions may also cause the desorption of a portion of the sorbate that is loosely and reversibly bound to the surface [44]. As a result, 0.2 g/200mL of MS is the optimal amount of mesoporous silica necessary to remove dye at a 100 mg/L concentration.

**Figure 9:** Effect of adsorbent amount (m) on: (A) the adsorption capacity ( $Q_t$ ) and (B) % R over the synthesized mesoporous silica ( $C_0 = 100 \text{ mg/L}$ ,  $V = 200 \text{ mL}$ ,  $T = 20^\circ\text{C}$ ,  $r = 300 \text{ rpm}$ ,  $\text{pH} = 2$ )

## 4. Use of synthesized mesoporous silica in the treatment of real industrial textile effluent

The potential use of synthesised MS in the treatment of a real textile effluent and its ability to reduce color, COD, and TOC were tested. Initial color, COD and TOC of the sample were 67 Pt-Co, 330 mg/L, and 96.6 mg/L respectively and its pH was 8.15.

For this experiment, the textile wastewater was first filtered, then the batch experiment was conducted in a 250 mL flask containing 100 mL of textile effluent and 0.1g of adsorbent at room temperature at an average shaker's speed of 300 rpm without changing the pH of the effluent. The mixture was then stirred overnight to reach equilibrium.

### 4.1 Effect of contact time

Figure 10 shows the effect of contact time on reduction of TOC concentration of the wastewater effluent.

**Figure 10:** Effect of treatment time on the reduction of TOC of the real textile effluent by adsorption on synthesized mesoporous silica ( $T = 30^\circ\text{C}$ ,  $\text{pH} = 8.15$ ,  $m = 1 \text{ g}$ ,  $V = 100 \text{ mL effluent}$ ,  $r = 300 \text{ rpm}$ )

It can be observed that during the first 60 minutes, there is a fast decrease in TOC concentration. The equilibrium is reached after one hour of contact time. At first, the solute molecules were adsorbed by the external surface of adsorbent particles, so the adsorption rate was fast. When the adsorption of the

external surface reached saturation, the molecules needed to diffuse through the pores of the adsorbent into the internal surface of the particle. This phenomenon may have taken a relatively long contact time[21]. A 60-minute time period was then used as contact time for color and COD treatment.

## 4.2 TOC, COD and color removal

Figure 11 provides the concentration reduction and removal percentage of TOC, COD and color of wastewater by adsorption on MS.

**Figure 11:** Percentage of removal, concentration of TOC, COD and color in treated and untreated wastewater compared to as-synthesized mesoporous silica

After adsorption, it can be seen that the concentration of TOC, COD and color decrease by 40% (from 96.6 mg/L to 56 mg/L), 31% (from 330 mg/L to 226.25 mg/l) and 39% (from 67 Pt-Co to 41 Pt-Co) respectively. These average values can be explained by the complexity of real effluents chemical composition.

## 5. Conclusions

This study determined that mesoporous silica was successfully synthesized from local raw clay (DD3) of Guelma province in Algeria as a source of silica. Before its use, the clay underwent two treatments: thermal and chemical. In addition, the pluronic L35 has been used as a structuring agent.

Several characterisation analyses were used to evaluate the textural and structural properties as well as the composition of the synthesized material. Mesoporous silica gives a surface area of 161 m<sup>2</sup>/g which shows promising results of adsorption to Acid Red 337 dyes in aqueous solutions.

In addition, it was noted that pH is the most important factor to affect the dye removal.

The adsorption properties of the synthesized mesoporous silica have been tested on real textile effluents and indicated promising treatment efficiency by reducing most of the parameters (color, COD and TOC). These results suggest that mesoporous silica material synthesized from low-cost and available clay would contribute to a more sustainable environmental process.

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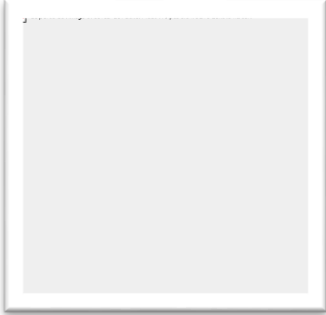
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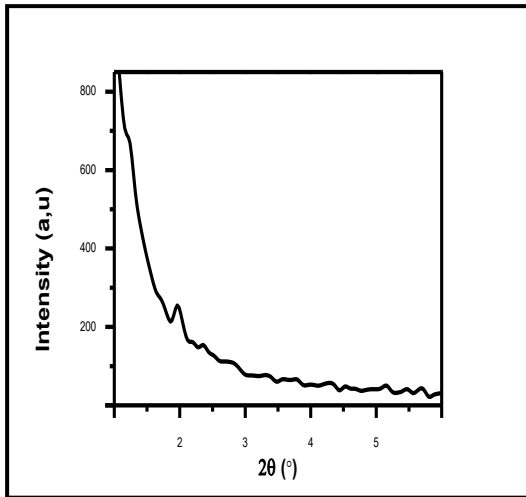
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**Table 1:** Main properties of Acid Red dye 337

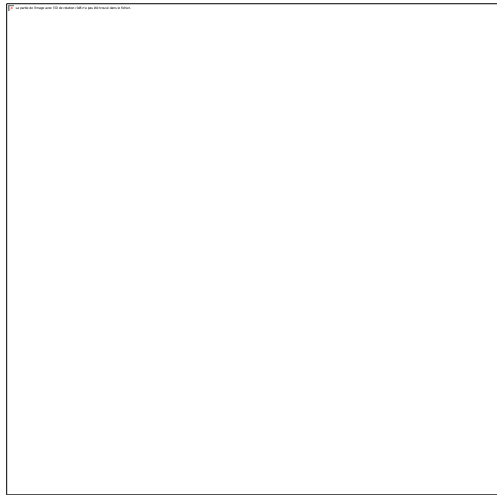
Characterization	Character/value
Chemical structure	
Molecular formula	C <sub>17</sub> H <sub>11</sub> F <sub>3</sub> N <sub>3</sub> NaO <sub>4</sub> S
Molar mass	433.337 g/mol
$\lambda_{\max}$	500nm
CAS	12270-02-9

**Table 2:** Chemical composition of natural Kaolin DD3 and as-synthesized mesoporous silica (wt %)

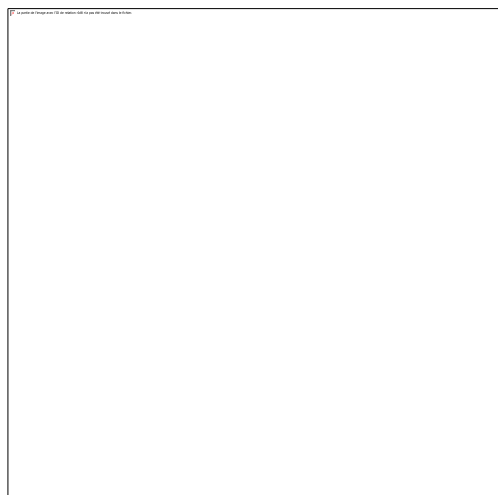
	SiO <sub>2</sub>	MgO	Al <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	K <sub>2</sub> O	CaO	TiO <sub>2</sub>
DD3	41.74	0.017	31.21	0.03	0.313	0.085	0.420	0.017
MS	89.3	0.015	0.51	0.003	0.045	0.017	0.01	0.006



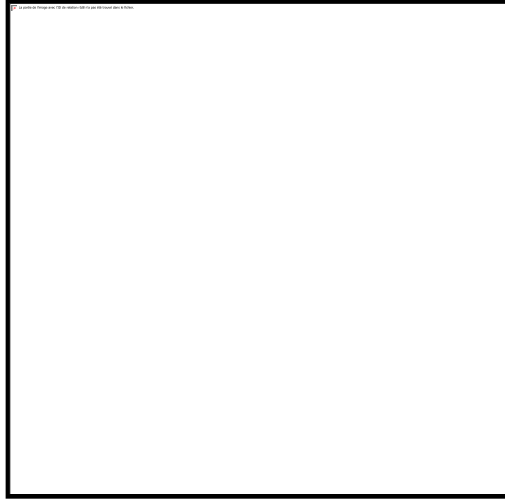
**Figure 1:** XRD pattern of as-synthesized mesoporous silica



**Figure 2:** TEM image of as-synthesized mesoporous silica



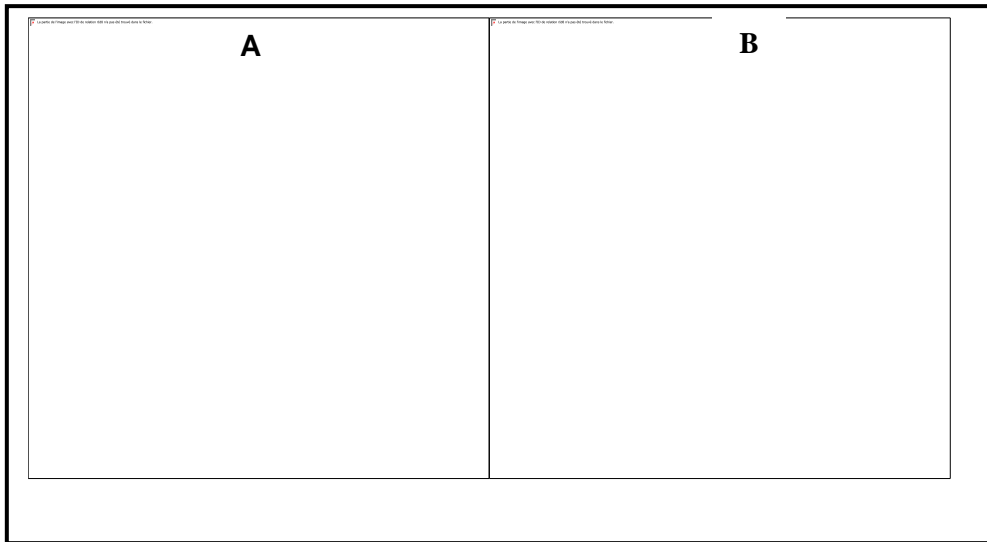
**Figure 3:** SEM microphotographs of as-synthesized mesoporous silica



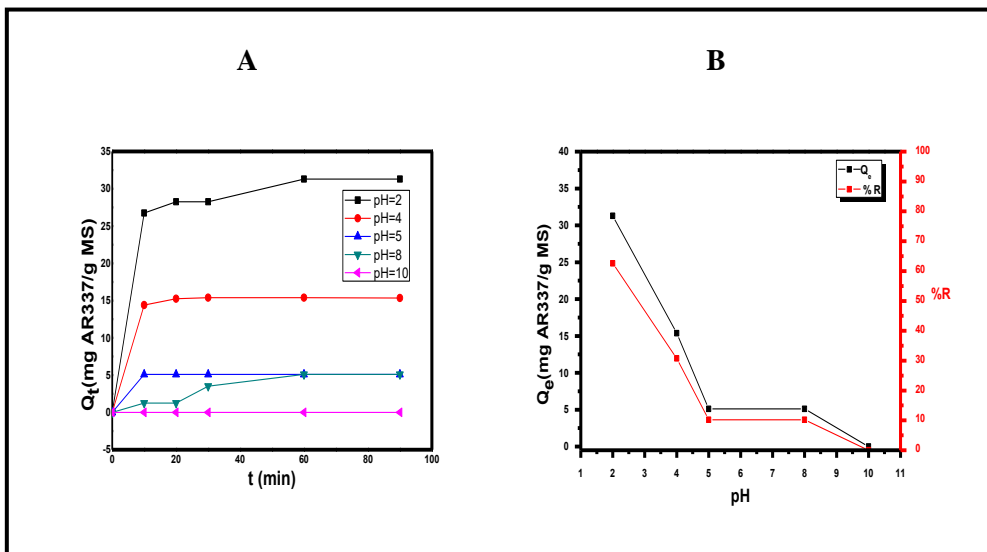
**Figure 4:** N<sub>2</sub> adsorption–desorption isotherms of as-synthesized mesoporous silica

**Table 3:** BET surface area, BJH surface area, total pore volume and pore size of DD3 Kaolin and as-synthesized mesoporous silica (MS)

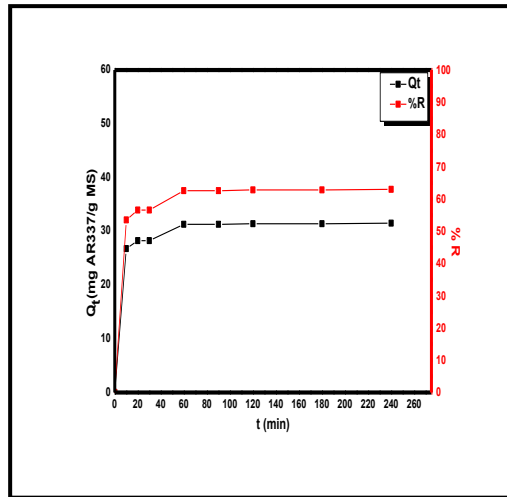
Parameter	DD3	MS
BET surface area (m <sup>2</sup> /g)	49.33	61.31
BJH surface area (m <sup>2</sup> /g)	11.04	83.390
Total pore volume (cm <sup>3</sup> /g)	0.00319	0.250
Pore Radius Å	7.5	15.73



**Figure 5:** TGA and DTA curves of (A) natural Kaolin (DD3), (B) as-synthesized mesoporous silica (MS)

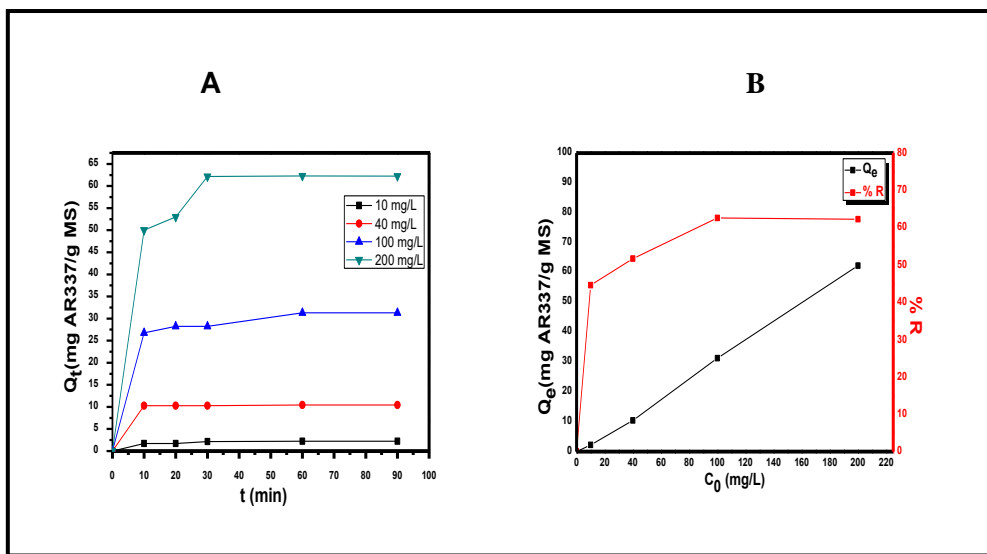


**Figure 6:** Effect of  $pH$  on the Acid Red 337 : (A) adsorption capacity ( $Q_t$ ) and (B) % R over the synthesized mesoporous silica ( $C_0 = 100 \text{ mg/L}$ ,  $V = 200 \text{ mL}$ ,  $T = 20^\circ\text{C}$ ,  $r = 300 \text{ rpm}$ ,  $m = 0.4 \text{ g}$ )

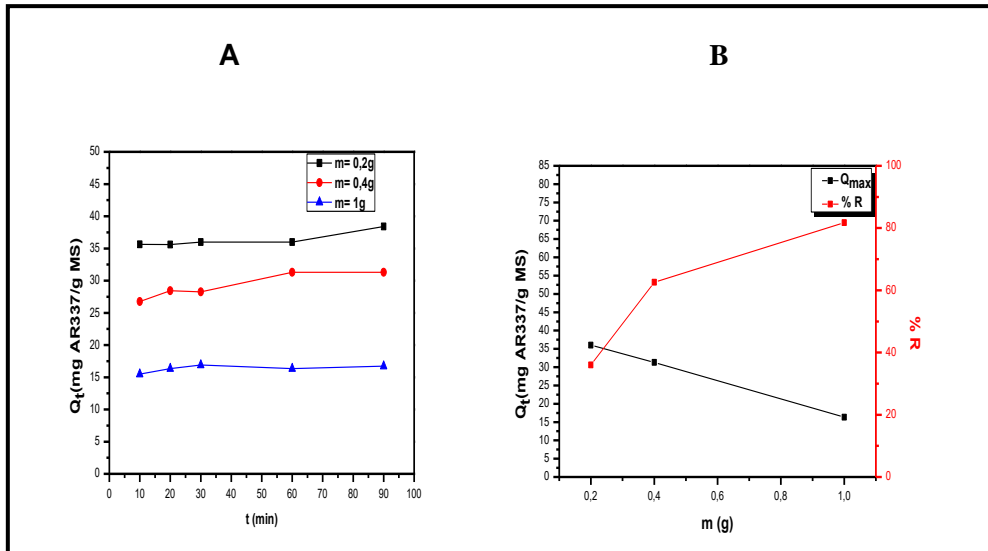


**Figure 7:** Effect of contact time ( $t$ ) on the Acid Red 337 adsorption capacity ( $Q_t$ ) and % R over the synthesized mesoporous silica ( $C_0 = 100 \text{ mg/L}$ ,  $V = 200 \text{ mL}$ ,  $T = 20^\circ\text{C}$ ,  $r = 300 \text{ rpm}$ ,  $\text{pH} = 2$ ,  $m = 0.4$

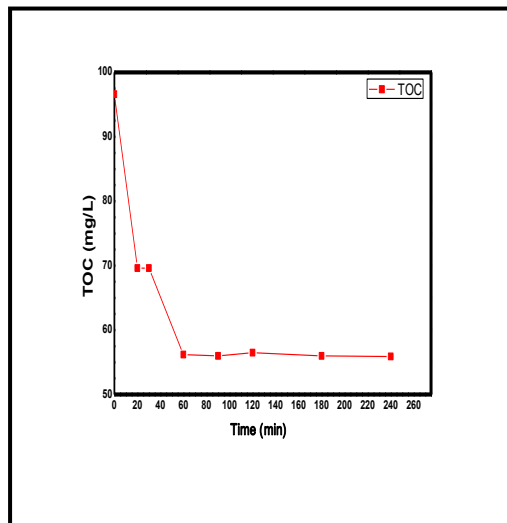
g)



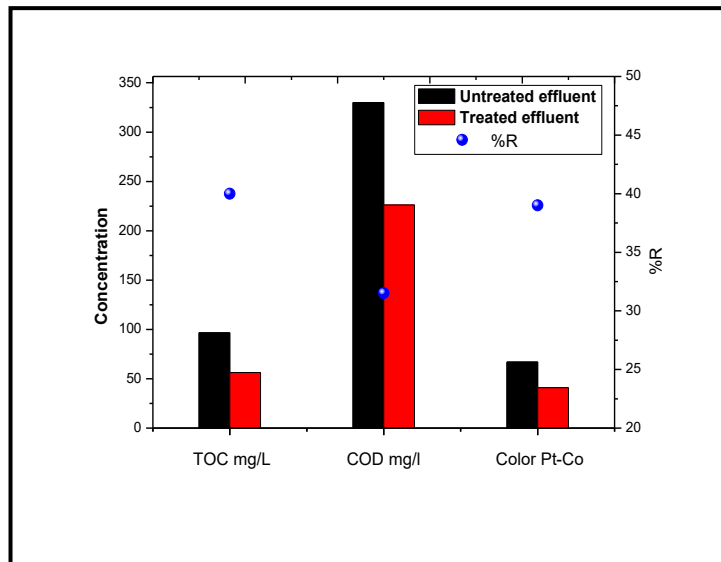
**Figure 8:**Effect of initial dye concentration ( $C_0$ ) on: (A) adsorption capacity ( $Q_t$ ) and (B) % R over the synthesized mesoporous silica ( $m = 0.4 \text{ g}$ ,  $V = 200 \text{ mL}$ ,  $T = 20^\circ\text{C}$ ,  $r = 300 \text{ rpm}$ ,  $\text{pH} = 2$ )



**Figure 9:** Effect of adsorbent amount ( $m$ ) on: (A) the adsorption capacity ( $Q_t$ ) and (B) % R of the synthesized mesoporous silica ( $C_0 = 100 \text{ mg/L}$ ,  $V = 200 \text{ mL}$ ,  $T = 20^\circ\text{C}$ ,  $r = 300 \text{ rpm}$ ,  $\text{pH} = 2$ )



**Figure 10:** Effect of treatment time on the reduction of TOC of the real textile effluent by adsorption on synthesized mesoporous silica ( $T = 30^\circ\text{C}$ ,  $\text{pH} = 8.15$ ,  $m = 1 \text{ g}$ ,  $V = 100 \text{ mL effluent}$ ,  $r = 300 \text{ rpm}$ )



**Figure 11:** Concentration reduction and removal percentage of TOC, COD and color of wastewater by adsorption on as-synthesized mesoporous silica