

Adsorption Kinetics of Alcohols over MCM-41 Materials

Farouq Twaiq, Mustafa Nasser, Siham Al-Hajri, Mansoor Al-Hasani

Abstract—Adsorption of methanol and ethanol over mesoporous siliceous material are studied in the current paper. The pure mesoporous silica is prepared using tetraethylorthosilicate (TEOS) as silica source and dodecylamine as template at low pH. The prepared material was characterized using nitrogen adsorption, X-ray diffraction (XRD) and scanning electron microscopy (SEM). The adsorption kinetics of methanol and ethanol from aqueous solution were studied over the prepared mesoporous silica material. The percent removal of alcohol was calculated per unit mass of adsorbent used. The 1st order model is found to be in agreement with both adsorbates while the 2nd order model fit the adsorption of methanol only.

Keywords—Adsorption, Kinetics, Mesoporous silica, Methanol

I. INTRODUCTION

INORGANIC porous solids have been found great utility as catalysts and adsorbents because of their large internal surface area. Nanoporous materials became more important and useful for separation of polluting species and recovery of useful ones due to their selectivity [1]. The first broad family of mesoporous molecular sieves (M41S) with three members that were well-known as hexagonal MCM-41, cubic MCM-48, and lamellar MCM-50 silica phases [2]. The mechanism for M41S formation involve strong electrostatic interactions and changed matching between micellar assemblies of quaternary ammonium cations (S^+), as structure-directing agents and anionic silicate oligomer species (I^-). A series of mesoporous silica molecular sieves had been prepared by electrostatic (charges) and natural (no charges) assembly pathways [3]. Mesoporous silicates, such as MCM-41 and SBA-15 are amorphous porous silicates with huge surface areas (normally $\geq 1000 \text{ m}^2/\text{g}$), large pore sizes (2 nm - 20 nm) and ordered arrays of cylindrical mesopores with very regular pore morphology [4]. The large pore size and ordered pore morphology allow one to be sure that molecules are small enough to diffuse into the pores [5]. It was found in all cases studied that the hexagonally packed pores are oriented in a circular manner around the micellar axis. Mesoporous silica fibers were one of the most interesting structures in application. The kinetics of fiber formation and the product distribution were vary, and strongly dependent on the silica source. A very interesting mesoporous silica fiber was obtained from a static two phase's acidic system. The fibers consist of hexagonally organized channels oriented parallel to the fiber axis.

The prepared mesoporous materials can be characterized to study their properties using different analytical techniques.

Most widely known is the determination of the Brunauer, Emmett, and Teller (BET) surface area by gas adsorption. BET analytical technique is designed to measure the adsorption characteristics of nitrogen molecules over porous materials maintained at a temperature of 77 K. Nitrogen adsorption method is used to measure the surface area, Barrett-Joyner-Halenda (BJH) pore volume and pore size distribution of a solid material. Nitrogen adsorption provides information of microporosity and mesoporosity distribution up to 10 nm [6].

X-ray diffraction (XRD) is used to measure crystal structure. The scanning electron microscope (SEM) is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition and other properties [1]. Transmission electron microscopy (TEM) is a microscopy technique where by a beam of electrons is transmitted through an ultra thin specimen, interacting with the specimen as it passes through. The TEM is useful in studying the pore structure and distributions.

The pollution of water with chemical contaminant has become one of the most crucial environmental problems [7]. The design of a suitable mesoporous molecular sieve with high surface area and adsorption capacity can be synthesized easily in the laboratories with manipulated pore sizes and surface composition [1]. The high surface area of mesoporous silicate can be utilized to adsorb organic compounds from wastewater with great capacity [8]. The seawater has been used widely in methanol industry in order to cool the equipment. This water is polluted with methanol due to losses of methanol from storage tanks of process vessels, leaks from piping and equipment. Because of growing environmental awareness has put up stringent regulations to control the emissions of this pollutant, the concern is to control and reduce the concentration of methanol before it could be recycled to the sea. Adsorption methods could be a good choice to separate the methanol from wastewater and can treat a large volume of wastewater if the proper adsorbent is selected [9].

The adsorption technique is one of the common methods used to recover the pollutants among many available methods widely applied. The adsorption process is two types, physical adsorption and chemisorption based on the interaction between adsorbate and adsorbent [7]. Activated carbon adsorption systems have been used and found to play important role in cleaning industrial effluents. Mesoporous materials are one alternative due to their large pores and ability for regeneration compare to activated carbons [5]. Other than that, due to their large specific surface area, high pore volume, uniform pore diameter and high thermal stability. Mesoporous materials become promising materials to be implemented in many industries involving adsorption, catalysis and ultra-filtration.

All Authors are with Department of Chemical Engineering, University of Nizwa, 616 Brikat Al-Mouz, Nizwa, Oman.

Farouq Twaiq, Farouq.twaiq@unizwa.edu.om, Mustafa Nasser, Mustafa.nasser@unizwa.edu.om

The mesoporous M41S molecular sieve materials showed a potential application as adsorbents of their large pore volume and the compositional flexibility [6].

In the current paper we aimed to synthesize and characterize mesoporous silica material which can be used as adsorbent for methanol and ethanol in aqueous solution. The adsorption kinetics for the adsorption of methanol and ethanol over the synthesized mesoporous material is evaluated using two different adsorption models that are pseudo 1st order and pseudo 2nd order models. The current work will differentiate between adsorption kinetics and mechanisms of different alcohols over the same adsorption material.

II. METHODOLOGY

A. Preparation of Mesoporous Materials

Mesoporous silica material was prepared by using sol-gel technique. The crystallization gel is prepared using 1 g of Tetraethylorthosilicate (TEOS), obtained from Merck with purity > 98%, as silica source dissolved in 160 mL of water and 8 mL hydrochloric acid (37%) and refluxed under vigorous stirring at 70°C for 4 h. A solution of 4 g of dodecylamine template obtained from Aldrich with purity > 99%, in 100 mL methanol is added to the previous mixture. The crystallization mixture is allowed to react at room temperature with stirring and kept for crystallization for 24 h. The solid produced from the crystallization is filtered, washed with deionized water and dried overnight in the room temperature prior to calcinations at 600°C in muffle furnace for 4 h.

B. Characterization of Mesoporous Materials

The prepared material was characterized by nitrogen adsorption and adsorption-desorption data was obtained using Automated Quantachrome 6B Autosorb at CombiCat research centre, Universiti Malaya, Kuala Lumpur, Malaysia. The sample was degassed at 120°C for 1 h before data are collected and analyzed to evaluate BET surface area and pore size and pore volume using BJH method. The structure of crystalline material is obtained using XRD measurement. The spectrum was collected in the range of 2 – 10° at step size of 0.02° per second. The XRD result was obtained using D8 advance diffractometer, Bruker AXS, at CombiCat research center, Universiti Malaya, Kuala Lumpur. The morphology of the synthesized material was viewed using scanning electron microscope (SEM) (Model Leica Cambridge S-360, DARIS research center, University of Nizwa).

C. Adsorption Test

Adsorption test was made on two alcoholic solutions, methanol and ethanol. Specified amount of alcohol (methanol and ethanol) was mixed with 1000 mL of deionized water for 10 min respectively. The initial concentration of the two solutions was measured using UV/Vis spectrophotometer (UVI Biomate, Chemistry Lab, University of Nizwa) at a scan rate of 300 nm/min. Adsorption experiments were performed by

adding 1 g of sorbent into each solution, respectively. The experiments were repeated for similar solutions using 2 g of sorbent. M-1 and M-2 are referred to methanol experiments treated with 1g and 2g adsorbent respectively, and E-1 and E-2 are the ethanol adsorbed using 1g and 2g adsorbent respectively. The concentration of the alcohol in the solution was measured at 10 min time intervals for 60 minutes.

III. RESULTS AND DISCUSSION

A. Preparation and Characterization of Mesoporous Materials

The adsorption-desorption data was collected at partial pressures (P/P_0) in the range of 0 to 1 as shown in Figure 1. The adsorption-desorption isotherm shows that the major nitrogen intake is found in the P/P_0 range above 0.7. The result indicates that a very high external surface area is formed. The mesoporous material was found of hexagonal mesoporous silica (HMS) type. The BET surface area of the material is measured using 5 points in the P/P_0 range of 0 to 0.1. The surface area was found to be 490 m²/g. BJH method was used to calculate the average pore size distribution and pore volume. The average pore size was found equal to 2.85nm and the pore volume is 0.32 cm³/g.

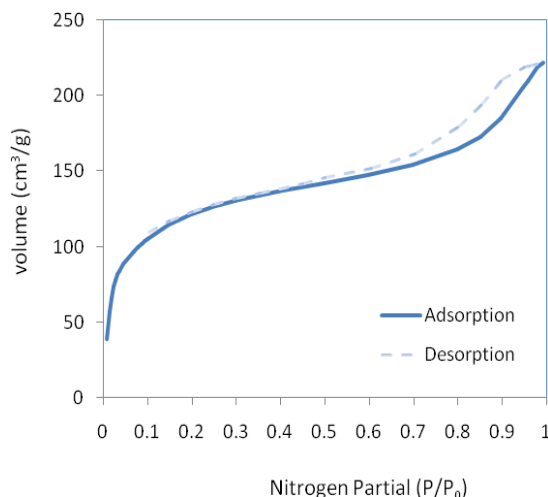


Fig. 1 Nitrogen adsorption-desorption isotherm for calcined HMS

Characterization of mesoporous material using X-ray diffraction (XRD) is necessary to identify the properties of the material crystallinity is shown in Figure 2. The X-ray scan was obtained in the range of 2 – 10°. Figure 2 shows XRD patterns of the products synthesized using HCl as acid source at ambient temperature. When the as-synthesized product is crystallized for 24 h, the XRD pattern displays a well-defined diffraction peak and two weak diffraction peaks in the range of 2 – 10°, which indicates high ordered hexagonal product. The results are in agreement of reported materials to mesoporous materials. Crystallinity with hexagonal pore structure is found as indicated by the number of peaks in the spectrum.

The first peak is narrow indicating a uniform pore structure however a thick wall is formed.

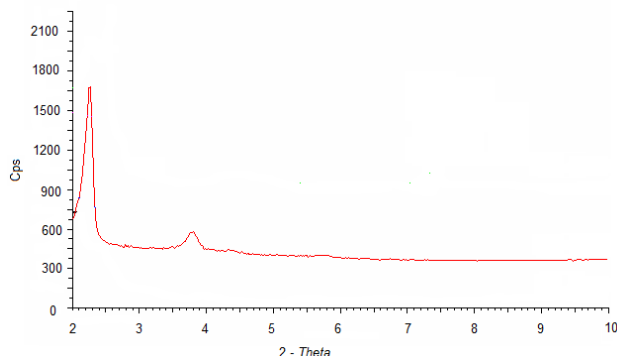


Fig. 2 XRD spectra for mesoporous material prepared by sol-gel technique

The morphology of the mesoporous materials is shown in Figure 3 by scanning electron microscopy (SEM). The scanning electron microscopy images displayed in Figure 3 exhibit micrometric spherical particles. Uniform particles of less than 1 μm were produced. The small uniform particles of high external surface area will enhance the adsorption, sorbents intake and access to the solid material.

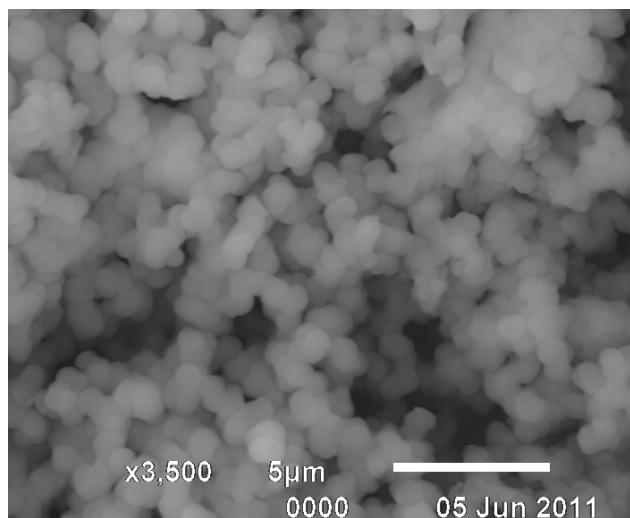


Fig. 3 SEM image of mesoporous silica material prepared by sol-gel technique

B. Adsorption Test

Methanol and ethanol solutions have been prepared at concentrations shown in Table 1. Methanol and ethanol have been adsorbed by using two different amounts of adsorbent 1g/L and 2g/L. Adsorption kinetics of methanol and ethanol over mesoporous silica material were performed at pH=7. Samples have been taken every 10 min, and the concentration has been measured by UV/Vis spectrometer. The UV/Vis data have been collected 3 times and the average concentration recorded. The data were reproducible within the accepted error. The amount of alcohol intake was calculated by Equation (1).

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (1)$$

where C_0 is the initial concentration of alcohol (g/L), C_t is the concentration of alcohol (g/L) remaining at time t , V is the volume of the solution (L) and W is the mass of adsorbent (g).

TABLE I
METHANOL ADSORPTION BY MESOPOROUS SILICA FIBER

Time(min)	M-1 g/L	M-2 g/L	E-1 g/L	E-2 g/L
0	0.550	0.395	0.800	0.800
10	0.525	0.369	0.770	0.710
20	0.457	0.358	0.640	0.630
30	0.441	0.349	0.580	0.540
40	0.440	0.349	0.490	0.500
50	0.440	0.347	0.430	0.400
60	0.440	0.347	0.410	0.330

The percentage of alcohol removal is calculated by Equation (2).

$$\text{Removal\%} = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (2)$$

The models describing adsorption mechanism are developed based on understanding the interactions over the silica surface. Three types of adsorbing centers of silica were proposed. Besides of the major adsorbing sites formed by free surface hydroxyl groups, there are also sites formed by paired – geminal – hydroxyl groups bound by Hydrogen Bridge, if the distance among the individual hydroxyl groups is suitable [10] as shown in Figure 4.

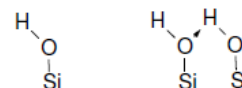


Fig. 4 Hydroxyl group formed by pure siliceous amorphous materials [10]

The models should take onto account the physical possibilities of the sorbate molecules to bind to the adsorbing centers, mainly by hydrogen bonding. Mirji et al [10] have proposed three mechanisms for methanol interaction with silica during adsorption as shown in Figure 5.

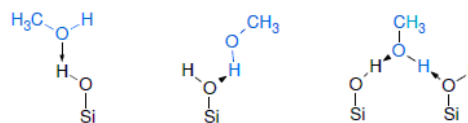


Fig. 5 Mechanisms of methanol interaction over siliceous material [10]

C. Kinetic Study

The study of adsorption kinetics describes the solute intake rate and evidently this rate controls the residence time of adsorbate intake at the solid-solution interface. The interaction of organic molecules with inorganic surfaces has attracted a great deal of attention due to its technological applications. Adsorption of organic solvents like methanol on inorganic

materials such as pure silica has been studied [10,11]. Figure 6 illustrates the removal of the alcohols from aqueous solution over mesoporous silica material. Mesoporous materials have very large surface area, ordered pore structure and extremely narrow pore size distribution. Methanol adsorption on these mesoporous materials can be interesting because of large surface area, and hence large adsorption sites, which may help to adsorb more quantity of methanol [11]. The kinetics of alcohol adsorption on the mesoporous silica material was analyzed using pseudo first-order and pseudo second-order kinetic models. The conformity between experimental data and the model predicted values is expressed by the correlation coefficients (R^2). A relatively high R^2 value closer to 1 indicates that the model successfully describes the kinetics of alcohol adsorption.

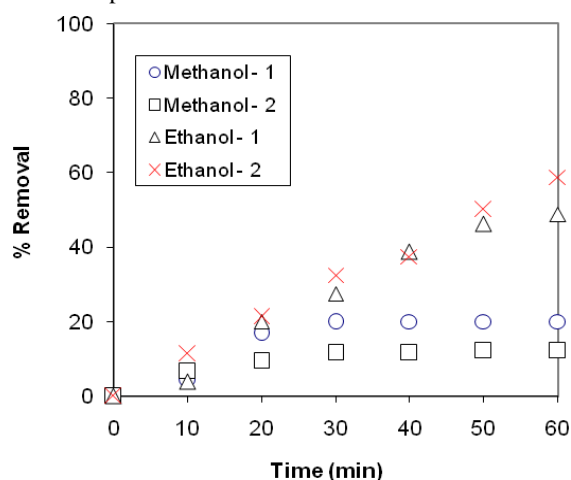


Fig. 6 Percent removal of alcohol over mesoporous siliceous materials

The pseudo first-order equation is generally expressed as follows [12],

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (3)$$

where q_e and q_t are the adsorption capacity at equilibrium and at time t , respectively (g/L), k_1 is the rate constant of pseudo first-order adsorption (1/min). After integration and applying boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the integrated form of Eq. (3) becomes.

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \quad (4)$$

Rearranging Eq. (4) to result q_t vs t as in Eq. (5)

$$q_t = q_e [1 - e^{(-k_1 t)}] \quad (5)$$

Nonlinear regression using Polymath software (version 5.1) was used to estimate the constant values of q_e and k_1 . Tables 2 illustrate the results of pseudo first-order model on the four experimental runs. In the 1st order model R^2 was calculated and found in the range of 0.92 – 0.99.

TABLE II
KINETICS OF METHANOL AND ETHANOL USING 1ST ORDER MODEL

	1 st order		
	k_1	q_e	R^2
M -1	0.0526	0.1223	0.92

M -2	0.0754	0.0490	0.99
E -1	0.0055	1.3888	0.97
E -2	0.0043	2.0090	0.99

Comparison between model and experimental q_t data are shown in Figure 7. The model data were in good agreement with the experimental data and pseudo first-order model said to represent the methanol and ethanol intake over the mesoporous silica surface. The first-order model support the mechanism that single site is responsible for adopting a single molecule of the alcohol at its surface. These results are in agreement with our unpublished data that Langmuir equilibrium model fitting the equilibrium results of methanol and ethanol over mesoporous silica materials.

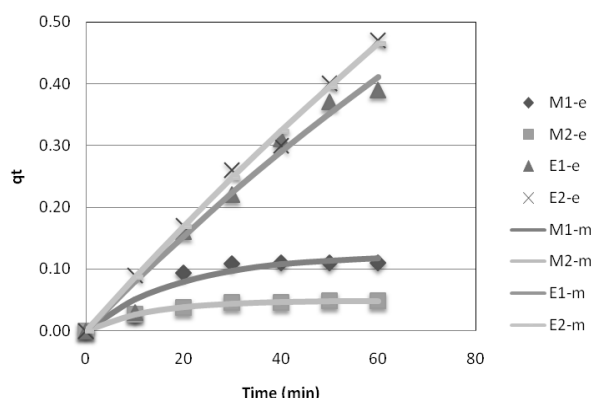


Fig. 7 Comparison between pseudo first-order model and experimental q_t data. Where in the legend: e is the experimental and m is the model

The pseudo second-order adsorption kinetic rate equation is expressed as [12].

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (6)$$

where k_2 is the rate constant of pseudo second-order adsorption (L/g·min). For the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the integrated form of Eq. (6) becomes

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} - k_2 t \quad (7)$$

which is the integrated rate law for a pseudo second-order.

Equation (7) can be rearranged to obtain Eq. (8), which has a linear form

$$\left(\frac{t}{q_t} \right) = \frac{1}{h} + \frac{1}{q_e} (t) \quad (8)$$

where $h = k_2 q_e^2$ (L/g·min).

The plot of (t/q_t) vs. t of Eq. (8) should give a linear relationship from which q_e and k_2 can be determined from the slope and intercept of the plot, respectively. Alternatively, polymath software using regression analysis was used to estimate the equation parameters. Table 3 is illustrating the values of h , q_e and R^2 for four experimental runs.

TABLE III
KINETICS OF METHANOL AND ETHANOL USING 2ND ORDER MODEL

	2 nd order		
	h	q_e	R^2
M - 1	0.0287	0.1190	0.99
M - 2	0.0067	0.0554	0.99
E - 1	0.0088	1.7830	0.65
E - 2	0.0097	3.3078	0.41

The results clearly show that pseudo second-order model well fitting methanol adsorption with $R^2 = 0.99$, however it fails to fit the ethanol adsorption. Figure 8 show a comparison between experimental data and model data for the four experimental runs.

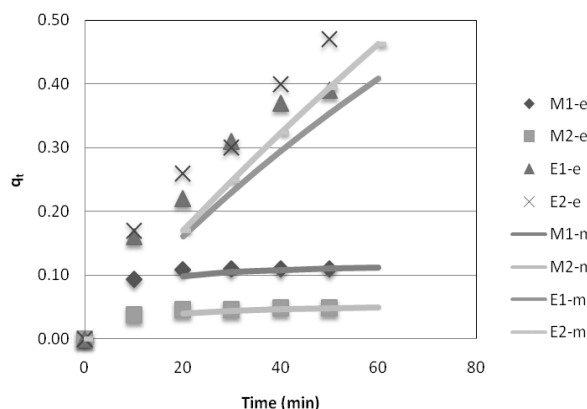


Fig. 8 Comparison between pseudo second-order model and experimental q_t data. where in the legend: e is the experimental and m is the model

In conclusion, hydrophilic HMS adsorbents provided low adsorption capacity than the hydrophobic ones. It should be noted that adsorption of alcohol on HMS due to interaction between silanol groups on surface and intermolecular hydrogen bonding part of alcohol molecule might be stronger than hydrogen bonding interacted with HMS surface. Moreover HMS hydrogen bonding caused by functional groups should be suggested to enhance the adsorption capacity comparing with HMS. Interaction between silanol group on HMS and might be stronger than hydrogen bonding interacted with materials loaded with functional group loaded on HMS surface.

IV. CONCLUSION

Mesoporous silica material having surface area of $490\text{ m}^2/\text{g}$ with adsorption capacity of $0.32\text{ cm}^3/\text{g}$ was synthesized. The synthesized mesoporous siliceous material was used as adsorbent for methanol and ethanol from aqueous phase. The methanol and ethanol intake over the mesoporous silica adsorbent surface was measured and percent removal was calculated and found to be 20% for methanol and 60% for ethanol. The experimental concentration – time data fit with 1st order model with good agreement. Furthermore, the 2nd order model fit the methanol adsorption only.

ACKNOWLEDGMENT

The authors would like to thank The Research Council (TRC) in The Sultanate of Oman for the financial fund for project No. ORG/EI/10/005.

REFERENCES

- [1] F. A. Twaig, A.R. Mohamed and S. Bhatia, "Liquid Hydrocarbon Fuels from Palm oil by Catalytic Cracking over Aluminosilicate Mesoporous Catalysts with Various Si/Al Ratios". Mesoporous Materials. 64, 2003, pp. 95-107
- [2] J.Y. Ying, and C.P. Mehnert "Synthesis and Applications of Supramolecular-Templated Mesoporous Materials", Angew. Chem. Int. Ed, 38, 1999, pp. 57 - 74.
- [3] S. Biz and M. L. Ocelli, "Synthesis and Characterization of Mesoporous Materials", Catal. Rev. Sci. Eng., 40(3), 1998, pp. 329 - 407.
- [4] B.G. Trewyn, I.I. Slowing, S. Giri, H.-T. Chen, V. S-Y Lin. "Synthesis and Functionalization of a Mesoporous Silica Nanoparticle Based on the Sol-Gel Process and Applications in Controlled Release". Accounts of Chemical Research. 40 (9), 2007, pp. 846-853
- [5] M. Yates, J. Blanco, M. A. Martin-Luengo and M. P. "Vapour adsorption capacity of controlled porosity honeycomb monoliths". Microporous Materials. 65 (2-3) 2003, pp. 219-231.
- [6] M. Vallet-Regí, F. Balas, D.Arcos "Mesoporous materials for drug delivery" Angew. Chem. Int. Ed. 46, 2007, pp. 7548-7558.
- [7] B. H. Hameed, "Equilibrium and kinetic studies of methyl violet sorption by agricultural by-product" Journal of Hazardous Materials. 154, (1-3), 2008, pp. 204-212.
- [8] H. A. Jamali, A. H. Mahvi and S. Nazmara. "Removal of Cadmium from Aqueous Solutions by Hazel Nut Shell". World Applied Science Journal. 5, 2009, pp. 16-20.
- [9] K. Kasim, N. Abu-bakur, S.N. Mustafa, A.M. and Mohamed Z.M. Daud. "Methylene Blue Removal from Simulated Wastewater by Adsorption Using Gandoderma Cultivation Waste Sawdust". World Applied Sciences Journal, 2009, pp. 104-113.
- [10] S.A. Mirji, S.B. Halligudi, N. Mathew, N.E. Jacob, K.R. Patil, A.B. Gaikwad. "Adsorption of methanol on mesoporous SBA-15". Materials Letters. 61, 2007, pp. 88-92.
- [11] A. Galíková and A. Galík. "The study of the adsorption kinetics of acetylene and methanol on silica gel by gravimetry and global fitting". 31th Intl Conf of SSCHE. Tatranské Matliare, Slovakia. May 24-28, 2004, pp.1.
- [12] E. Demirbas, M. Kobyab, E. Senturkb, T. Ozkana. "Adsorption kinetics for the removal of chromium (VI) from aqueous solutions on the activated carbons prepared from agricultural wastes". Water SA, 30 (4), 2004, pp. 533-5337.