

Adsorption of Thymol From Aqueous Solution Using Granulated Surfactant Initiated Modified Bentonite via Packed Column Method

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Abstract

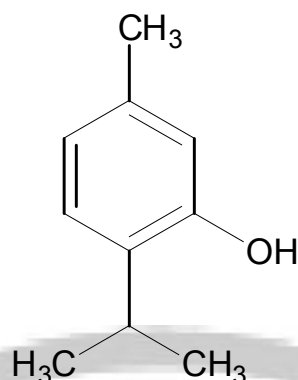
The adsorption study of thymol, was carried out at $(25\pm 0.1)^\circ\text{C}$, using granulated surfactant modified Iraqi Na – montmorillonite clay (initiated modified bentonite); in a down-flow packed column, the modified mineral was characterized by FT-IR spectroscopy. A linear calibration graph for thymol was obtained, which obey Beer's law in the concentration range of 5-50 mg/L at 274 nm against reagent blank. Single-factor-at-a-time approach; showed that the equilibrium time required for complete adsorption was 45 minute with flow rate (4.0drop/ mint). The adsorption of thymol increased with rising pH of the adsorbate solution, increase of solute uptake when the initial adsorbate concentration is increased. The adsorption is mostly physically in nature and fitted with Langmuir model. The result indicated that the pseudo-second-order kinetic models is fitted very well with the experimental data.

Keywords : adsorption, thymol, Na – montmorillonite, clay, packed column.

Introduction

Phenolic compounds are the most important contaminants present in the environment. It can be originated naturally due to the degradation of humic substances, tannins, lignins and many of environment processes, These compounds are used in several industrial processes to manufacture chemicals such as pesticides, explosives, drugs and dyes. They are also used in the bleaching process of paper manufacturing. Apart from these sources, phenolic compounds have substantial applications in agriculture as herbicides, insecticides and fungicides [1, 2].

Thymol (Scheme1) is phenolic monoterpene, isolated from *Thymus vulgaris*, *Origanum vulgare*, *Satureja thymbra* and *Thymbra capitata* plants [3], confers antimicrobial properties to these oils. In addition, this phenolic compound is currently used in conjunction with chlorhexidine to inhibit oral bacteria. It has been postulated that thymol decreases enzyme activity and/or disrupts membrane integrity by altering protein reactions [4]. Studies have shown that thymol inhibits Gram-positive and Gram-negative bacteria and possess multiple biological properties such as anti-inflammatory, anti-leishmanial, antioxidant [5], hepatoprotective and anti-tumor activities [6]. It have been shown to be an efficient acaricide molecule against the *Varroa destructor*, an external parasitic mite that attacks honey bees [7]. Many methods are used for determination of thymol such as liquid chromatographic methods by making a comparison between the use of a silica-based monolithic column and a RP-Amide C16 column for the separation of phenol, thymol and carvacrol [8], NMR [9] and HPTLC [10].



Scheme 1: The chemical structure of thymol

Clays are hydrated alumino silicates, composed of mixture of fine-grained minerals, crystals of other minerals and oxides. Natural mineral clays possess specific surface chemical properties, e.g., cation exchange capacity, and adsorptive affinity for some organic and inorganic compounds, which have led to investigate on the potential use of clays as adsorbents for treating heavy metals and organic pollutants, or as coagulant aids for improving the settling performance in coagulating low particle content water. By replacing the natural inorganic exchange cations with alkyl ammonium ions, clay surfaces are converted from being primarily hydrophilic to hydrophobic, which enable them to interact strongly with organic vapors and organic compounds dissolved in water [11].

Clays obtaining montmorillonite are referred to bentonite which belongs to the 2:1 clay family composed of two tetrahedrally coordinated sheet of silicon surrounding an octahedrally coordinated sheet of aluminum ions [12]. While the number of Al ions in tetrahedral sites determines the net negative charge of the host layer, which can adopt a number of interesting stacking arrangements to form ordered, partially ordered, or disordered three-dimensional structures. Another interesting feature of clay is swelling [13], indicating that the interlayer of some clay can reversibly incorporate amounts of polar molecules, such as water and cations.

Much attention has been drawn to the modification of clay mineral properties, because it has low cost and readily available in several technological applications [14]. Clays can be modified to increase the attenuation of some organic compounds and improve its sorption ability. Since hydration of exchangeable alkali and alkaline earth metal cations creates a hydrophilic environment on the surface and in the interlayer region of natural clays [15]. The adsorbent properties can be improved by replacing the natural inorganic cations with organic cations such as quaternary ammonium cations of the $(\text{CH}_3)_3\text{N}^+(\text{CH}_2)_{15}\text{CH}_3$ form. The main purpose of such modification is to increase the hydrophobic nature of the mineral surface and consequently enhance the affinity towards organic compounds. Organo clays show different hydrophobic properties depending on the organic cations structure and its uptake into the gallery. This is an important feature because the treatment of the mineral can be adjusted according to need [16].

Another very important attribute when clay modification is proposed for organo clay is the cation exchange capacity (CEC). Vermiculite and bentonite are clay minerals with high CEC.

The CEC for vermiculite, for instance, is approximately 100–150 meq per 100 g [15].

West Iraqi (Traifawi) bentonite consists mostly of calcium – montmorillonite. The percent of montmorillonite is between (60 – 65 %) of crude bentonite, table (1) shows the chemical analysis of West Iraqi (Traifawi) bentonite, therefore it is necessary to remove the impurities before the bentonite is ready to use.

Apparatus

A Cintra 5 spectrophotometer with 1 cm quartz cells was used for absorbance measurements. Sartorius BL 210S (± 0.0001 g) scientific balance, scientific shaker with thermal control (GCA precision), pH-meter DW-9421 from Philips instrument, a glass column (70 cm X 15 mm i.d.) and Pentium 4 computer (DELL 1545) was used for data processing

Experimental

Material and Reagents

All Chemicals used were of analytical reagent grad unless otherwise is mentioned, bentonite mineral clay obtained from the General Company for Geological Survey and Mining in Baghdad; Iraq, thymol crystal (Riedel- De Haen).

Standard solution

Thymol stock solution (250 mg/L), was prepared by dissolving 0.025 gm of thymol in 5ml ethanol and diluting to 100 ml in volumetric flask with distilled water. Working solutions were freshly prepared by subsequent dilutions.

General Recommended procedure for determination of thymol

1 ml aliquots of thymol standard solution containing (25-250 mg/L) were transferred into a series of 5 ml volumetric flask; and diluted with distilled water. Measure the spectrum at 274nm against a reagent blank prepared similarly without addition of thymol.

Procedure for synthesis of granulated surfactant modified Iraqi Na – montmorillonite clay

a. Initiation

In this study the bentonite was beneficiated to improve its Smectite (Montmorillonite) content by attrition – scrubbing at high solid concentration (50%) and at high impeller speed (2500 r.p.m.) for 1 h, using flotation cell. Then is converted calcium - montmorillonite to sodium - montmorillonite by process of activation using ion-exchange technique, by mixing the bentonite preconcentrate with Na – form activated amberlight orange ion exchanger followed by agitation for 1 h, at 150 r.p.m[17].

The clay was separated from the mixture by filtration, washed about five times with distilled water. Each washing step involved stirring the slurry in distilled water, followed by centrifugation and removal of the supernant, then Na – monmorillonite was treated with 0.5 M NaCl to ensure complete transformation to the Na – form, then the treated clay was washed with distilled water to remove excess NaCl[17].

b. Modification

Then the sodium-form montmorillonite was modified with a surfactant Hexadecyltrimethyl ammonium bromide (HDTMA) to form organic modified clay ready to use in our research, it was done by adding (50 m mol/L) solution of (HDTMA) TO A 7% aqueous clay suspension. The mixture was stirred in a mixer for 3h, at 350 r.p.m. The organic modified clay was separated from the mixture by filtration and washed about five times with distilled water[18].

c. Granulation

The organic modified montmorillonite turned to a granules of (2mm) diameter using granulating machine (GK Dry Granulating Machine) and dried at 110 °C for 3h, until constant mass, to make an ion – exchange column ready to adsorb thymol from aqueous solution. The surface area of 5 gm mass of adsorbent was calculated physically and it equals to (75.09cm²).

Adsorption Experiments

A glass column (70 cm X 15 mm i.d.) filled with known mass (5gm) of adsorbent (modified organic Na – montmorillonite) corresponding to bed heights of 3cm, percolated with 5 ml of (5-50 mg/L) thymol solution adjusted to different pH values 2.5, 5.5 and 10.8 (optimum 5.5) by ~ 0.1 N NaOH or ~ 0.1 N HCl, and different contact time (from 5 to 120 minutes) with flow rate (4.0drop/ mint).The equilibrium adsorption uptake (q_e mg/g) and percentage removal of thymol from the aqueous solution was determined or calculated using the following relationship[19].

Amount adsorbed $q_e = (C_0 - C_e) V / W$
(mg of adsorbate / g of adsorbent)

$$\% \text{ removal} = 100 (C_0 - C_e) / C_0$$

Where C_0 is the initial sorbate concentration (mg/L), C_e the equilibrium sorbate concentration(mg/L), V is the volume of solution in L and w is the mass of the adsorbent in (g).

Results and Discussion

Characterization of clay

Natural Iraqi bentonite FTIR spectrum[20] showed adsorption band at 3628.10 cm⁻¹ (Al-Al-OH)(Mg-OH-Al) corresponding to stretching vibration of structural OH groups coordinating to Al-Al pair or Mg-OH-Al fig(1). Adsorbed water gives broad bands from 3406.29 cm⁻¹ to 3533.59cm⁻¹ corresponding to H₂O- stretching vibration . Al, Mg bound water molecules gives H-O-H stretching vibration bond at 1643cm⁻¹. Also three bands at 1546.91, 1427.32 and 1384.89 cm⁻¹ corresponding to H..O..H weak . The complex broad band around 1033 cm⁻¹ belongs to Si-O stretching vibration . Two bands at 914.26 cm⁻¹ and 837.11 cm⁻¹ are most characteristic for quartz. Finally the bands from 420.00 cm⁻¹ to 516.93 cm-1 are related to Al-O-Si , Si-O-Si deformations.

Initiated bentonite FTIR spectrum fig(2) showed the same bands of fig(1) but with higher transmittance percent and sharper than bands of FTIR spectrum of natural bentonite. Nevertheless H..O..H weak disappear in this spectrum. Adsorbed water band appear at 3421.72 cm⁻¹,two bands belong to Al, Mg bound water molecules observed at 1654.92 cm⁻¹ and 1641.42 cm⁻¹. The broad complex band becomes single band at 1039 cm⁻¹ belongs to Si-O stretching vibration. Also we observe two bands belongs to Al...OH stretching vibration at 937.04 cm⁻¹ and 916.19 cm⁻¹ with higher transmittance percent .The quartz characteristics band from 694.37 cm⁻¹ to 839.03 cm⁻¹ become boarder. Finally Al-O-Si , Si-O-Si and Si-O stretching vibration bands from 426.27 cm⁻¹ to 522.71 cm⁻¹ become sharper and triplet bond[18]

Hexadecyl trimethyl ammonium bromide modified Iraqi bentonite FTIR spectrum (Figure 3) showed two adsorption bands, the first at 2927.94 cm⁻¹ corresponding to C – H of (-CH₂) groups assymmetric stretching vibration, and the second at 2854.65 corresponding to C – H of (-CH₃) groups stretching for tetrahedral carbon[18].

Also we see an adsorption band at 1475.54 cm^{-1} corresponding to C – H bending of (- CH₃) groups, and a band at 1456.26 cm^{-1} corresponding to C – H scissoring in (- CH₂) groups. C – N stretching adsorption band of quaternary aliphatic amine doesn't appear due to low force constant of this C – N bond of 4^o aliphatic amine.

The adsorption spectrum of thymol adsorbed on initiated modified Iraqi bentonite fig.(4), showed a band at 3545.16 cm^{-1} corresponding to O – H stretching free sharp band. Also two bands at 1643.35 cm^{-1} and 1475 cm^{-1} corresponding to C – C aromatic stretching. Another band appears at 1311.59 cm^{-1} corresponding to C – O stretching of thymol. Out of plane bending C – H bands appears at 939.33 cm^{-1} .

Absorption spectrum

Fig.(5) shows the absorption spectrum of (25 mg/L) thymol against the reagent blank (distilled water), the maximum absorption wavelengths at 274nm.

Calibration graph

Employing the experimental conditions, linear calibration graph for thymol were obtained fig (6), which show that Beer's law obey in the concentration range of (5-50 mg/L), The regression equations, correlation coefficients, molar absorptivities, and sandell sensitivities in addition to other parameters are given in table (2).

Effect of time of adsorption(contact time)

In order to establish the equilibrium time for adsorption, the effect of contact time was studied table (3) shows the results for the effect of contact time on the removal of thymol from aqueous solution at an initial concentration of 25 mg/l. about 52.040 % of thymol had been removed within the first fifteen minutes of adsorption and 67.876% within thirty minutes of adsorption.

This is as a result, the adsorption capacity generally increases with the increase in contact time until reaches the equilibrium time of adsorption at 45 minutes with 77.072% had been removed.

Effect of pH

The pH of the thymol solution will effect on the ability of adsorption, increases the pH of (25mg/ L) thymol solution from 2.5 to 5.5 leads to increase 3.5% of the % adsorbate removal, until when reaches to pH 10.8 leads to increase 4.1% of the % adsorbate removal, dissociation of thymol into (C₁₀H₁₃O⁻) will be repressed at pH > pKa[18]; (pKa value of thymol is 10.59 ± 0.10) [21], resulting in higher repulsion between the positive surface charge of the adsorbate and the anion.

Effect of initial concentration

The influences of thymol concentration on the adsorption activity are illustrated, This means that an increase in initial adsorbate concentration resulted in increasing of solute uptake fig.(7).

The initial solute concentrations provide an important driving force to overcome all mass transfer resistance of adsorbate between aqueous and solid phase, the higher initial solute concentration will decrease the mass transfer resistance. Hence, higher initial concentration of adsorbate enhances adsorption process with the result of higher interaction between solute and the adsorbent[22,23].

Adsorption isotherm

The equilibrium adsorption isotherm is important in the design of adsorption systems. Because it's useful to describe how solutes interact with adsorbents and very important to evaluate the feasibility of the adsorbate-adsorbent system. The set of experimental results as

presented in (Figure 8) at room temperature (25 ± 0.1) was fitted with the Freundlich and Langmuir model. Adsorption isotherms were obtained and the adsorptive capacity interpreted using both models.

Freundlich isotherm

The Freundlich expression [23] is an empirical equation describing sorption onto heterogeneous surface. The isotherm assumes that the surface sites of the adsorbent have a spectrum of different binding energies. The linear equation is presented as:

$$\log q_e = \log k_F + 1/n \log C_0$$

where K_F is The Freundlich constant (L/g) and $1/n$ is the adsorption intensity. The value of n indicates the favorable adsorption ability. , the values of $\log K_F$ and $1/n$ can be calculated from the intercept and the slope of the linear plot of $\log q_e$ versus $\log C_e$ fig.(9).

Langmuir isotherm

The Langmuir model [24] is widely used for modeling equilibrium data. The isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. It can be described by the linear form:

$$1/q_e = 1/q_{\max} + 1/q_{\max} K_L \cdot 1/C_e$$

where q_{\max} is the adsorption capacity at saturation (mg/g) and K_L (L/mg) is the adsorption coefficient related to energy of adsorption, the values of q_{\max} and K_L can be evaluated from the intercept and the slope of the linear plot of experimental data of $1/q_e$ versus $1/C_e$ fig.(10).

The Langmuir isotherm can also be expressed by a separation factor [25], which is given by the equation .

$$R_L = 1 / (1 + K_L \cdot C_0)$$

Where, ' C_0 ' is the initial concentration of thymol in mg/L and ' K_L ' is the Langmuir constant in g/L. The separation factor ' R_L ' indicates the nature of the adsorption process[26] as given in (Table 4).

The results reveal that the adsorption of thymol was best fitting with Langmuir model rather than Freundlich table(5), as indicated by higher R^2 values, the low value of the Freundlich constant ($k_F = 0.001$ L/g), which indicates the effectiveness of the thymol- Na – montmorillonite clay system and the value of adsorption intensity, ' n ' is found to be 0.633 did not satisfy the condition of heterogeneity, i.e., $1 < n < 10$ as well as $0 < 1/n < 1$ [27]. While the higher magnitude of ' q_{\max} ' (0.170 mg/g) for Langmuir mode indicates that the amount of thymol per unit weight of sorbent (to form a complete monolayer on the surface) seems to be significantly higher, also a relatively lower ' K_L ' value (0.018 L/mg) implies low surface energy ($K_L < 0.3$), thus indicating a probable stronger bonding between thymol and sorbents [28].

Adsorption kinetics

Kinetic models are used to examine the rate of the adsorption process in the present work, the kinetic data obtained from the studies have been analyzed by using pseudo-first-order and pseudo-second-order models.

The pseudo first order equation of Lagergren is generally expressed as follows[29].

$$dq/dt = k_1(q_e - q_t)$$

where q_e is the amount of thymol adsorbed at equilibrium (mg/g), q_t is the amount of thymol adsorbed at time t (min^{-1}), and k_1 is the rate constant of pseudo-first-order adsorption. If it supposed that $q=0$ at $t=0$, then:

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

The pseudo-second-order kinetic rate equation is expressed as follows [30].

$$dq_t/dt = k_2(q_e - q_t)^2$$

Where k_2 is the rate constant of pseudo-second-order sorption (g/mg/min). The integrated form of equation when ($t=0 \rightarrow t$ and $q_t=0 \rightarrow 0q_e$) the following expression is obtained:

$$t/q_t = 1/k_2 q_e^2 + t/q_e$$

The rate constant k_1 , k_2 and q_e calculated from the slopes and intercepts of the linear plot of $\ln(q_e - q_t)$ or (t/q_t) against t respectively fig(11 and 12). It is seen that thymol removal well described by the pseudo second order reaction kinetic. Moreover, the correlation coefficient (R^2), of pseudo-second-order reaction kinetic(0.991) is higher than that of the pseudo-first-order reaction kinetic(0.989) and greater value of rate constant for the adsorption data. While the value of q_e experimental is approximately equal q_e calculated for the both first and second order reaction kinetic; Table(6) shows the rate constants, q_e (experimental, calculated) and correlation coefficient (R^2) for pseudo first and second order reaction kinetic.

Analysis of Thymol

The concentration of residual thymol (after adsorption) was determined spectrophotometrically according to the standard methods, at 274nm.

Accuracy and precision

The accuracies of the proposed methods were confirmed by analyzing three replicate analyses of four different amounts of thymol; within Beer's law (before and after adsorption) by calculating the relative error percentage. The results indicated good accuracies of the method. The precision was determined by calculating the percentage relative standard deviation (RSD %) for three determinations at each of the studied concentration level tables (7 and 8).

Conclusion

In this study, the adsorption of thymol from aqueous solution was investigated using granulated surfactant initiation modified bentonite. The results indicated that adsorption capacity of the adsorbent was considerably affected by contact time, initial pH, and initial thymol concentration. The results indicated that the uptake of thymol took place at a pH in the range of (2.5-10.8); the adsorption of thymol increased with increase of pH. The result also showed that the amount of thymol adsorbed increased the increase of initial thymol concentration. The results reveal that the adsorption of thymol obeys Langmuir adsorption isotherms.

The pseudo-first and second-order kinetic models were used to analyze the data obtained for thymol adsorption from aqueous solution. The result indicated that the pseudo-second-order equation provided the better correlation coefficient (R^2) and the greater value of rate constant for the adsorption data.

References

- Nielson, A. H.; Allard, A. S.; Hynning P. A. and Rememberger, M. (1991) Distribution, fate persistence of organochlorine compounds formed during production of bleached pulp, *J. of Toxicol. Environ. Chem.*, **30**: 3-41.
- Cristina, M. S.; Zoraida, S. F.; Esther, M. T. P. and José, J. S. R. (2009) Review-Methodologies for the Extraction of Phenolic Compounds from Environmental Samples: New Approaches, *J. of Molecules* , **14**: 298-320.
- Chandra, S. M.; Krishna, K. S. and Vivek, K. G. (2010) Synthesis and Inevetro Antibacterial Activity of Thymol and Carvacrol Derivatives, *J. of Acta Poloniae Pharmaceutica*, **67** (4): 375-380.
- Jeff, D. E. and Scott ,A. Ma. (2000) Effects of Thymol on Ruminant Microorganisms, *J. of Current Microbiology* , **41**: 336–340.
- Al-Malki, A. L. (2010) Antioxidant Properties of Thymol And Butylated Hydroxytoluene in Carbon tetrachloride – Induced Mice Liver Injury, *J. of KAU: Sci.*, **22** (1): 239-248.
- Juven, B.J. ; Kanner, J. ; Schved F. and Weisslowicz, H. (1994) Factors that interact with the antibacterial action of thyme essential oil and its active constituents, *J. of Appl. Bacteriol* **76**: 626-663.
- Lis-Balchin ,M. and Deans, S. G. (1997) Bioactivity of selected plant essential oils against *Listeria monocytogenes*, *J. of Appl. Microbiol*, **82**: 759–762.
- Pilar, V. ; Mar'ia, J. S. and Manuel, H. C. (2006) Liquid chromatographic determination of phenol, thymol and carvacrol in honey using fluorimetric detection, *J. of Talanta*, **69**: 1063–1067.
- Nadja, B.W. ; Till, K. D. M. and Oliver, Z. (2005) determination of natural products using new methods of NMR spectroscopy, *J. of Chemistry & Biodiversity*, **2**(2): 147-177.
- Jayant, K. V. and Anil, V. (2006) Rapid HPTLC method for identification and quantification of curcumin, piperine and thymol in an ayurvedic formulation, *J. of Planar Chromatography*, **19** (111): 398-400.
- Zhao, H.T. and Vance, G.F.(1998) Sorption of trichloroethylene by organo-clays in the presence of humic substances, *J. of Water Res.* **32**: 3710-3716.
- Brindley,G.W. and Brown, G.(2010) Crystal Structures of Clay Minerals and their Xray Identification, Mineralogical Society, London, edited by [IdentifierBot](#) 31-July Last edited:1-495.
- van Olphen, H.(1977)An Introduction to Clay Colloid Chemistry: For Clay Technologists, Geologies', 2nd edition, Wiley Interscience, New York.316-318
- Zadaka, D.; Mishael, Y.; Polubesova, T.; Serban, C. and Nir, S. (2007) Modified silicates and porous glass as adsorbent for removal of organic pollutants from water and comparison with activated carbons, *J. of Applied Clay Science*, **36** (1-3): 174–181.
- Abate, G. and Masini, J. C. (2005). Sorption of atrazine, propazine, deethylatrazine, deisopropylatrazine and hydroxylatrazine onto organovermiculite, *J.of the Brazilian Chemical Society* , **16** (5): 936–943.
- [Sandro, F.](#); [Raquel, F M.](#); [Willian, F.](#) and [Marcelo, R. E.](#)(2009) Water Remediation by Adsorption of Phenol onto Hydrophobic Modified Clay, *J. of [Water, Air, & Soil Pollution](#) . 199 (1-4)*,):107-113.p

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17. Hassan, M.S. ; Abdel-Khalek, N.A. (1998) Beneficiation and applications of an Egyptian bentonite, *J. of Applied Clay Science* 13(2): 99-115.
18. Uday, F. A.; Abduljabar, A. M. and Ammar, H. Al. (2009) The removal of phenol from aqueous solutions by adsorption using surfactant-modified bentonite and kaolinite, *J. of Hazardous Materials*, 169 (1-3): 324-332.
19. Zlem, C. and Demet, B. (2000) Adsorption of Some Textile Dyes by Hexa decyltrimethylammonium Bentonite, *J. of Turk Chem*, 25: 193-200.
20. Russell, J.D. and Fraser, A.R. (1994) Clay Mineralogy-Spectroscopic and chemical determinative methods (Wilson M.J. editor) Chapman and Hall, London. Chapter two(Infrared methods)11-67.
21. Budavari, S. (2001) "The Merck index", New Jersey, Merck Company, Inc..
22. Hawaiah, I. M.; Bassim, H. H. and Abdul Latif, A.(1996) adsorption equilibrium of phenols from aqueous Solution using modified clay, *J. of Jurutera Kimia Malaysia*, 3:85 – 96.
23. Uddin, M. T.; Islam, M. S. and Abedin, M. Z. (2007) Adsorption of phenol from aqueous solutions by water hyacinth , *J. of Engineering and Applied Sciences (ARPN)*. 2 (2):11-17.
24. Mahvi, A. H.; Maleki, A. and Eslami, A. (2004) Potential of Rice Husk and Rice Husk Ash for Phenol Removal in Aqueous Systems *J. of American Applied Sciences*, 1(4): 321-326.
25. Juang, R.S.; Wu, F.C.; Tseng, R.L.(1997) Ability of activated clay for the adsorption of dyes from aqueous solutions.*J. of Environ. Technol.*18:525-535.
26. Srihari, V.; Das, A. (2009) Adsorption of phenol from aqueous media by an agro-waste (*Hemidesmus indicus*) based activated carbon. *J. of Applied Ecology and Environmental Research*. 7(1): 13-23.
27. Khalid, N., Ahmad, S. and Toheed, (2000): A Potential of Rice Husk for Antimony Removal. *J. of Applied Radiation and Isotopes* 52:30-38.
28. Aksu, Z. and Yener, J. (2001) A comparative adsorption/biosorption study of monochlorinated phenols onto various sorbent. – *Waste management* 21 (8): 695-702.
29. Lagergren, S. (1998) Zur theorie der sogenannten adsorption gelöster stoffe, *Kungliga Svenska Vetenskapsakademiens. J. of Handlingar*, 24:1-13.
30. Ho, Y.S. and McKay, G. (1999) Pseudo-second-order model for sorption process. *J. of Process Biochem.* 34 (5): 451-465.

Table (1): Chemical analysis West Iraqi (Traifawi) bentonite.

Iraqi (Traifawi) bentonite	Compound (wt, %)
55.81	SiO ₂
14.91	Al ₂ O ₃
5.78	Fe ₂ O ₃
5.72	CaO
3.5	MgO
1.29	Na ₂ O
0.41	K ₂ O
0.67	LiO ₂
----	SO ₃
10.86	L.I.O.
98.95	Total

Table (2): Spectral characteristics and statistical data of the regression equations for determination of thymol.

Thymol	Parameter
274nm	λ_{\max} (nm)
colorless	Color
5-50	Linearity range (mg/L)
1922.816	Molar absorptivities (l.mol ⁻¹ .cm ⁻¹)
A = 0.0128 [Thymol(mg/L)] + 0.0245	Regression equation
0.0128	Calibration Sensitivity
78.125	Sandell's Sensitivity ($\mu\text{g.cm}^{-2}$)
0.9983	Correlation of Linearity (R ²)
0.9991	Correlation coefficient (R)

Table (3): Effect of contact time on the adsorption of (25mg/L) thymol from aqueous solution.

Equilibrium Time (minute)	q_e (mg/g)	% Removal	Equilibrium Conc. (C_e) (mg/L)	Time (minute)	Initial Conc. (mg/L)
45	0.0088	35.376	16.156	5	25.000
	0.0112	44.808	13.798	10	
	0.0130	52.040	11.990	15	
	0.0146	58.296	10.426	20	
	0.0169	67.876	8.031	30	
	0.0186	74.484	6.379	40	
	0.0193	77.072	5.714	45	
	0.0193	77.072	5.714	60	
	0.0193	77.072	5.714	75	
	0.0193	77.072	5.714	90	
	0.0193	77.072	5.714	120	

Table(4): The process nature of separation factor.

Type of process	R_L Value	S.No.
Unfavorable	$R_L > 1$	1
Linear	$R_L = 1$	2
Favorable	$0 < R_L < 1$	3
Irreversible	$R_L = 0$	4

Table(5): Freundlich and Langmuir isotherm parameters for the adsorption of thymol at $(25 \pm 0.1)^\circ\text{C}$ under optimum conditions.

Langmuir isotherm parameters				Freundlich isotherm parameters		
R_L^*	R^2	K_L (L/mg)	q_{\max} (mg/g)	R^2	n	K_F (L/g)
0.526-0.917	0.990	0.018	0.170	0.988	0.633	0.001

* for (5-50 mg/L) initial concentration of thymol.

Table(6): The pseudo- first and second- kinetic order parameters for the adsorption of 25 (mg/L) of thymol at (25±0.1) °C under optimum conditions.

The pseudo-second-order kinetic models			The pseudo-first-order kinetic models			q _e Expe. (mg/g)
R ²	K ₂ (g/mg/min)	q _e cal. (mg/g)	R ²	K ₁ (min ⁻¹)	q _e cal. (mg/g)	
0.992	4.167	0.023	0.989	0.069	0.016	0.0193

Table (7): Evaluation of accuracies and precisions for thymol before adsorption.

R.S.D.* %	Relative Error* %	Concentration ((mg/L)	
		Found* Before Adsoption	Taken
1.212	1.030	9.897	10
1.158	0.900	24.775	25
1.371	1.070	39.572	40
2.816	2.244	48.878	50

*Average of three determinations.

Table (8): Evaluation of accuracies and precisions for thymol after adsorption at optimum conditions.

R.S.D.* %	Relative Error* %	% Removal	Concentration (mg/L)	
			Found(C ₀)* After Adsoption	Taken
1.701	1.427	69.860	3.014	10
1.663	1.383	77.144	5.714	25
1.874	1.522	78.822	8.471	40
2.987	2.721	80.072	9.964	50

*Average of three determinations.

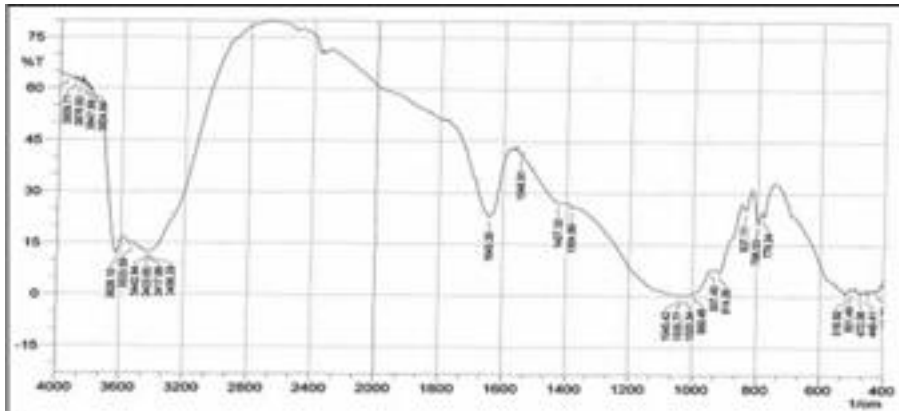


Fig. (1): FTIR spectrum for crude Iraqi bentonite (Trifawi).

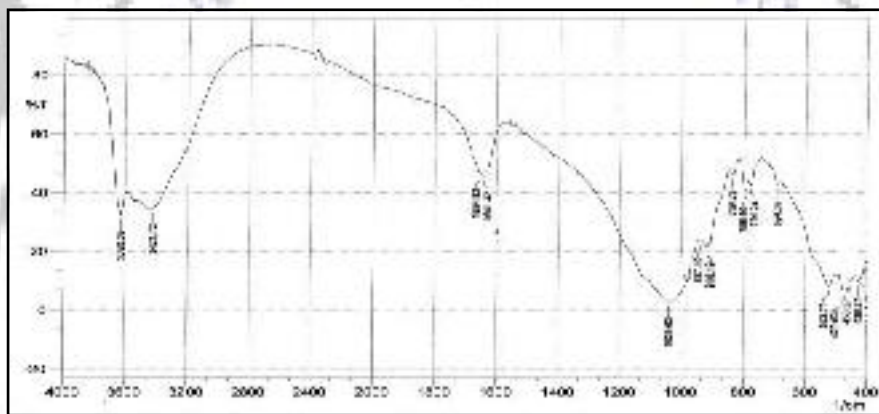


Fig. (2): FTIR spectrum for initiated Iraqi bentonite (Trifawi).

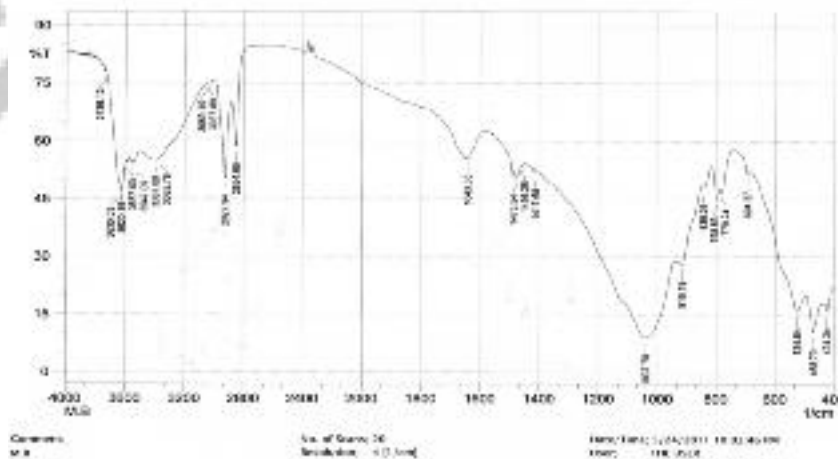


Fig. (3): FTIR spectrum for initiated modified Iraqi bentonite (Trifawi).

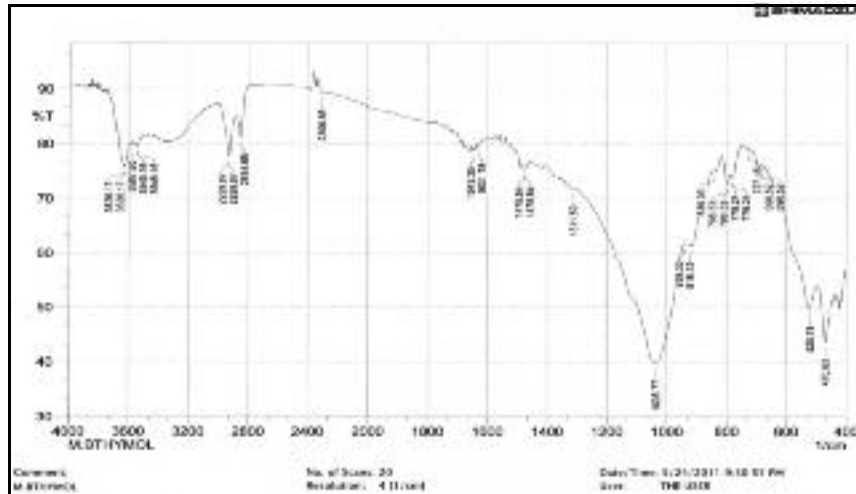


Fig. (4): FTIR spectrum for thymol adsorbed on initiated modified Iraqi bentonite.

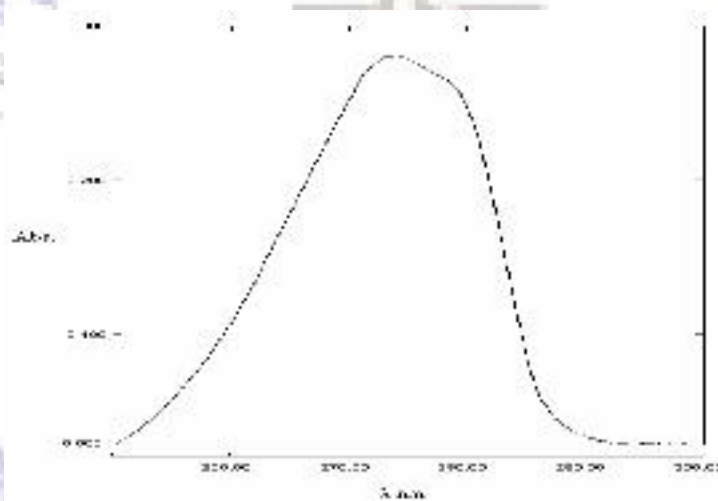


Fig. (5): Absorption spectrum of (25mg/L) thymol, against reagent blank (distal water).

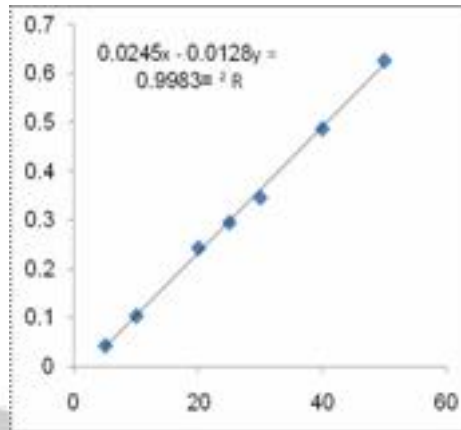


Fig. (6): Calibration curve for thymol against reagent blank (distilled water) at 274nm.

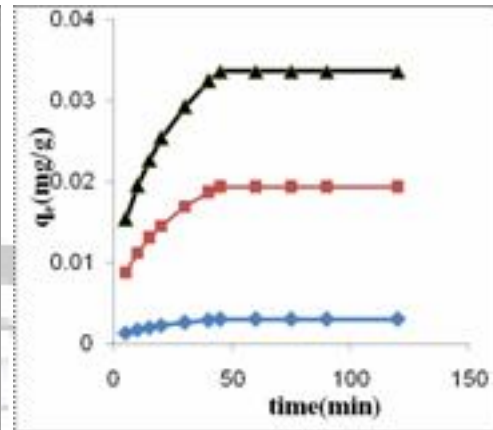


Fig.(7): Effect of initial concentration onto adsorption of (10, 25 and 40)mg/L of thymol solution

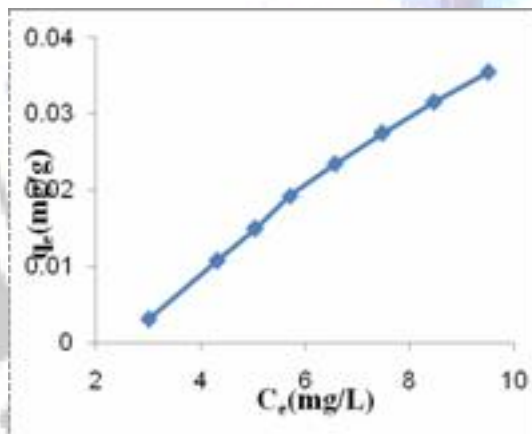


Fig.(8): Adsorption isotherm for thymol at (25±0.1) °C under optimum conditions.

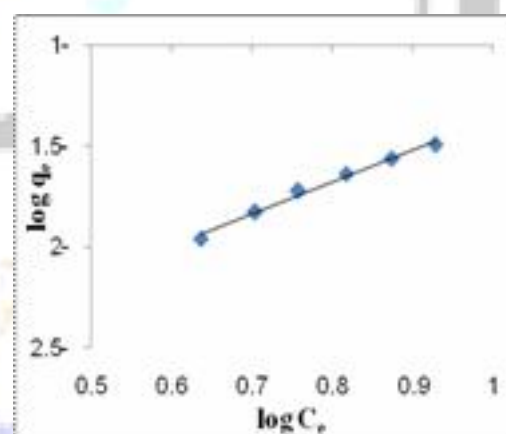


Fig.(9): Freundlich isotherm for the adsorption of thymol at (25±0.1) °C under optimum conditions.

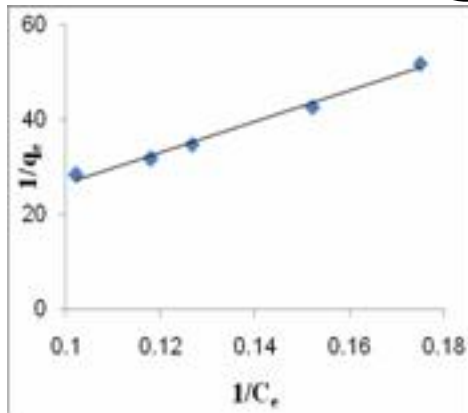


Fig.(10): Langmuir isotherm for the adsorption of thymol at $(25\pm 0.1)^\circ\text{C}$ under optimum conditions.

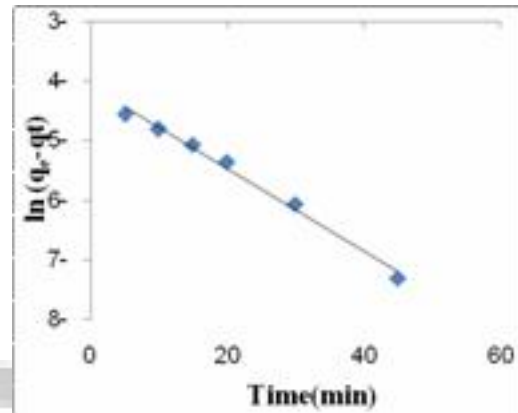


Fig.(11): The pseudo-first-order kinetic models for the adsorption of 25(mg/L) thymol at $(25\pm 2)^\circ\text{C}$ under optimum conditions.

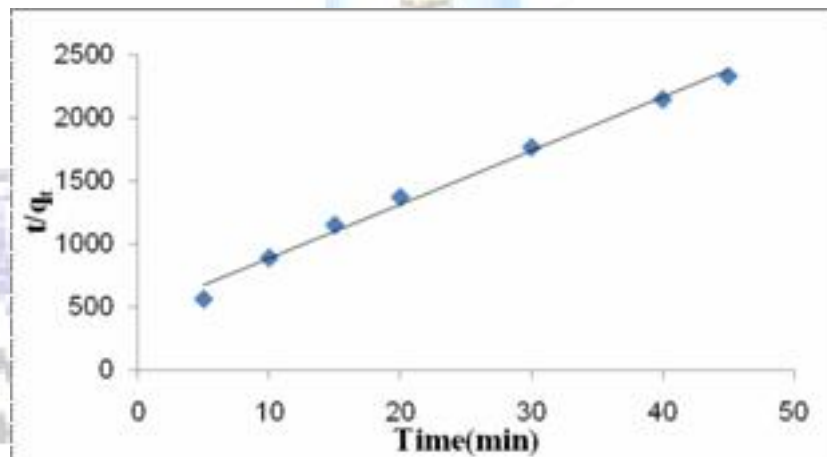


Fig.(12): The pseudo-second-order kinetic models for the adsorption of 25 (mg/L) of thymol at $(25\pm 0.1)^\circ\text{C}$ under optimum conditions.

امتزازالثايمول من محلوله المائي بأستعمال طين البنتونايت المنشط والمحورعضوياً بطريقة العمود المعبأ

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الخلاصة

اجريت دراسة لأمتزاز الثايمول من محلوله المائي بدرجة حرارة الغرفة، بأستعمال طين البنتونايت العراقي المنشط على هيئة المونتموريلونايت والمحور عضوياً، اذ استعملت طريقة العمود في عملية الامتزاز. شخص البنتونايت المنشط والمحور بأستخدام طيف الاشعة تحت الحمراء، قبل امتزاز الثايمول وبعده كما تم الحصول على منحني تدريجي خطي لمحلول الثايمول وبمطابقة لقانون لامبرت بير لمدى من التراكيز يتراوح بين (5-50) ملي غرام/ لتر، وعند الطول الموجي 274 نانو متر، ضد محلول الخلب. درست المتغيرات المؤثرة في عملية الامتزاز، اذ وجد ان الزمن اللازم لحصول عملية الاتزان هو 45 دقيقة، وبسرعة جريان 4 قطرات لكل دقيقة. ولوحظ زيادة في امتزاز المحلول بزيادة الدالة الحامضية (pH)، وازيادة التركيز الابتدائي للمادة الممتزة. كما وجد ان طبيعةعملية الامتزاز نوسكل فيزيائي في الاغلب، وينطبق عليها ايزوثيرم لانكماير للامزاز. وأظهرت النتائج ان عملية الأمتزاز تتبع تماماً حركية المرتبة الثانية الكاذبة.

الكلمات المفتاحية: امتزاز، ثايمول، صوديوم-مونتموريلونايت، طين، طريقةالعمود

