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Adsorption of Anionic Dye from Equeous Solution by Modified Synthetic Zeolite

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Abstract

The adsorption of Congo red (CR) dye on modified synthetic zeolite 5A , the general name of which is Linde Type A (LTA)which is modified by amino mercepto thiadiazole (AMT) and have been characterized by using fourier transform infrared (FT-IR) , x-ray diffraction (XRD) spectroscopies, atomic force microscopy (AFM) and scanning electron microscope (SEM) analysis. In this work Modified zeolite was utilized as adsorbent to remove (CR) dye from aqueous solution by adsorption. Batch experiments were conducted to study the effects contact time , initial concentration of adsorbate and temperature on dye adsorption. The equilibrium adsorption data were analyzed by using several isotherm models (Freundlich , Langmuir , temkin , Dubinin-Radushkevitch and Redlich–Peterson)models. The best results were achieved with the Redlich–Peterson isotherm equilibrium model. The equilibrium adsorption capacity (q_e) increases with the increase of the initial concentration of dye. The values of qe were found to be decreased with the increase of solution temperatures. The thermodynamic parameters ΔG° , ΔH° and ΔS° have been calculated.

Key words: Adsorption, (LTA) zeolites, Congo red, several isotherm models, thermodynamic parameters .

Introduction

Synthetic dyes and pigments are extensively used for dyeing and printing in industry over 7×10^5 tons and approximately 10000 dyes are produced annually worldwide, Azo dyes (N= N group) are the largest class of synthetic dyes with the greatest variety of colours approximately 10-15 % of the dyes are released into the environment during dyeing of different substrates, such as synthetic and natural textile fibres, plastics, leather, paper, ineral oils, waxes, and even foodstuffs and cosmetics[1,2], In addition, many dyes are toxic to some organisms causing direct destruction of aquatic communities. Some dyes can cause allergic dermatitis, skin irritation, cancer and mutation in man[3].

(CR) dye is an anionic dye, very stable in aqueous medium. It is moderately resistant to light and oxidation agents, thus, it is very difficult to be biodegraded. Congo red contains an azo (-N=N-) chromophore and an acidic auxochrome (-SO₃H) associated with the benzene structure figure (1) [4,5]. (CR) is also called acidic diazo dye, (CR) dye is a benzidine-based, direct, anionic diazo dye. Its molecular structure and physicochemical characteristics are presented in Table (1). Congo red is the first synthetic azo dye produced that is capable of dying cotton directly. Congo red containing effluents are generated from a number of industrial activities: textiles, printing and dyeing, paper, rubber, plastics industries [6,7].

There are common methods of textile wastewater treatment including: adsorption [8], biosorption [9] coagulation/flocculation [10], to remove dyes from aqueous solution. The use of natural materials as clays and siliceous materials for waste water treatment is increasing because of their high abundance, availability and low cost. The removal of dyes and organics in an economic way, however, remains an important problem although a number of systems have been developed with adsorption technique. Adsorption is a very effective separation technique and now it is considered to be superior to other techniques for water treatment in terms of initial cost, simplicity of design, high abundance, availability, ease of operation and insensitiveness to toxic substances [11,12].

Also, dyes can be effectively removed by an adsorption process in which dissolved dye compounds attach themselves to the surface of adsorbents. Various adsorbents such as: activated carbon [13]; bentonite [14] polymers [15], zeolite [16], etc. have been widely studied for dye removal from aqueous solution.

Zeolites are hydrated microcrystaline aluminosilicates containing exchangeable cations of alkaline metals and of alkaline earth metals. They are made up of three-dimensional cage-like frameworks of silica (SiO_4^{-4}) and alumina (AlO_5^{-4}) molecules linked together through oxygen atoms, the number of water molecules contained in the zeolite, which have the number of (SiO_4^{-4}) and (AlO_5^{-4}) tetrahedrons contained in a basic cell. The tetrahedron units form cavities of various size, total volume of which is usually 20 - 50%. The effective size of channels and cavities is 0.3 - 0.7 nm. The most important properties of zeolites are as follows:

• Vigorous and partially selective cation exchange properties.

• Adsorption ability of different capacities for a number of compounds (including metal-ions, vapors and gases).

• High chemical-, temperature- and radiation stability.

• Low density and large void volume of dehydrated samples.

• Specific physical and catalytic properties.

Modification of clay minerals and zeolites with organic cations - surfactants is undergoing the extensive study because of their potential use as environmental sorbents. Zeolite minerals have surface chemistry similar to clays, but display superior hydraulic properties [17], The present study undertaken to evaluate the efficiency of a zeolite modified for the removal of dye in aqueous solution. In order to design adsorption treatment systems, knowledge the applicability of masstransfer isotherm models for the adsorption of congo red dye onto modified zeolite was reported.

Merialsats and Instrumental Materials

The Synthetic Zeolite 5A with chemical formula ($Ca.Na.Al_3Si_3O_{12}$) used in the present work was supplied from Petroleum Research & Development Center) of Ministry of Oil of Iraq with the chemical formula of and chemically characterized in the state company of Geological Survey and Mining-Ministry of Industry using x-ray florescence spectra. Table (2) shows the composition of this Zeolite 5A.

1-Chemicals

Ethanol(BDH), Thiosemicarbazide (Fluka), lead nitrate (BDH), anhydrous sodium carbonate(BDH), carbon disulphide (Merck), congo red (BDH)

2-Methods

2-1 Preparation of 2- amino -5 - mercapto-1,3,4-thiadiazole (AMT)[18].

A mixture of (2g, 0.02 mol.) of thiosemicarbazide and (2.33g, 0.02mol.) of anhydrous sodium carbonate were dissolved in 25 ml. abs. ethanol . To this solution (3.2g, 0.04 mol.) of carbon disulphide was added. The resulting mixture was heated under reflux for 10 hrs. The reaction mixture was then allowed to cool down at room temperation. Most of solvent was removed under reduced pressure and the residue was dissolved in 20 ml of distilled water, carefully acidified with cold con. Hydrochloric acid to give pale yellow precipitate . The crude product was filtered and washed with cold water , recrystallized from hot water to give the desired product as yellow needles , yield (75%), m.p (230-232)C^o.

2-2-Preparation of Modified Zeolite by Lead amino,merchapto-thiadiazole (PbAMT) complex

The sieved zeolite (10 g) suspended in aqueous solution(200 ml) then added (5ml) of lead nitrate (0.06 M) to suspension solution of zeolite with continues stirring (Centrifuge tubes. Hettich (EBA-20) for half hr .The zeolite was separated from the mixture by decantation, washed about seven times with distilled water, and dried in an oven at a temperature of 60 C^o for 2 hours. then the dry zeolite was added to (200 ml) of absolute ethanol with continuous stirring for 10 minute Then added a certain amount of AMT compound to suspension solution of zeolite + Pb with continuous stirring (QA9010X - Hot Plate Stirrer, Ceramic Surface) for half hr The zeolite +Pb(AMT)₂ complex was separated from the mixture by filteration, and dried in an oven (Daihan Labtech Oven LDO - 060E) at a temperature of 60 C^o for 2 hours.

2-3-Adsorption Procedure

Wavelength of maximum absorbancy (λ_{max}) was found 498 nm for congo red by using (Uv-Visible spectrophotometer double beam (shimadzu UV-1800)). This value were utilized for estimation of quantity of C-R dye adsorbed .Adsorption studies were performed by the batch technique (spectrophotometer single beam (CECIL,CE1011) to obtain equilibrium data. Batch adsorption studies were performed at different temperatures, dyes initial concentrations with known weight of adsorbent modified zeolite (0.1 g) to obtain equilibrium isotherms. For isotherm studies, a series of 50 mL conical flasks were employed. Each conical flask was filled 10 mL of congo red dye solution of varying concentrations (10,15,20,25,30,40,50 ppm) at pH 7 and uniform particle size ($\leq 150 \ \mu$ m) The contents were shaken(Labtech shaking water bath) by using shaker with a speed of (120 rmp) After equilibrium, the solution was allowed to settle for 10-15 min, and separated by centrifuged (Centrifuge tubes. Hettich (EBA-20) and volumes of 3ml supernatant were taken for spectro -photometrically measurements of dye content. The quantity of dye adsorbed can be calculated by using the following equation [19]:

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m: weight of adsorbent (g). C₀: initial concentration (mg/l). C_e: equilibrium concentration (mg/l). V : volume of solution (L). The percentage adsorption of dye on d modified zeolite was calculated using the equation :

Adsorption % =
$$\frac{(C_\circ - C_e)}{C_\circ} \times 100$$
 ------ (2)

The effect of contact time on the removal of dye by the adsorbent in a single cycle was determined by keeping particle size, initial concentration, dosage, pH and concentration of other ions as constant.

Results and Discussion

Characterization of Zeolite and Modified Zeolite

Figure(3 - zeolite) XRD pattern (XRD-6000shimadzu) of LTA zeolite before modified showed high purity and a good crystallinity of zeolite. These results are in good agreement with those reported in the literature [20]. Figure (3 -zpb (AMT)2) XRD pattern of LTA zeolite after modified shows that there are no changes in the positions of the diffraction peaks of zeolite after loading of pb (AMT)₂cluster into the framework voids (figure 3 - ZpbAMT). This means that loading of pb (AMT)₂cluster into the framework voids of zeolite A does not distort the zeolite framework. The change in the relative intensities of peaks is caused by higher stress by pb (AMT)₂ cluster on the zeolite framework atoms (Al, Si, O) and compensating sodium and calcium ions [21].

Figure (4-zeolite) FTI R spectra (iraffinity-1 FTIR spectro-photometer (shimadzu 8400 s) of LTA zeolite is shown in Figure 1. The bands at 450 to 1200 cm⁻¹ are known to assignable to Si-O-Al, Si-O-Si, Si-O, Si-Al and T-O species [22]. The peaks at 403.cm⁻¹ are assigned to the structure insensitive internal (TO₄) tetrahedral bending peaks of zeolite A in literature. Peaks 1633 cm⁻¹ and 3033 cm⁻¹ are assigned to the external linkage asymmetrical stretching and internal tetrahedral symmetrical stretching respectively. In the other hand, the broad bands at 3350 to 3700 cm⁻¹ are attributed to Si-OH, Si-OH-Al and -OH hydroxyl groups. The band at 668 cm⁻¹ is known to assignable to Si-O-M where M is the exchangeable Na⁺ ion metal species. The absorption band at 672 cm⁻¹ in LTA is visible which is in corporate with Na atoms in the zeolite framework [20]. Figure (4- zeolite- pb (AMT)₂) FTI R spectra of LTA zeolite modified by pb (AMT)₂ is in agreement with XRD results by changing in the relative intensities of peaks.

The AFM images (SPMAA3000Atomic force microscope-USA 2008) (in two and three-dimensional) and granularity distribution charts for the synthetic zeolite and Pb(AMT)2-Zeolite in Figure (5). it shows that the diameter of the particles for zeolite (0.58 nm) and for $Pb(AMT)_2$ – zeolite (13.35 nm), the average particle size for zeolite was (95.13 nm) and for the Pb(AMT)₂ - zeolite (77.33 nm). This result indicates that average particle size for Pb(AMT)₂ - zeolite more than zeolite.Figure (6-zeolite) shows the SEM image (SEM-- T-Scan ,Vega-111,Czech) of zeolite and Pb(AMT)₂ - zeolite particles with magnification of 25000, Scanning electronic micrographs show uniform morphology and cubic shape of particles for LTA zeolite. The average diameter of the particle observed from SEM analysis is smaller than 1 µm, Figure (6-zeolite-Pb(AMT)₂) shows the changes on the surface of the AMT - zeolite up to 300 nm and this indicates on pb(AMT)₂ cluster from pores to zeolite surface.

Adsorption Batch

Effect of Contact Time

The experimental results of adsorptions of at various concentrations (10, 20, 30,40, 50 and 60 mg/L) with contact time are shown in figure (7). which showed the adsorption rates of congo red dye onto zeolite -Pb(AMT) observed to be very fast within the first few minutes and gradually decrease and become almost constant after a period of 30 min ,percent adsorption of (CR) dye increased with increase in time, become almost constant after a period of 30 min. It means that amount of dye reached to saturation, suggesting the possible monolayer coverage of the dye on the modified zeolite surface [23].

Effect of Initial Concentration

The quantities adsorbed (q_e) were plotted versus equilibrium concentration (C_e) to obtain the general case of the adsorption isotherms as shown in figure (8) which represents the isotherms of (CR) dye on the zeolite- pbAMT at different temperatures, and as shown the (CR) equilibrium isotherm for modified zeolite is a L-type isotherm. L-shaped adsorption isotherm indicates the adsorbed solute molecules are most likely being adsorbed in a flat geometry, which is based on the assumption of high adsorption affinity between the dye and the surface [24,25].

Quantity adsorption decreased with increase in initial dye concentration, but the actual amount of dye adsorbed per unit mass of modified zeolite increased with increase in dye concentration. It means that the adsorption is highly dependent on initial concentration of dye. It is because of that at lower concentration, the ratio of the initial number of dye molecules to the available surface area is low subsequently the fractional adsorption becomes independent of initial concentration. However, at high concentration the available sites of adsorption become fewer and hence the percentage removal of dye is dependent upon initial concentration [23,26].On the other hand we note decrease of quantity with increase of temperature of the modified zeolites and that was indicated of adsorption of (CR) dye on zeolite – PbAMT exothermic process [27].

Equilibrium Isotherm Modelling

Adsorption properties and equilibrium parameters, commonly known as adsorption isotherms, describe how the adsorbate interact with adsorbents and comprehensive understanding of the nature of interaction. Isotherm helps to provide information about the optimum use of adsorbents. In order to optimize the design of an adsorption system to remove dye from solutions, it is essential to establish the most appropriate correlation for the equilibrium curve. There are several isotherm equations available for analyzing experimental sorption equilibrium parameters.

The Freundlich Isotherm Model

The Freundlich equation is an empirical model that considers heterogeneous adsorptive energies on the adsorbent surface and the equation expressed as follows: The linear form of Freundlich isotherm [28] is:

$$\ln q e = \ln k_{F} + \frac{1}{n} \ln C e^{------(3)}$$

Where K_F is a constant, indicating the relative adsorption capacity of the adsorbent (l/g^{-1}) and n is a the heterogeneity factor, representing the intensity of adsorption, Plotting ln q_e versus ln(C_e) (Equation (3) figure (9-a) results in a straight line of slope 1/n and intercept ln (k_F).

The Langmuir Isotherm Model

Langmuir model is the most widely used isotherm equation, which has the linear form as follows [29,30]

$$\frac{C_{e}}{q_{e}} = \frac{1}{a_{L}k_{L}} + \frac{C_{e}}{a_{L}} - \dots - (4)$$

where a_L and K_L are Langmuir isotherm parameters, representing the maximum uptake capacity per unit mass of adsorbent (mg/g), and the Langmuir constant (l/mg) respectively. Plotting C_e /q_e versus C_e (Equation (4))figure (9-b) results in a straight line of slope 1/a_L and intercept 1/a_L k_L .

The Temkin Isotherm Model

The Temkin isotherm model assumes that the adsorption heat of all molecules decreases linearly with the increase in coverage of the adsorbent surface, and that adsorption is characterized by a uniform distribution of binding energies, up to a maximum binding energy. The Temkin isotherm can be described by Equation [31]:

$$q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e - \dots - (5)$$

where K_T is the equilibrium binding constant (L mol⁻¹) corresponding to the maximum binding energy, b_T is related to the adsorption heat, R is the universal gas constant (8.314 J K^{-1} mol⁻¹) and T is the temperature (K). Plotting q_e versus $ln(C_e)$ (Equation (5)) figure (9-c) results in a straight line of slope RT/b_T and intercept (RT ln K_T)/b.

The Dubinin and Radushkevich Isotherm Model

The experimental adsorption data were applied to The linear form of Dubinin and Radushkevich isotherm equation is expressed as follows [32]:

The constant B gives the mean free energy E of sorption per molecule of the sorbate when it is transferred to the surface of the solid from infinity in the solution and can be computed using the relationship:

$$E = \frac{1}{\sqrt{(2B)}}$$
 -----(7)

Plotting (\mathcal{E}^2) versus ln (q_e) (Equation (7) figure (9-d) results in a straight line of slope (β) and intercept(q_{max})

The Redlich-Peterson Isotherm Model

The experimental adsorption data were applied to the linear form of Redlich-Peterson isotherm equation is expressed as follows is [33]:

$$\frac{C_{e}}{q_{e}} = \frac{1}{K_{R}} + \frac{a_{R}}{K_{R}}C_{e}^{\beta} - \dots$$
(8)

Plotting(C_e/q_e) versus (C_e^{β}) (Equation (8) figure (9-e) results in a straight line of slope(a_R) and intercept(K_R) .constants of isotherms were previously recorded in Table (3)

Table(3) shows the values of the constants of the Freundlich isotherm at different temperature, for zeolite -PbAMT where (n > 5) for all temperatures indicates that the adsorption of (CR) dye on zeolite -PbAMT is more easily achieved than adsorption on zeolite and the value of K_f decreases with increase of temperature indicates that process is a favourable physical

adsorption ,the values of ($R^2 > 0.83$) for the Freundlich model was not higher for all the temperatures evaluated, and this indicated that model not fitted to experimental data for all the temperatures.

Table(3) shows the values of the constants of the Langmuir isotherm at different temperatures for zeolite -PbAMT the maximum adsorption capacity (a_L) of (CR) dye on zeolite decreased with an increase in temperatures , showing that (a_L) is enhanced at lower temperatures. on the other hand, the energy of adsorption(k_L) is enhanced at middle temperatures on zeolite -pbs surface, because it was oscillated with a increase in temperatures , the values of ($R^2 > 0.99$) for the Langmuir model was higher for all the temperatures evaluated, and this indicated that model fitted better to experimental data for all the temperatures [34].

Table(3) shows the values of the constants of the temkin isotherm at different temperatures for zeolite-PbAMT which have heat of adsorption b_T within(15-25) kJ.mol⁻¹, This means that the values of b_T zeolite -PbAMT smaller than zeolite and that indicates that zeolite - PbAMT favorable for the physical adsorption at all different temperatures, the values of ($R^2 > 0.83$) for the temkin model were not higher for all the temperatures evaluated, and this indicated that model not fitted to experimental data for some the temperatures.

Table(3) shows the values of the constants of the Dubinin and Radushkevich (D-R) isotherm at different temperatures for zeolite-PbAMT is not useful because they have values of ($R^2 = 0.58$ to 0.85) for all the temperatures, and this indicated that model is not fitted to experimental data for some the temperatures.

Table(3) shows the values of the constants of the Redlich-Peterson (R-P) isotherm at different temperatures for zeolite-PbAMT which have values of β (0.85-1.00) and this leaded to applying of experimental data under of the ideal Langmuir condition with the low concentration limit the Redlich-peterson isotherm exhibit extremely high(R² > 0.99) values indicating, superficially at least, that it produces a considerably better fit compared to the preceding two-parameter isotherms. This equation reduces to a linear isotherm at low surface coverage, to the Freundlich isotherm at high adsorbate concentration and to the Langmuir isotherm when $\beta = 1$ [35], according values of R² of the isotherm models for zeolite –pbAMT at all temperatures are as following order:-

(Big R^2) R-P > langmuir > freundlich > temkin > D-R (small R^2)

Thermodynamic Studies

The effect of temperature (at 288,298,308, 318 K) on the adsorption of congo red dye by modified zeolite was studied at 0.1 g adsorbent and initial dye concentrations (10,15, 20, 25,30,40,50 ppm) at pH 7 and uniform particle size ($\leq 150 \mu m$ for 30 minutes contact time.

Thermodynamic parameters including the change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were used to describe thermodynamic behavior of the congo red adsorption onto zeolite – pb(AMT)₂. The equilibrium constant (K_e) for the adsorption process at each temperature is calculated from division of the quantity of dye adsorbed on the zeolite and zeolite – pbs form the equation [36,37]:

$$K = \frac{Qe * 1000}{Ce} \quad ----- \quad (9)$$

Where (0.1g) represent the weight of the clay that has been used and (0.01 L) represents the volume of the dye solution used in the adsorption process, The change in free energy (ΔG°) could be determined from the equation [**38**]:-

Where R is the gas constant (8.314 J.mole⁻¹. K⁻¹) and T is the absolute temperature. The heat of adsorption (Δ H^o) may be obtained from the vant Hoff's equation:-

 $\ln K = \frac{-\Delta H^{\circ}}{RT} + cons \quad \tan t \quad -----(11)$

Where K is the equilibrium constant when C_e approaches to zero at certain temperature. Figure (10) is obtained from plotting (Ln K) of each concentration against corresponding Ce. Plotting (In K) versus (1/T) should produce a straight line with a slope =($-\Delta H^{\circ}/R$) from which the enthalpy (ΔH°) of the adsorption process is obtained .The change in entropy (ΔS°) was calculated from Gibbs equation:

 $\Delta G \circ = \Delta H \circ - T \Delta S \circ \quad -----(12)$

the equilibrium constant (K_e), free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were recorded in table (4)

From table (4) for zeolite- pbAMT the negative value of ΔG° confirms the feasibility of the process and the spontaneous nature the increase in ΔG° values with an increase temperature shows an increase in feasibility of adsorption at lower temperatures. The value of ΔH° was negative, indicating that the nature of the adsorption is exothermic. The positive ΔS° value suggests an increase in the randomness at sorbate - solution interface during the adsorption process.

References

1- Minussi, R. C; de Moraes, S. G; Pastore, G. M and Duran, N. (2001), Biodecolourization screening of synthetic dyes by four white rot fungi in solid medium. Possible role of siderophores. Letters of Applied Microbiology., **33** (1): 21-25.

2- Gharbani, P; Tabatabaii, S. M and Mehrizad, A. (2008). Removal of congo red from textile wastewater by ozonation. International Journal of Environmental Science and Technology., **5** (4): 495-500.

3- Vaidya, A.A. and Datye, K.V., , (1982) "Environmental Pollution During Chemical Processing of Synthetic Fibers", Colourate, 14, 3-10.

4- Vimonses, V. Lei, S. Jin .B; Chow ,C.W.K and Saint ,C. (2009) ,Kinetic study and equilibrium isotherm analysis of Congo Red adsorption by clay materials, Chem. Eng. J. **148(2-3):** 354–364.

5- Purkait, M.K; Maiti , A.; Gupta , S.D and De.S., (2007)Removal of congo red using activated carbon and its regeneration, , J. Hazard. Mater. **145** :287–295.

6- Sabnis, R.W. (2010), Handbook of Biological Dyes and Stains. Synthesis and Industrial Applications (John Wiley & Sons, New Jersey, Canada, Springer, pp. 106-107).

7- Chatterjee, S; Chatterjee, B.P and Guha ,A.K., (2007) ,Adsorptive removal of congo red, a carcinogenic textile dye by chitosan hydrobeads: Binding mechanism, equilibrium and kinetics, Colloid Surface A **299** (1–3) :146–152.

8-. Mahmoodi, N. M., (2011), Equilibrium, kinetics, and thermodynamics of dye removal using alginate in binary systems J. Chem. Eng. Data, **56**: 2802-2811.

9. Sivaramakrishna ,M. C.; L. and Varada Reddy, A., (2012) , The use of an agricultural waste material, Jujuba seeds for the removal of anionic dye (Congo Red) from aqueous medium. Somasekhara Reddy, J. Hazard. Mater, **118** :203-204.

10. Man, L. W.; Kumar, P.; Teng, T. T. and Wasewar, K. L., (2012). Design of experiments for Malachite Green dye removal from wastewater using thermolysis–coagulation–flocculation. Desalin. Water Treat., **40**:260-271.

11- Sen.K; Afroze, S. and Ang ,H.M., (2011) , Equilibrium, kinetics and mechanism of removal of methylene blue from aqueous solution by adsorption onto pine cone biomass of Pinus radiate, .,Water Air Soil Poll. **218** :499-515.

12- Abd EI-Latif, M.M; Ibrahim ,A.M and EI-Kady ,M.F., (2010) ,Adsorption equilibrium, kinetics and thermodynamics of methylene blue from aqueous solutions using biopolymer oak sawdust composite, J. Am. Sci. **6** (6) :267-283.

13- Khaled, A.; El Nemr, A.; El-Sikaily, A. and Abdelwahab, O., (2009).Removal of Direct N Blue-106 from artificial textile dye effluent using activated carbon from orange peel: adsorption isotherm and kinetic studies. J. Hazard. Mater., **165**, 100-110.

14- Bulut, E.; Özacar, M. and Şengil, İ. A., (2008). Adsorption of malachite green onto bentonite: Equilibrium and kinetic studies and process design. Micropor. Mesopor. Mat., 115: 234-246.

15- Kim, H. and Guiochon, G., (2005). Adsorption on molecularly imprinted polymers of structural analogues of a template. Single-component adsorption isotherm data. Anal. Chem., 77:6415-6425.

16- Mesko, V.; Markovska, L.; Minceva, M. and Burevski, D., (2001). Equilibrium isotherms for adsorption of basic dyes from aqueous solutions on different adsorbents. Macedonian J. Chem. Chem. Eng., **20**:143-150.

17- Senesa, L. R.; Dutta, P.; Datskos, P.G. and Sepaniak, M., J., (2006), Analyte species and concentration identification using differentially functionalized microcantilever arrays and artificial neural networks. *Anal Chim Acta*, 558:94-101.

18- Nadia, A. S., (2005), Ph. D. Thesis, Synthesis of new heterocyclic compounds derived from 2-Amino -5- Mercapto - 1,3,4-Thiadaiazole College of Science, Al-Nahrain University, Iraq.

19- Belhachemi, M. and Addoun ,F. (2012) /Adsorption of congo red onto activated carbons having different surface properties: studies of kinetics and adsorption equilibrium, Desalination and Water Treatment 37,122–129.

20- Kugbe, J., Matsue ,N. and Henmi ,T. (2009), "Synthesis of Linde Type A Zeolite-Goethite Nanocomposite as an Adsorbent for Cationic and Anionic Pollutants," Journal of Hazardous Materials,**164**, No. 2-3: 929-935.

21- Treacy, M. M. J. and Higgins ,J.B., in Collection of simulated XRD powder patterns for zeolites, Elsevier, Amsterdam (2001) :212.

22- Thompson, R. W. and Huber, M. J., (1982), "Analysis of the Growth of Molecular Sieve Zeolite NaA in a Batch Precipitation System," Journal of Crystal Growth, **56**, No. 3: 711-722.

23- Namasivayam, C.; Muniasamy, N.; Gayathri, K.; Rani, M. and Renganathan, K. (1996), Removal of dyes from aqueous solutions by cellulosic waste orange peel . Biores. Technol. **57**: 37-43.

24- Giles, C. H.; Macewan, T. H.; Nakhwa, S. N. and Smith, D., (1960). Studies in adsorption. In diagnosis of adsorption mechanisms and in measurement of specific surface areas of solids. J. Chem, Soc., 786:3973-3993.

25- Ash, S.G.; Everett, D. H. and Findenegg, G. H., (1968). Multilayer theory for adsorption from solution. Mixtures of monomers + dimmers , Trans. Farad. Soc., 64:2645-2666 .

26- Namasivayam, C. and Yamuna, R. T., (1995), Adsorption of direct red 12 B by biogas residual slurry: Equilibrium and rate processes Environ. Pollut., 89, 1-7.

<u>27-</u> Chatterjee, S.; Chatterjee, S.; Chatterjee, B. P. and Guha, A. K., (2007), Adsorptive removal of Congo Red, a carcinogenic textile dye by chitosan hydrobeads: Binding mechanism, equilibrium and kinetics. Colloids and Surfaces A: Physicochemical and Engineering Aspects, **299**:146-152.

28- Ho, Y. S.; Porter, J. F. and McKay, G., (2002). Equilibrium isotherm studies for the sorption of divalent metal ions onto peat: copper, nickel and lead single component systems. Water Air Soil Pollut., **141**: 1-33.

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29- Dursun, A.Y. and Kalayc, C. S., (2005).equilibrium ,kinetic and thermodynamic studies on the adsorption of phenol onto chitin, J. Hazard. Mater., **B123**: 151–157 .

30-Liu, H.; Chen, B.; Lan, Y. and Cheng, Y. (2004).Biosorption of Zn(II) and Cu(II) by the indigenous Thiobacillus thiooxidans.,Chem. Eng. J., 97: 195-201.

31- Mall, I. D.; Srivastava, V. C.; Agarwal, N. K. and Mishra, I. M., (2005). Removal of congo red from aqueous solution by bagasse fly ash and activated carbon: kinetic study and equilibrium isotherm analyses. Chemosphere,**61**: 492–501.

32- Dubinin, M. M. and Radushkevich ,L. V., (1947), Equation of the characteristic curve of activated charcoal, Chem. Zentr. 1: 875.

33- Mckay, G. (1984), "Two Resistance Mass Transfer Modles for the Adsorption of

Dyestuffs from Aqueous Solution Using Activated Carbon" J. Chem. Technol. Biotechnol., **34A**: 294.

34- Vinod, V.P., and Anirudhan, T.S., (2001). "Sorption of Tannic Acids on Zirconium Pillared Clay", J. Chem. Technol. Biotechnol., 77:92-101.

35- Jossens, L; Prausnitz ,J.M ; Fritz ,W; Schlünder ,E.U and Myers ,A.L., (1978)

,Thermodynamics of multi-solute adsorption from dilute aqueous solutions, Chem. Eng. Sci.**33** :1097 –1106.

36- Valdimir, P.; Zlatko, K. and Slaro, C., (1974). "Adsorption on Solids", Butter Worths, London, 301-304, 572-604.

37- Kipling, J. J., (1965)."Adsorption from Solutions of Non-Electrolytes", Academic Press, London, 3, 101-168, 257-259.

38- Kapoor, K. L., (1994)."A Text Book of Physical Chemistry", Macmillan IndiaLimited, India,: 449-481.

CA Index name	1-Naphthalenesulfonic acid, 3,3'-[(1,1'-biphenyl)- 4,4'-diylbis(2,1-				
	diazenediyl)]bis[4-amino-,sodium salt (1:2)]				
Molecular formula	$C_{32}H_{22}N_6Na_2O_6S_2$				
Molecular weight	696.66 g mol ⁻¹				
Molecular surface area	557.6 Å ²				
Physical form	brounish-red powder				
Solubility	soluble in water, ethnol; very slightly soluble in acetone; practically				
	insoluble in ether, xylene				
Density	0.995 g cm ⁻³ at 25°C				
Dye Class	Azo				
Melting point	> 360oC				
pH range	3.0-5.0				
Colour	Blue (pH 3.0) to red (pH 5.0)				
рКа	4.1; 3.0				
Absorption wavelength	498 nm				
(λ _{max})					

Table No.(1) : physiochemical characteristics of (CR) dye

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Ta	able No.	(2)	The c	compos	ition	of Zeo	lite 5A	mine	ral	
										_

HUPAS

Constituent	SiO ₂	Al ₂ O ₃	Na ₂ O	CaO	L.O.I.
Weight %	32.52	27.64	4.20	11.38	24.25

Table No. (3):	Several isotherms	constants for (CR dye u	ptake by	y zeolite - PbAMT
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T/V	Freundlich isotherm						
1/K	K _F (L/g)			n	\mathbf{R}^2		
288	0.984		8.461			0.968	
298	0.948		11	1.618		0.939	
308	0.714		7.	.042		0.833	
318	0.707		5.	.899		0.969	
			Langmui	r isotherm			
1/K	K _L (L/mg)		a _L (mg/g)		R ²	
288	0.606		1	.570		0.996	
298	0.781		1	.340		0.997	
308	1.028		1	.151		0.998	
318	0.492		1	.319		0.999	
			Temkin	isotherm			
1/K	K _T (L/mg)		bT			R ²	
288	974.095		16.849			0.944	
298	19825.535		25.999			0.919	
308	169.563		19.012			0.833	
318	47.628		15	15.403		0.987	
T/V	The Dubinin and Radushkevich isotherm						
1/K	βmol ² /KJ	Ε	KJ/mol	q _{max} (mg/g)		\mathbb{R}^2	
288	5.8X10 ⁻⁸		2.995	1.33		0.608	
298	4.6X10 ⁻⁸		3.291	1.19		0.589	
308	4.5X10 ⁻⁷	1.051		1.051 1.09		0.835	
318	4.4X10 ⁻⁸		1.059	1.17		0.855	
T/V	The Redlich-Peterson isotherm						
1/K	ar (Lmg ⁻¹) Kr		$(L g^{-1})$	β		\mathbb{R}^2	
288	-20.371	-	18.292	0.850		1.000	
298	15.652		14.381	0.900		0.999	
308	1.028		1.183	1.000		0.998	
318	0.894		0.973	0.950		1.000	

Table No.(4): Thermodynamic parameters of adsorption process of C-R dye on the
adsorbent at different temperatures

uuson bene ut unier ent temper utur es								
T/K	$\Delta G (J mol^{-1})$	ΔH (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)	Ke				
288	-11454.6	-8.497	10.27	119.6				
298	-11224.1	-8.497	9.15	92.8				
308	-11277.4	-8.497	9.03	81.8				
318	-11793.0	-8.497	10.37	86.5				





Figure No. (2): Structure of AMT











Figure No.(5) : AFM image of zeolite , zeolite-AMT



Figure No. (6): SEM image of zeolite, zeolite-AMT



Figure No. (7). Effect of contact time on the removal of CR = 40 mg/L; pH = 7; adsorbent dose = 100 mg/10 mL



Figure No. (8): Adsorption isotherms of dyes on zeolite and zeolite-pbs at different temperatures



Figure No. (9): Adsorption isotherms models of CR dye on zeolite-AMT:a- Freundlich, b- Langmuir, c- Temkin, d- Dubinin and Radushkevich, e- Redlich-Peterson.at different temperatures



Figure No. (10): Plot of ln K_e against reciprocal absolute temperature for adsorption of CR dye on zeolite-AMT

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استلم البحث في: ٣ تشرين الثاني ٢٠١٤ ، قبل البحث في ٢١ كانون الاول 2014

الخلاصة

قمنا بامتزاز صبغة الكونغو الاحمر بواسطة زيولايت صناعي معدل 5A والذي اسمه العام Lind صنف A اذ تم تعديل السطح قيد الدراسة بواسطة مركب امينومركتوثايادايزول (AMT) وتم تشخيص السطح المعدل عن طريق مطيافية الاشعة تحت الحمراء ومطيافية الاشعة السينية ومجهر القوى الذرية ومجهر الماسح الالكتروني . تعتبر صبغة الكونغو الاحمر من الملوثات البيئية، لذلك استعمل في هذه الدراسة الزيولايت المعدل كسطح ماز لازالة صبغة الكونغو الاحمر من محلولها المائي بواسطة الامتزاز اذ تم اعتماد تجارب الدفعات لدراسة تاثير زمن الاتزان والتركيز الابتدائي المادة الممتزة و تاثير درجة الحرارة في امتزاز صبغة الكونغو الاحمر ، حللت بيانات التوازن للامتزاز تم تحليلها عن طريق تطبيق عدة معادلات مثل (فريندليش ، لانكماير ، تمكين ،دوبنن-رودشكيفج ، ريدليش- بيترسون) وجصلنا على افضل النتائج من تطبيق معادلة تم حساب الدوال الثرموديناميكية °Δ من الابتدائي للصبغة وكما تقل مع زيادة درجة الحرارة كم حساب الدوال الثرموديناميكية محين . 200 من معاد الابتدائي الصبغة وكما معادلة معادلات مثل المنتزاز معنعة الكونغو الاحمر ، حللت بيانات التوازن للامتزاز تم تحليلها عن طريق تطبيق عدة معادلات مثل المن ويندليش ، لانكماير ، تمكين ،دوبنن-رودشكيفج ، ريدليش- بيترسون) وجصلنا على افضل النتائج من تطبيق معادلة ريدليش – سيترسون . اذ تزداد سعة الامتزاز تزداد بريادة التركيز الابتدائي للصبغة وكما منه معاد الدرارة كذلك تم حساب الدوال الثرموديناميكية °Δ ، 40°, من .

الكلمات المفتاحية: الامتزاز، صبغة الكونغو الحمراء، ايزوتيرم، دوال ثرموديناميكية.

مجلة إبن الهيثم للعلوم الصرفة و التطبيقية