Experimental studies of Thermodynamics parameters : as a model
Adsorption and Removal of Textile

Aseel M. Aljeboree1, Sadiq Jaafer Baqir 2, Ayad F. Alkaim 3
1,3Department of Chemistry, College of Science for women, University of Babylon, Hilla, Iraq
2Al-Mustaqbal University College, Babylon, Hilla, IRAQ
Corresponding author:
Aseel M. Aljeboree
E-mail: alkaimayad@gmail.com

ABSTRACT

Study the adsorption and removal of (Maxilon Blue GRL Basic) textile dye from aquatic solution via AC/Clay surface. The adsorbent was characterized with (XRD) X-Ray Diffraction, (FT-IR) Fourier transform infrared spectrophotometer, and (SEM)Scanning electron microscope. Several physio-chemical parameters for example, agitation time, primary concentration dye GRL "50-150 mgL⁻¹", adsorbent dosage (0.005-0.125)g, pH of solution dye about 3-11 and solution temperature (15, 30, 50) °C. For GRL dye adsorbent surfaces maximum adsorption found to be at pH = 6. In fact adsorption found to decrease with increase in solution pH. The application ability of adsorption model to study the adsorption behavior has too been analyzed via Langmuir, Freundlich and Tempkin models was utilized to explain the experiential isotherms and constants isotherm's. It was found Langmuir model give good fittings when compare with Freundlich and Tempkin model. The amplitude of the adsorption reduction with increased the temperature. Keywords: AC/Clay surface, Maxilon Blue GRL, textile dye, Adsorption model, X-Ray Diffraction (XRD).
Introduction

Textile sewage water have a great quantity of solids suspended, in added to BOD (biochemical oxygen demand), COD (chemical oxygen demand), basicity, color, heat, acidity and other pollutants inorganic more impurities, excluding color, container to removal through traditional wastewaters treatment works[1]. Dyes tricky to removal due to their origin synthetic, chemical compound which do them so constant [2]. The existence of even so decrease of dyes concentrations in effluents is very visible and unwanted [1, 3, 4]. There are a great multiplicity of dyes (basic, dispersive, direct, sculpture, reactive, acid, and dye metallic) that fall in to the nonionic, cationic or category anionic. Acid, reactive dyes and Direct are anionic while dyes basic are cationic. The utmost levels of toxicity present in diazo direct and basic dyes [5].

The industrial sewage water usually contains a set of the compound organic and substances toxic which are hurtful to fish and other life eques. Several manufacture like dyes, paper, textile, and plastics, utilized the dyes to color their products. Thus they have a major amount of wastewater colored. Color is the initial pollutants to be known in sewage water [6-8]. The presence of exact lesser quantities of dyes in water (for some dyes less than 1ppm) is greatly visible and undesirable. The dye sewage water has been a large ecological issue all the country. The essential bases of sewage water dye from printing, textile, extra industries related.

Activated carbon is an efficient but costly adsorbent due to its rise price of industrial. They have lead several workers to search for the utilize of inexpensive and effective alternate materials. Like eggshell waste, lignocelluloses waste, rice husk, peanut shell, coconut husk, bottom ash, coconut copra meal, coconut shell fibre, de-oiled soya [9-13].

Thus, the objective in the study was to explore the potential of the surface AC/Clay very low inexpensive adsorbent for the dye removal from eques solution. The present study the affects of primary conc., agitation time, pH, mass of adsorbent, temp. on GRL adsorption amount have studied. Isotherms was too reported and estimated.

Experimental part

Methods and Materials

Maxilon Blue GRL was gained from M/s Merck. The chemical structures appear in Fig. 1. The experiment all the solutions was prepared after the stander solution dilution by distilled water. A stander solution was prepare via dissolving 1 g (1000 mg/L) as an suitable amount of (GRL) dye in 1 L double D.W. using the solutions Working of concentrations desired were prepared via dilution successive. The naturel solution pH of dye GRL was appear to be 6.20.
Preparation of Apricot stone activated carbon AC/Clay surface (CAC):

Apricot stone was attained from the market at the Hilla/Iraq. Apricot stone was filtered by a 3-2 mm mesh, washed again and again by D. W to eliminate surface impure, soluble contaminations, and dry at 100.5 °C at 45 hour. should improve its adsorption capability in an try to estimate the basic dyes properties of adsorption an inexpensive Apricot stone, abundantly obtainable in Babylon. The clean bio-mass and filtered to give a powder with mesh <50 μm. After that using clay bentoneuet 5g 160ml distilled water, was added with 3g AC powder and mixed for 25min by magnetic stirrer. Then was put in oven at 100ºC for 48h. The powder washed with distilled water several times with ultrasonication until the pH of the wash became neutral (pH =7). Finally, it was dried at 80ºC for 24h.

Adsorption studies

Batch data was agreed to calculate the effect of initial dye concentration, agitation time, adsorption mass and pH solution for the elimination of dye GRL on AC/Clay from aqueous solutions. In all data except for the primary conc., 0.5 mg AC/Clay in 100 mL aquatic solution of dye GRL with 50 mg.L⁻¹. After agitation on a water bath for predetermined equilibrium time, the solution having AC/Clay and GRL dye and additional to centrifugation. The residual conc. of solution dye was limited by prepare a calibration curve at the corresponding max. wavelength (590 nm) utilizing a UV-visible spectrophotometer (UV meni 1240 shimedzu). The quantity of adsorbed dye GRL, Qₑ (mg.g⁻¹), determine by utilizing the following equation:

\[ Qₑ = (C₀ - Cₑ) \frac{V}{M} \]  \hspace{1cm} (1)

Cₑ, C₀ are the equilibrium and initial conc. (mg.L⁻¹), at the same order, M mass (gm) of AC/Clay. The adsorption efficacies of dye under several conditions were determined of the several among the C₀ and Cₑ. The affect the pH of removal GRL dye was studied above a pH about (3–11). The primary pH of GRL dye solution was adjusted via added of 0.1 N of HCl or NaOH solution. The concentration of solution GRL dye about of 50 - 150 mg.L⁻¹ to study the adsorption model. The results were expressed as the removal...
efficiency ($E\%$) of the adsorbent for GRL dye which was defined as determined utilizing the following equation:

$$E\% = \frac{C^0 - C_e}{C^0} \times 100$$

\[(2)\]

**Results and discussion**

**Effect of primary concentration GRL dye and contact time**

The primary concentration consider very significant driving force to overcome all quantity resistances transfer of totally molecules among the solid and aqueous phases [14, 15]. The dye concentrations was altered and intervals time assessed until no adsorption of adsorbate on AC/Clay take place. Figure. 2 appear the affects of agitation time on the quantity of GRL dye adsorbed via AC/Clay under several primary concentrations GRL dye. As appear, the adsorption increases with increasing primary concentration of GRL dye [16]. The percentage% of GRL via adsorption onto AC/Clay was found to be fast at the original period of agitation time and then to decrease with increasing in agitation time. This was make happen via forces attractive among of dye molecule and the adsorbent like forces Vander Waals and attractions electrostetic [17, 18]. Usually, adsorption includes a reaction surface method, the adsorption primary is fast. after that, a reduces adsorption should follow the obtainable active sites adsorption Usually decrease [19, 20].

![Figure 2: Effect of primary con. on the removal percent GRL dye on to AC/ Clay (Exp. Cond.: Temp. = 30 °C, agitation time 24 hour, and pH 6).](image-url)
Comparative between (0.2AC/Clay, 0.1AC/Clay, 0.05 AC/Clay, AC and Clay) surfaces as Adsorbents. The best results of the percentage of removal (E%) and adsorption capacity for GRL dye the order increasing (0.2AC/Clay > 0.1AC/Clay > 0.05 AC/Clay > Clay and AC). The good results of the percentage of removal (E%) 98.1.9%, 82,812%, 74.22%, 68.45%, 58.66% and adsorption capacity 50.01mg/g, 44.2mg/g, 36.51mg/g, 27.11mg/g for GRL dye respectively show in Fig3.

Figure 3: Comparative between (0.2AC/Clay, 0.1AC/Clay, 0.05 AC/Clay, AC and Clay) (Exp. Cond.: Temp. = 30 °C, agitation time 24 hour, and pH 6).

**Effect of weight of adsorbent**

The effect of AC/Clay mass onto (adsorption) removal dye GRL at 25 ±1 °C. Figure. 4 displays the percentage % of GRL rise with increase the weight of the AC/Clay (0.005–0.125 gm). The increase in the removal dye with increasing mass AC/Clay was due to the rise in surface area as extra active sites was obtainable for adsorption. But after a specified adsorbent mass (0.05 gm) the % of the removal dye not increase significantly and that mass was careful as an dose optimum [21].The dye adsorption capacity was 94.13% at the best dose AC/Clay, thus, results in an increase of the quantity of dye adsorbed. The density of the adsorption decrease with an rise in the amount mass is generally because of active places adsorption stay un-saturated through the reaction adsorption while the number of active places obtainable for adsorption active place increases via increasing the mass dose [22, 23].
Figure 4: Effect of weight of adsorbent AC/Clay onto removal percentage and quantity of adsorbed dye GRL. (Exp. Cond.: Temp. = 30 °C, agitation time 24 hour, and pH 6).

**Effect of solution pH on dye uptake**

Numerous investigator have proposed the solution pH dependence of GRL dye bound method on several materials [24]. The affect of solution pH on the adsorption of GRL via AC/Clay is show in Fig5. was studied within pH about 3–11. The pH Solution should effect thought aqueous chemistry and surface binding places of the mass dosage [25]. Removal Percentage % of GRL dye that minimum at pH 11 (22%) and rise up to pH 6, reached maximum (94.13 %) above the primary pH 3–11. The absence of sorption at pH low can be explicated via the fact that at this pH acidic, H+ can compete with dye ions for the active places adsorption of adsorbent, there via inhibiting the adsorption of GRL. At greater pH solution, the AC/Clay can give charge negative, which improves the charge positive cations dye by forces electrostetic of attraction. Alike result of solution pH affect was too reported adsorption of GRL on to AC/Clay [26, 27] and the adsorption of GRL from aqueous solution through dried activated sludge [28].
Surface characterizations

(SEM) have been a primary instrument for characterizing the morphology surface and important physical properties of the adsorbent. SEM of adsorbent material was taken before and after adsorption dye GRL on AC/Clay (Fig. 6). From (Fig. 6a), it is clear, there is a best probability for GRL dye to be trapped and adsorbed into these holes. The pictures SEM of adsorbed samples appear very distinguished dark spots which can be taken as a sign for affective adsorption of molecules dye in the cavities and holes of this adsorbent. The micrographs presented in (Figs. 6b and c) appear clearly 0.05AC/Clay and 0.2AC/Clay. The GRL molecules seem to have formed a void-free film masking the reliefs of particles and porosity of the aggregates [29-31]. On the other hand, the decorated carbon micrographs of samples (Figure 6) showed changes in morphology of phase for new irregular bulky particles presence on the surface. This leads to increased surface texture protuberance and coarseness that are absent before carbon loading [32, 33].
Figure 6: SEM image of (a) activated carbon before adsorption and (b) Clay before adsorption (c) 0.05 AC/Clay after adsorption of GRL dye (d) 0.2 AC/Clay after adsorption of GRL dye.

**X-Ray Diffraction (XRD)**

X-ray diffraction was measured to study the crystal phases and the purity components of nanomaterials. It gets detailed information about the lattice factor, lattice strain, crystallite size, lattice defects, (in case of nanoparticles) and the kind of bond molecular of phase crystalline. Therefore, for estimation of the average size of the particles[34].

\[ D = \frac{k\lambda}{\beta \cos \theta} \]

\[ \text{… (3)} \]

D is the average particle size, k is the so-called factor shape, which generally takes a value of 0.9, \( \lambda \) is the wavelength of the radiation X-ray (0.15418 nm for Cu-K\( \alpha \)), \( \beta \) is (FWHM) of the peak diffraction measured at 2\( \theta \) (that is broad due to the crystallite dimensions), and \( \theta \) is the angle at maximum diffraction intensity curve.

Figure 7 appear the X-ray of the AC/Clay. In this Figure, all patterns are very similar; There are no diffracted signals of the AC as a source of Carbon, which attributed to the low weight percentage or non-crystallinity of doping materials on the crystal surface.

Figure 7: XRD patterns of the clays including AC.

**FT-IR characterization for adsorbent/adsorbate**

Technique FTIR was utilized to examine the surface groups responsible for adsorption GRL dye. Adsorbent surfaces (Apricot stone) and dye GRL-loaded adsorbent sample after adsorption was located in furnace at 85 °C for 4 hour. Sample was made as pellet
and then the spectra infrared of GRL on adsorbent before and after the adsorption method were recorded about of $4000 – 400 \text{ cm}^{-1}$ on a Bio Rad FTS 175C spectrophotometer. Fig.8. The adsorption stretching band of OH in the structure crystal of the adsorbent is observed at $3445 \text{ cm}^{-1}$ assigned to free hydroxyl and diminished after adsorption with dye adsorbent. All these findings suggest the attachment of GRL dye onto Apricot stone [9-12]

![Figure 8: FT-IR spectra for adsorption of GRL on the surface of Apricot stone.](image)

**Isotherms Adsorption**

For liquid-solid method, the adsorption equilibrium is one of the significant physiochemical aspects in the explanation of the behavior adsorption. In the project, three famous isotherms of Langmair, Tempkin, Freundlich model are calculated. The Langmair model assumes adsorption mono-layer on to a surface having a finite number of the active sites adsorption with no transmigration of the adsorbate in the plane of the surface [35] This isotherm is the mostly utilized three -factor equation, usually expressed in the form via the following equation:

$$q_e = q_{\text{max}} K_L C_e / (1 + K_L C_e)$$  \hspace{1cm} (4)

$$q_e = K_f C_e^{1/n}$$ \hspace{1cm} (5)

Where, $q_e$ is the quantity adsorbed (mg/g). $C_e$ is the concentration equilibrium solution (mg/L). $K_L$ and $Q_{\text{max}}$, the constants Langmiuir represent the maximum adsorption efficiency (mg/g) at complete mono-layer coverage and energy of adsorption at the same order. [36]

This parameter can indicate while the adsorption method $(R_L = 1)$ linear, $(R_L = 0)$ irreversible, $(R_L > 1)$ unfavorable $(0 < R_L < 1)$ favorable Freundlich model is defined as:[37] The non-linearized form of Tempkin model is exemplified via Eqn (6):
\[ q_e = \frac{R_T}{b} \log (K_T C_0) \]  

(6)

Where \( b \) constant Tempkin related to the heat of adsorption (kJ/mol), \( R \) : constant Gas (8.314 J/mol.K), \( T \) : Temp. (K), and \( K_T \) : Empirical constant Tempkin linked to the equilibrium binding constant related to the maximum binding energy (L/mg), (L/mol)

Langmair and Freundlich isotherms for the GRL AC/Clay system are shown in the Figs. 9 -11 at the same order. the parameters Isotherm and the determination coefficients was determined in Table 1. Appear in the table, isotherm Langmair by coefficient correlation of 0.9999 represents a good fit of data than isotherm Freundlich by coefficient correlation of 0.8668. It indicates the mono-layer adsorption of dye GRL takes place of the homogeneus mesoporous surface absorbent. The quantity of computed maximum mono-layer capacity for the deletion dye GRL from aqueous media via Langmair isotherm was present in 293.1 mg/L. Furthermore, the values of the dimensionless constant \( R_L \) (0.0098 – 0.168) indicate that the adsorption is favorable and rather irreversible. As appear in Table 1, the value of \( 1/n \) was too create to be among zero and one, indicating the great intensity adsorption.

Figure 9 : Isotherm model plot GRL adsorbed AC/Clay surface at several temp. Exp. Cond. adsorbent conc.0.5 g.L⁻¹, contact time 24h, agitation speed=120 rpm, pH6
Figure 10: isotherm model plot GRL adsorbed AC/Clay surface at several temp.. Exp. Cond. adsorbent conc.0.5 g.L⁻¹, contact time 24h , agitation speed=120 rpm , pH6

Figure 11: isotherm model plot GRL adsorbed AC/Clay surface at several temp.s. Exp. Cond.s adsorbent conc.0.5 g.L⁻¹, contact time 24h , agitation speed=120 rpm , pH6

Table 1: model of Freundlich, Langmuir and Templin model for GRL dye adsorbed on the surface of AC/Clay at 35 °C.

| Isotherm models | Parameter | GRL dye 288K | GRL dye 303K | GRL dye 323K |
|----------------|-----------|---------------|---------------|---------------|
| Langmuir       | qm (mg.g⁻¹) | 138.968 ± 4.32645 | 162.0984 ± 6.28009 | 175.9586 ± 4.4003 |
|                | K_L (L.mg⁻¹) | 0.25319 ± 0.03747 | 0.32891 ± 0.05885 | 0.46032 ± 0.05271 |
Adsorption thermodynamics

The thermodynamic factors of the adsorption GRL dye via AC/Clay for example the standard change Gibbs energy (ΔG), the change standard enthalpy (ΔH), and the change standard entropy (ΔS) can be determined from the variation of maximum adsorption with temperature (T). The values experimental found from the following equations inform while process of the adsorption was nonspontaneous or spontaneous [38].

\[ \Delta G = -RT \ln K_d \]  

(6)

where ΔG is the Gibbs free energy; Kd is the distribution coefficient expressed as Kd = qe/Ce; T, the absolute temperature (K) and R is the universal constant gas (8.314 J/Kmol).

The relationship among ΔG, ΔH and ΔS is expressed as:

\[ \Delta G = \Delta H - T \Delta S \]  

(7)

Substitution of equations (6) to equations (7) gives

Van’t Hoff equation was utilized to conclude the average change standard enthalpy, the equation is expressed as

\[ \ln K_d = \Delta H / RT + \Delta S / R \]  

(8)

The value of ΔS and ΔH can be found from the interception and slope from the plot of lnKd against 1/T.

The value of thermodynamic factors calculated are tabulated in Table 2. The value ΔG is negative for all methods, indicates that the adsorption method is spontaneous [39]. The temperature increase leads to greater negative value ΔG. Therefore the adsorption
method was favorable at the temperature higher. The value positive of $\Delta H$ for all systems indicates that the adsorption method is endothermic. Meanwhile, the value positive of $\Delta S$ for all method reflects the increased randomness at the solution solid interface through adsorption. This too implies that is irreversible adsorption. Thus regeneration of the adsorbent is improbable.

Figure12: Van't Hoff range of adsorption GRL AC/Clay

Conclusion

Equilibrium adsorption of basic dye GRL on to AC/Clay was studied in a batch type process of different factors first concentration GRL, pH, temperature, and mass of adsorbent. The results appear the adsorption of basic GRL dye increase with increasing in primary concentrations GRL dye, pH and solution temp. whereas it decreased with increase in adsorbent weight. All results conform models isotherm was select in the study then most appropriate of isotherm Freundlich that gave the better correlations for the dye GRL onto surface AC/Clay.

Reference

1. Alidadi, H., et al., *Enhanced removal of tetracycline using modified sawdust: Optimization, isotherm, kinetics, and regeneration studies*. Process Safety and Environmental Protection. 117: p. 51-60.

2. L.D.T. Prola, E.A., E.C. Lima, C.S. Umpierres, J.C.P. Vaghetti, W.O. Santos, S. Laminsi, P. Djifon, *Comparison of Jatropha curcas shells in natural form and treated by non-thermal plasma as biosorbents for removal of Reactive Red 120 textile dye from aqueous solution*. Ind. Crop. Prod., 2013. 46: p. 328340.-
3. P. Nigam, G.A., I.M. Banat, D. Singh, R. Marchant,, Physical removal of textile dyes and solid state fermentation of dye-adsorbed agricultural resides, Bioresour. Technol, 2000. 72 p. 219-226.

4. N.F. Cardoso, E.C.L., I.S. Pinto, C.V. Amavisca, B. Royer, R.B. Pinto, W.S. Alencar, S.F.P. Pereira Application of cupuassu shell as biosorbent for the removal of textile dyes from aqueous solution. J. Environ. Manage :92 .2011, p. 1237-1247.

5. T. Robinson, G.M., R. Marchant, P. Nigam, Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative, Bioresour. Technol., 2001. 77 p. 247-255.

6. Aljeboree, A.M. and A.N. ALSHIRIFI, Spectrophotometric Determination of phenylephrine hydrochloride drug in the existence of 4- Aminoantipyrine: Statistical Study. International Journal of Pharmaceutical Research, 2018. 10(4).

7. Abdulrazzak, F.H., et al., Sonochemical/hydration-dehydration synthesis of Pt-TiO2 NPs/decorated carbon nanotubes with enhanced photocatalytic hydrogen production activity. Photochemical and Photobiological Sciences ;(11) 15 .2016p. 1347-1357.

8. I.M. Banat, P.N., D. Singh, R. Marchant, Microbial decolorisation of textile dye containing effluents: a review,Bioresour. Technol. 58 (1996) 217-227. Bioresour. Technol. 1996. 58: p. 217-227.

9. Aljeboree, A.M. and A.N. Alshirifi, Colorimetric Determination of phenylephrine hydrochloride drug Using 4-Aminoantipyrine: Stability and higher sensitivity. Journal of Pharmaceutical Sciences and Research, 2018. 10(7): p. 1774-1779.

10. A. Mittal, V.T., V. Gajbe, Adsorptive removal of toxic azo dye Amido Black 10B by hen feather, Environ. Sci. Pollut. Res20 .2013, p. 260-269.

11. B.H. Hameed, D.K.M., A.L. Ahmad, Equilibrium modeling and kinetic studies on the adsorption of basic dye by a low-cost adsorbent: Coconut (Cocos nucifera) bunch waste,. J. Hazard. Mater., 2008. 158 p. 65-72.

12. U.R. Lakshmi, V.C.S., I.D. Mall, D.H. Lataye, Rice husk ash as an effective adsorbent: Evaluation of adsorptive characteristics for Indigo Carmine dye, J. Environ. Manage. , 2009. 90. p. 710-720.

13. J. Mittal, V.T., A. Mittal, Batch removal of hazardous azo dye Bismark Brown R using waste material hen feather,. Ecol. Eng 60 .2013 , p. 249-253.

14. Y.S. Ho, T.H.C., Y.M. Hsueh, Removal of basic dye from aqueous solutions using tree fern as a biosorbent,. Process Biochem :40 .2005, p. 119-124.

15. M. Do´gan, M.A., O. Demirbas, Y. Ozdemir, C. Ozmetin, Adsorption kinetics of maxilon blue GRL onto sepiolite from aqueous solutions,. Chem. Eng. J 2006 ,. 124p. 89-101 .

16. Aljeboree, A. and A. Alshirifi, Effect of Different Parameters on the Adsorption of Textile Dye Maxilon Blue GRL from Aqueous Solution by Using White Marble. Asian Journal of Chemistry. 5813-5816.

17. M.A. ALJEBOREE, A., Adsorption and Removal of pharmaceutical Riboflavin (RF) by Rice husks Activated Carbon. International Journal of Pharmaceutical Research 2019. 11( 2): p. 255-261.

18. Y. Bulut, H.A., A kinetics and thermodynamics study of methylene blue adsorption on wheat shells,. Desalination 2006. 194: p. 194.
19. Aseel M. Aljeboree, H.Y.A.-G., Mohammed H. Said and Ayad F. Alkaim, *THE EFFECT OF DIFFERENT PARAMETERS ON THE REMOVAL OF VITAMIN B12 DRUG (AS A MODEL BIOCHEMICAL POLLUTANTS) BY AC/ CLAY.* Biochem. Cell. Arch., 2019. 19(1): p. 000-000.

20. C.-H. Weng, Y.-F.P., *Adsorption characteristics of methylene blue from aqueous solution by sludge ash,* Colloids Surf. A. Physicochem. Eng. Aspects-154 (2006) :274.162.p. 154-162

21. Ayesha Wasti a, M.A.A., *Adsorption of textile dye onto modified immobilized activated alumina,* J. of the Association of Arab Universities for Basic and Applied Sciences. (2014)

22. Enas M Alrobayi, A.M.A., Aseel M Aljeboree, Ayad F Alkaim, Falah H Hussein, *Investigation of photocatalytic removal and photonic efficiency of maxilon blue dye GRL in the presence of TiO2 nanoparticles.* Particulate Science and Technology, 2017. 35(1): p. 14-20.

23. Aseel M. Aljeboree , A.S.A., *Removal of Pharmaceutical (Paracetamol) by using CNT/ TiO2 Nanoparticles.* Journal of Global Pharma Technology, 2019. 11(01): p. 199-205.

24. R. Han, Y.W., P. Han, J. Shi, J. Yang, Y. Lu, *Removal of methylene blue from aqueous solution by chaff in batch mode,* J. Hazard. Mater. B137 (2006) Hazard. Mater. B, 2006 137 p. 550-557.

25. E.C. Lima, B.R., J.C.P. Vaghetti, N.M. Simon, B.M. da Cunha, F.A. Pavan, E.V. Benvenutti, R.C. Veses, C. Airoldi, *Application of Brazilian-pine fruit coat as a biosorbent to removal of reactive red 194 textile dye from aqueous solution.* Kinetics and equilibrium study, J. Hazard. Mater., (2008) 155 p. 536-550.

26. Liqiang Jin a, Quucun Sun b, Qinghua Xu b, Yongjian Xu Adsorptive removal of anionic dyes from aqueous solutions using microgel based on nanocellulose and polyvinylamine* Bioresource Technology, 2015( 197 ): p. 348-355.

27. G. Annadurai, R.S.J., D.J. Lee, G. Annadurai, R.S. Juang, D.J. Lee, *Use of cellulose-based wastes for adsorption of dyes from aqueous solutions,* J. Hazard. Mater. B92 (2002) 263-274. J. Hazard. Mater. B 92. (2002) p. 263-274.

28. S. Senthilkumaar, P.R.V., K. Porkodi, C.V. Subbhuraam, Adsorption of methylene blue onto jute fiber carbon: kinetics and equilibrium studies, J. Colloid Interface Sci. , 2005. 284 p. 78-82.

29. Salman, J.M., E. Abdul-Adel, and A. F. AlKaim, *Effect of pesticide Glyphosate on some biochemical features in cyanophyta algae Oscillatoria limnetica.* International Journal of PharmTech Research, 2016. 9(8): p:365-355.

30. Alkaim, A.F., Alrobayi, Enas M, Algubi, Abrar M and Aljeboree, Aseel M, *Synthesis, characterization, and photocatalytic activity of sonochemical/hydration–dehydration prepared ZnO rod-like architecture nano/microstructures assisted by a biotemplate.* Environmental technology, 2017. 38(17): p. 2119-2129.
31. Aljeboree, A.M., *Removal of Vitamin B6 (Pyridoxine) Antibiotics Pharmaceuticals From Aqueous Systems By ZnO*. International Journal of Drug Delivery Technology 2019. 9(2): p. 125-129.

32. Edathil, A.A., P. Pal, and F. Banat, *Alginate clay hybrid composite adsorbents for the reclamation of industrial lean methyldeethanolamine solutions*. Applied Clay Science, 2018. 156: p. 213-223.

33. Gao, J., et al., *Preparation and properties of novel eco-friendly superabsorbent composites based on raw wheat bran and clays*. Applied Clay Science, 2016. 132-133: p. 739-747.

34. Abazari, R., A.R. Mahjoub, and S. Sanati, *A facile and efficient preparation of anatase titania nanoparticles in micelle nanoreactors: morphology, structure, and their high photocatalytic activity under UV light illumination*. RSC Advances, 2014. 4(99): p. 56406-56414.

35. Langmuir, I., J. Am. Chem. Soc., 1916. 38 p. 2221-2295.

36. Langmuir, I., *The constitution and fundamental properties of solids and liquids*. J. Am. Chem. Soc 1916. 38 p. 2221-2295.

37. H.M.F., *Freundlich Die adsorption in lusungen* Z. Phys. Chem., 1906. 57 p. 385-470.

38. ALJEBORI, A.M.K.A., ABBAS NOOR, *Effect of Different Parameters on the Adsorption of Textile Dye Maxilon Blue GRL from Aqueous Solution by Using White Marble*. Asian Journal of Chemistry, 2012. 24(12): p. 5813-5816.

39. A F Alkaim, M.B.A., *Adsorption of basic yellow dye from aqueous solutions by Activated carbon derived from waste apricot stones) ASAC): Equilibrium, and thermodynamic aspects*. international journal of chemical sciences, 2013. 11(2): p. 797-814.