ISSN NO. 2320-5407

RESEARCH ARTICLE

Removal of some organic dyes from aqueous solution by peanut husk.

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Manuscript Info	Abstract
	Adsorption is one of the most promising decolorization techniques in dyeing waste water treatment. Adsorption is a useful and simple technique, which allows kinetic and equilibrium measurements without any highly sophisticated instruments. The main advantage of adsorption recently became the use of low-cost materials, which reduces the procedure cost. Peanut husk (PH) was developed for the removal of acid violet 19 (AV19) and basic red 2 (BR2) in single and binary systems from aqueous solutions. The variation of pH, dose of adsorbent, initial concentration of dyes and temperature were investigated where the removal percent of dyes increase with increasing dose and temperature and decrease with increasing concentration. SEM and IR were used to analyze the morphology and chemical groups of the (PH) and (TPH) before and after dye sorption and also the point of zero charge of adsorbent was investigated. Langmuir and Freundlich isotherm models were used to investigate the adsorption process. It was found that the Langmuir model best described the experimental data. Also the kinetic obtained data were analyzed using pseudo first order, pseudo second order, intraparticle where the experimental results fit well with the pseudo- second- order model. And thermodynamics properties of the process were investigated where adsorption of dyes onto peanut husk (PH) was found to be spontaneous and endothermic in nature.

Introduction:-

Water, whether fresh; salted; rain; surface or underground-water may be contaminated with materials that make it harmful. Polluted water is the cause of various diseases that can seriously affect public health. Human are not the only one to suffer the consequences of water pollution, fauna and flora are also victims **(Zamouche and Hamdaoui, 2012)**. Textile industries produce a lot of wastewater, which contains a number of contaminants, including acidic or caustic dissolved solids, toxic compounds, and any different dyes, Many of the organic dyes are hazardous and may affect aquatic life causing various diseases and disorders **(Mohammed. 2014)**. It has been estimated that the total dye consumption in textile industry worldwide is more than 10,000 tonnes per year and about 10–15% of these dyes are released as effluents during the dyeing processes **(Sara and Tushar, 2014)**.

Dyes can have acute and/or chronic effects on exposed organisms depending on the exposure time and dye concentration **(Bharathi and Ramesh, 2013)**. Moreover dye causes eye burns, which may be responsible for permanent injury to the eyes of human and animals. If swallowed, the dye causes irritation to the gastrointestinal tract with symptoms of nausea, vomiting and diarrhea. It may also cause methemoglob inemia, cyanosis, convulsions, tachycardia and dyspnea, if inhaled **(Hamdaoui and Chiha, 2007)**.The main components of dye molecules are: the chromophores, which are responsible for producing the color, and the auxochromes, which can not only supplement the chromophore but also render the molecule soluble in water and give enhanced affinity (to attach) toward the fibers **(Gupta and Suhas,2009)**.Color is a visible pollutant and the presence of even a very minute amount of coloring substance makes it undesirable due to its appearance When the color interferes with

penetration of daylight into waters it retards photosynthesis and inhibits the expansion of aquatic aggregation and interferes with gas solubility in water bodies **(Zohreh and Anita, 2014)**.

The removal of color from dye-bearing effluents is a major problem due to the difficulty in treating such waste waters by conventional treatment methods **(Pragathiswaran *et al* ., 2016)**.Wastewater containing dyes must be appropriately treated before being discharged into the water bodies **(Gbekeloluwa *et al*.,2014)**.The conventional methods for the treatment of colored wastewater are physical, chemical and biological treatments **(Mohammed *et al* .,2014).** However the application of these technologies is sometimes restricted due issues including; incomplete dye removal, requirement of expensive equipment and monitoring systems, high reagent or energy requirements or generation of toxic sludge and other waste products **(Gbekeloluwa *et al*.,2014).** Among these physico-chemical methods like adsorption and electrochemical coagulation are the most popular methods in recent days **(Arun *et al*., 2014)**. Since adsorption is more effective because adsorption removes the entire dye molecule, leaving no fragments in the effluent **(Sara and Tushar 2014).**

Dyes can be classified as : anionic (direct, acid and reactive dyes), cationic (basic dyes) and non-ionic (dispersive dyes) **(Bharathi and Ramesh, 2013)**. Acid dyes are belonging to anionic group which there are acid group (sulphonate ,carboxyl) in their molecular structure **(Davoud *et al*.,2016).** Acid dyes are used with silk, wool, polyamide, modified acrylic and polypropylene fibers. they have a harmful effect on human beings since they are organic sulphonic acids **(Mohamad *et al*.,2011)**. While cationic dyes are also called basic dyes due to the presence of positive ions in the molecule's structure. Basic dyes are water soluble and they are highly visible in water even at very low concentration. Basic dyes consist of monoazoic, diazoic and azine compounds. Cationic dyes are used to color wool, silk, nylon, mod-acrylic and polyester materials. Cationic functionality is found in various types of dyes such as cationic azo dyes, methane dyes, anthraquinone, di- and tri-arylcarbenium, phthalocyanine dyes, poly carbocyclic and solvent dyes. Basic dye are toxic and can cause allergic dermatitis, skin irritation, mutations and even cancer. Also, cationic dye scan cause increased in heart rate, shock, vomiting, cyanosis, jaundice, quadriplegia, heinz body formation and tissue necrosis in humans. **(Sara and Tushar,2014)**

Research in the past few years was focused on utilizing waste materials from agricultural products because they are inexpensive, ecofriendly, and renewable **(Alshabanat *et al*.,2013).**Peanut is an oil plant, which is extensively cultured in China. Thus, peanut husk is an abundant and inexpensive agricultural by-product. The exploitation and utilization of this biomaterial must bring obvious economic and social benefits **(Binglu *et al*.,2014)**. Peanut husk are the newly thought adsorbents because of their extended surface area, micro porous structure, high adsorption capacity and high degree of reactivity. Peanut husk are totally new adsorbents for waste water treatment. **(Mahmudur *et al*.,2014).** Peanut husk or Groundnut shell is easily available at zero prices. Nut shell is carbonaceous, fibrous solid waste, which creates a disposal problem and is generally used for its fuel value. **(Bharathi and Ramesh , 2013).** Natural peanut husk(NPH) is composed of cellulose, hemi-cellulose, lignin, etc. There are some inorganic elements confirmed by the X-ray fluorescence analysis, such as Si, Ca, K, Fe, Mg, Al, etc. The contents of main inorganic elements (as oxides) for NPH were SiO_2 19.5%, CaO 45.8%, K_2O_2.63%, MgO 5.48%, Fe_2O_3 4.37%, and Al_2O_3 6.64%, respectively.**(Binglu *et al*.,2014 and Nahal and Azza, 2014).**

Materials and Methods:-

All the chemicals used throughout this study were of analytical-grade reagents and the adsorption experiments were carried out at room temperature (25 ± 2 °C)

1. Adsorbent:-
1.1. Peanut Husk (PH):-
Fresh biomass of peanut husk was collected from its natural habitats in the farmland. The collected biomaterial was extensively washed with tap water to remove soil and dust, and washed with distilled water, next dried in an oven at 80°C for complete dryness. Dry peanut husk was crushed into powder crusher and sieved to different particle sizes 0.335 and 0.850mm and then preserved in the desiccator for use. **(Nahal and Azza, 2014 and Taha and El-Maghraby,2016) .**

1.2 Treated peanut husk (TPH):-
A sample of 20 g peanut husk was added to 500 ml of 10% NaOH into three necks round bottom flask and agitated for 1h at room temperature. The half of the solution was removed and immediately 100 ml of distilled

water and 160 ml of epoxy chloropropan were added .The mixture was then heated at 65°C and stirred for 6 h those were carried out in shaking water bath (BS-21) .The solution was removed from heat and 220 ml of 34% tri ethyl amine solution was added .The mixture was heated in 80°C water bath and agitated for 3 h .The product was washed with ethanol and distilled water. The solution pH was then adjusted around 7 using 0.1M NaOH and 0.1M HCl. Finally, the product was cleaned with distilled water until the pH was around 7. The treated peanut husk (TPH) was dried at 60°C for 12 h. The dried (TPH) was grounded in a domestic mixer grinder. After grinding, the powder was again washed and dried. Different sized adsorbents 0.335 and 0.850mm were stored in plastic container for further use. (**Xiaoyu et al.,2013).**

**1.3. Determination of the point of zero charge:-**
   The point zero charge (pHpzc) of adsorbent was determined by the solid addition method. The net charge of surface is zero on the adsorbent surface at pHpzc. Batch equilibrium method was used for the determination of point of zero charge. To each of the flask 1 g of adsorbent was added including 50 ml solution KNO_3 (0.01 N) in the pH range between 2.0 to 10.0.
   The initial pH of solutions were adjusted by adding drops of (0.01 N) KOH and (0.01 N) HNO_3 solutions and each flask was sealed and shaken thoroughly for 48 h at room temperature and the final pH of the solution was measured and recorded. The total charge adsorbed on untreated and treated of (PH) surface was determined by ΔpH (the difference in the value of pH of the solution before and after 48 h). The intersection of obtained curve with pH$_o$ axis indicated the pHpzc value. (**Oladoja and Aliu, 2009; Mohamad et al., 2012; Noureddine et al.,2016 and Moawed and El-Shahat,2016**)
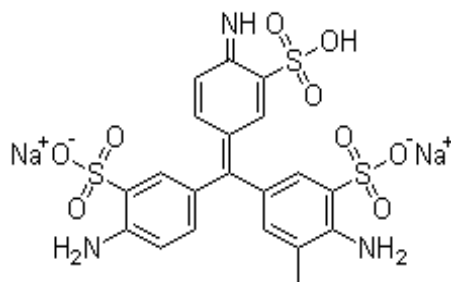
2. Adsorbate:-
2.1. Chemical dye structure:-
   The following dyestuffs under investigation are a cationic dye basic red 2(BR2) obtained from El-Gomhoria Company , Egypt having molecular formula $C_{20}H_{19}N_4Cl$ (M.wt 350.85 and Acid violet 19(AV19) obtained El-Gomhoria Company, Egypt having molecular formula $C_{20}H_{17}N_3Na_2O_9S_3$ (M.wt 585.54 g /L) scheme (1).
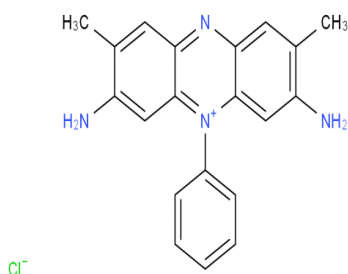
Scheme (1) a-Chemical structure of (BR2)   **b- Chemical structure of (AV19)**

2.2. Dye Solutions:-
   A stock dyes solution of basic red 2 was prepared by dissolving 1.75g in 500 ml distilled water and acid violet 19 was prepared by dissolving 2.93 g in 500 ml distilled water.

3. Effect of some parameters on dye adsorption
   The effects of various experimental parameters have been investigated using a batch adsorption technique to obtain information on treating effluents from the dye industry.

3.1. Effect of pH on dye adsorption by PH
   The effect of pH on the removal of AV19 and BR2 was analyzed over the pH range 2.0 – 9.0. The pH was adjusted using 0.05 M NaOH or 0.05 M HCl solutions. In this study 150 ml of dyes solutions with fixed initial concentrations 5.85 mg/L and 3.51mg/L, respectively was taken in a conical flask at room temperature (25°C) and was agitated at 130 rpm with 0.75 g of untreated and treated of PH. The particle size of adsorbent was 0.335 mm.

3.2. Effect of initial concentration

The effect of initial concentration on the removal of AV19and BR2 was analyzed at (5.85, 11.71, 17.57, 23.42 and 40.99mg/L) and (3.51, 7.02, 10.52, 14.03 and 24.55 mg/L), respectively. In this study 150 ml of dyes solutions at pH5, pH6for (TPH and PH), respectively were taken in a conical flask at room temperature ($25^{o}C$) and were agitated at 130 rpm with 0.75 g of untreated and treated of (PH). The particle size of adsorbent was 0.335 mm.

3.3. Effect of dose:-

The effect of untreated and treated of (PH) dose on the amount of AV19 and BR2 adsorbed was obtained by contacting 150 ml of dyes solutions with initial concentration 5.85 mg/L and 3.51 mg/L, respectively with different amount of (TPH) are 0.25g, 0.5g, 0.75g, 1g at pH5 and different amount of (PH) are 0.25g, 0.5g, 0.75g, 1g and 1.5g at pH6, respectively into a number of 250 ml conical flask and at room temperature($25^{o}C$). The flasks were agitated at 130 rpm. The particle size of adsorbent was 0.335 mm.

3.4. Effect of temperature:-

The effect of temperature on AV19 and BR2 dyes solutions was obtained by contacting 150 ml of dyes solutions with initial concentration (5.85 and 3.51) mg/L with 0.335 mm of treated and untreated of (PH), 0.75g of PH (treated and untreated) into a number of 250 ml conical flask at pH5 ,pH6 of (TPH and PH), respectively and at different temperature values ($30^{o}C$, $50^{o}C$ and $70^{o}C$).

4. Adsorption isotherm:-

The results obtained for adsorption of dye were analyzed by use of well-known models given by the Langmuir and Freundlich isotherms. **(Smitha and Santhi,2015).**

4.1. Langmuir isotherm:

The Langmuir model is based on the assumption that adsorption takes place at specific homogenous sites within the adsorbent .The saturated monolayer curve can be represented by the expression**(Sohn and Kim ,2005 ;Mohammad and Md,2012 ;Babatunde *et al.*,2014 ; and Dahri *et al.*,2016).**

$$q_e = q_{max} K_L C_e / (1 + K_L C_e) \qquad (II.1)$$

a linear form of this expression is:

$$C_e / q_e = 1/ q_{max} K_L + C_e / q_{max} \qquad (II.2)$$

Where C_e is the concentration of the dye solution (mg L^{-1}) at equilibrium, q_e the amount of dye adsorbed per unit weight of adsorbent (mg g^{-1}) and K_L is the constant related to the free energy of adsorption (L mg^{-1}). q_{max} is the maximum adsorption capacity (mg g^{-1}).

4.2. Freundlich isotherm:-

The Freundlich model is an empirical equation based on adsorption onto a heterogeneous surface given below by equation (II.3) **(Akar *et al.*, 2013 ; Zohreh and Anita,2014 ;Manimekalai *et al.*,2015 and Eldien *et al.*,2016)**:

$$q_e = K_F C_e^{1/n} \qquad (II.3)$$

Where K_F is roughly an indicator of the adsorption capacity and 1/n of the adsorption intensity and can be written as:

$$\ln x/m = \ln q_e = \ln K_f + 1/n \ln C_e \qquad (II.4)$$

Where x is the amount of adsorbate (mg), m the weight of the adsorbent used (g), q_e or x/m the amount of dyes adsorbed per gram of adsorbent mg/g at equilibrium, C_e the dyes concentration (mg/L) at equilibrium and K_F and n are the Freundlich constants which are related to adsorption capacity and intensity, respectively.

5. Kinetic studies:-
5.1. Pseudo-first-order kinetic model:-

The pseudo-first order kinetic of Lagergren (1898) is given in the form**(Suteu *et al.*,2011 ; Mohamed .2013 ; Arockiaraj *et al.*,2014 ; Hongxiang *et al.*,2016 and Eldien *et al.*,2016)**

$$dq_t/ dt = k_1(q_e - q_t) \qquad (II. 5)$$

After definite integration by applying the initial conditions *t*= 0 to *t* and q_t= 0 to q_t, equation (II.5) becomes:

$$\log (q_e - q_t)= \log q_e - k_1 t /2.303 \qquad (II.6)$$

where q_e and q_t is the amount of dye sorbed per unit weight of sorbent (mg/g) at equilibrium and at time t (min) respectively, k_1 is the rate constant of the pseudo-first order sorption (min^{-1}). The plot of log ($q_e - q_t$) versus t gives a straight line for the pseudo-first-order adsorption kinetics. The values of k_1 and q_e were obtained from the slopes and intercept of the straight lines.

5.2. Pseudo second-order kinetic model:-

The pseudo-second order rate equation (**Ho. 2006 ; Mohamed .2013; Nahal and Azza , 2014 ; Davoud *et al*.,2016 and Fakir *et al*.,2016**) can be expressed as:

$$dq_t/dt = k_2(q_{e2} - q_t)^2 \tag{II.7}$$

Integrating equation (II.11) for the boundary conditions t= 0 to t= t and q_t= 0 to q_t= q_t , gives:

$$1/(q_{e2} - q_t)= 1/q_t + k_2 t \tag{II.8}$$

Where k_2 is the equilibrium rate constant of pseudo-second order sorption (g/mg min). Equation (II.12) can be rearranged to obtain a linear form :

$$t/q_t = (1/ k_2 (q_{e2})^2) + (1/ q_{e2}) t \tag{II.9}$$

The equilibrium adsorption capacity (q_{e2}), (mg/g) and the second-order constants k_2 (g/mg min), can be determined experimentally from the slope and the intercept of plot t/q_t versus t.

5.3. The intraparticle diffusion kinetic model:-

The dyes sorption is usually governed by either the liquid phase mass transport rate or the intraparticle mass transport rate (**Han *et al*.,2008 ; Ho and Mckay,2009 ; Sun *et al* .,2013 ;Frederick *et al* .,2014; Manimekalai *et al*.,2015 Fakir *et al*.,2016**). An intraparticle diffusion model is defined in equation (II.10):

$$q_t = k_i t^{1/2} + C \tag{II.10}$$

Where C (mg/g) is constant and k_i is the intra particle diffusion rate constant (mg/g min$^{1/2}$) which determined from the intercepts and slopes.

6. Thermodynamic parameters:-

The thermodynamic parameters provide in-depth information regarding the inherent energetic associated with adsorption; therefore, they should be properly evaluated.

The thermodynamic parameters such as change in standard free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o) were determined by using the following equations (**Bekci *et al*.,2006 ; Li *et al*., 2010 ; Rahulkumar *et al* .,2014 ; Noureddine *et al*.,2016 ; Dahri *et al*.,2016**):

$$\ln K_d = \Delta S^o/R - \Delta H^o/RT \tag{II.11}$$

$$G^\circ = - RT\ln K_d = -RT\ln \tag{II.12}$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \tag{II.13}$$

where R (8.314 J/mol K) is the gas constant, T (K) the absolute temperature and K_d (l/g) is the standard thermodynamic equilibrium constant defined by q_e/C_e. By plotting a graph of $\ln K_d$ versus 1/T the values ΔH^o and ΔS^o can be estimated from the slopes and intercepts.

Results and Discussion:-

1. Solid state analysis:-

The peanut husk (PH) was analyzed before and after treatment and measured point of zero charge of it. As well as studies of dye sorption are focused on one-component and competition between dyes for sorption sites before and after adsorption. SEM and IR were used to analyze the morphology and chemical groups of the (PH) and (TPH) .

1.1. Scanning electron microscopy (SEM):-

The results of SEM of PH are shown in Fig.III.1 (a-e).Fig. III.1 (a) shows (PH) before treatment and after treatment with tri ethyl amine solution Fig.III.1 (b), it was found that TPH surface occupies with amino groups which modified the surface and increases the positivity of the surface. Fig.III.1(c and d) shows clear protuberances due to good possibility for dyes to be trapped and adsorbed into these pores. The SEM micrographs of (TPH) samples show very distinguished dark spots which can be taken as a sign for effective adsorption of dye molecules in the cavities and pores of this adsorbent Fig.III.1 (e) illustrated that SEM of AV19 and BR2 adsorbed by (TPH)in binary system (**Taha and El-Maghraby,2016).
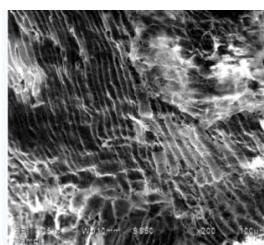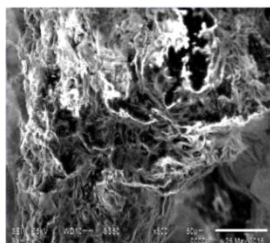
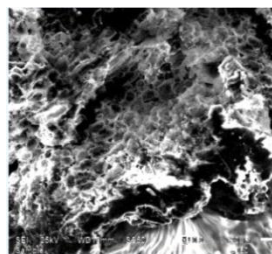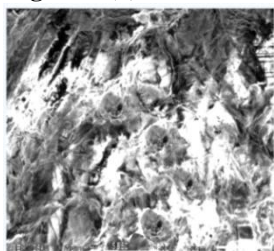| Fig.III.1 (a):PH. | Fig.III.1 (b): TPH. | Fig.III.1(c):AV19 adsorbed on TPH |

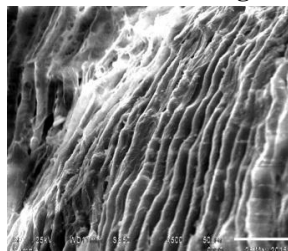

.   Fig.III.1(d):BR2 adsorbed on PH   Fig.III.1 (e):AV19 and BR2 adsorbed on TPH.

Fig.(III.1): The SEM micrographs of (PH) (a) and after treatment (b) and
after adsorption of AV19 (c) and BR2 (d) and after adsorption of
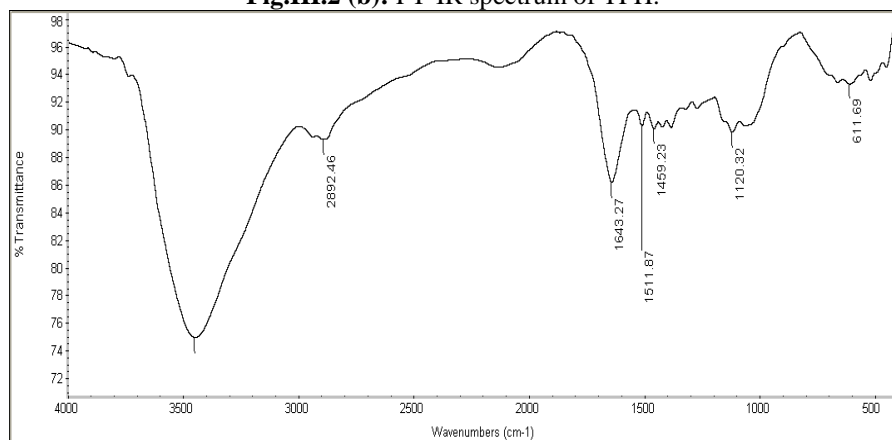binary system (AV19 and BR2)on TPH (e).

### 1.2. Fourier transformed infrared spectroscopy studies:-

The FTIR technique was an important tool to identify functional groups, which are capable of adsorbing pollutant dyes. FTIR spectroscopy was therefore, done for preliminary quantitative analysis of major functional groups presented in PH **(Nahla and Azza,2014)**.

While Fig.III.2 shows the infrared spectra of the PH and TPH. In Fig.III.2(a) the most prominent peak at around $3415cm^{-1}$ was attributed to -OH group and the band at $(2923$ and $1377cm^{-1}$) could be assigned to the C–H asymmetric stretching of methyl group **(Panneerselvam *et al*., 2011;Nahla and Azza, 2014 and Taha and El-Maghraby,2016)**. The band at 1738 cm^{-1} represented contribution from C=O stretching vibration of non-ionic carboxyl group. The band at 1650 cm^{-1} assigned to asymmetric stretching vibration of the C=O bonds of ionic carboxyl group. The presence of absorption peak at 1511 cm^{-1} was confidently to the stretching vibration of the aromatic ring skeleton **(Zhuhong *et al*.,2014 and Binglu *et al*., 2014)**.There are peaks appear at 1265 cm^{-1} due to the asymmetric bending vibration of the -CH3 group and at $(1460$ and $1039cm^{-1})$ corresponds to C-O stretching **(Noureddine *et al*.,2016)**since the peak appears at 596 cm^{-1} due to C-H bend (alkenes) **(Maher *et al*., 2016)**.

Some distinct changes are noted in the spectrum between PH and TPH Fig.III.2 (a and b) where the bands at $(1738,$ 1377 and 1039 $cm^{-1})$ were disappeared but two new peak appears at 1420 and1139 cm^{-1}. Moreover, the peak at 2923 cm^{-1} shifted to 2937 cm^{-1}.These peaks indicate that NaOH treatment in the first stage of the synthesis process further removed some soluble lignin in TPH. Epoxy chloropropane introduced new CH_2 groups to the cellulose molecules. There is a new adsorption peak associated with the stretching vibration of C-N band at$1420cm^{-1}$,and abroad band of the skeletal vibration of the quaternary ammonium salt, which was successfully grafted onto the cellulose skeleton **(Cao *et al* .,2011).**

Fig.III.2(c and d) shows the TPH and PH after AV19 and BR2 molecules adsorbed respectively where some peaks are shifted but some new peaks appear on the other hand some peaks are disappeared.
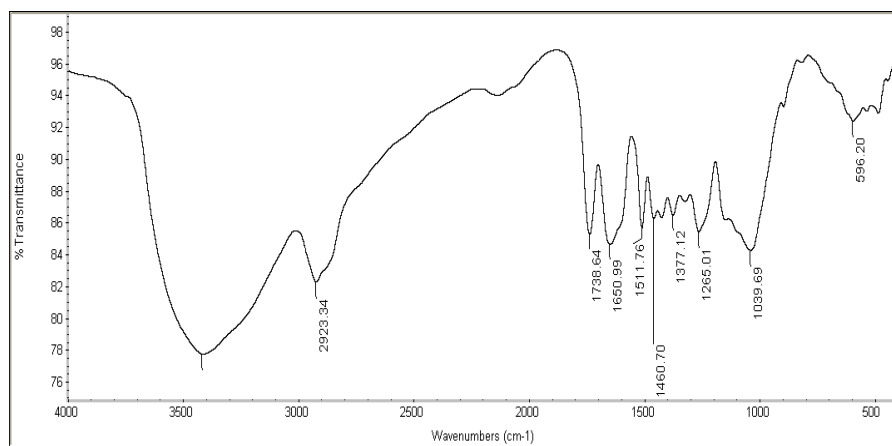
Fig.III.2 (a): FT-IR spectrum of PH.
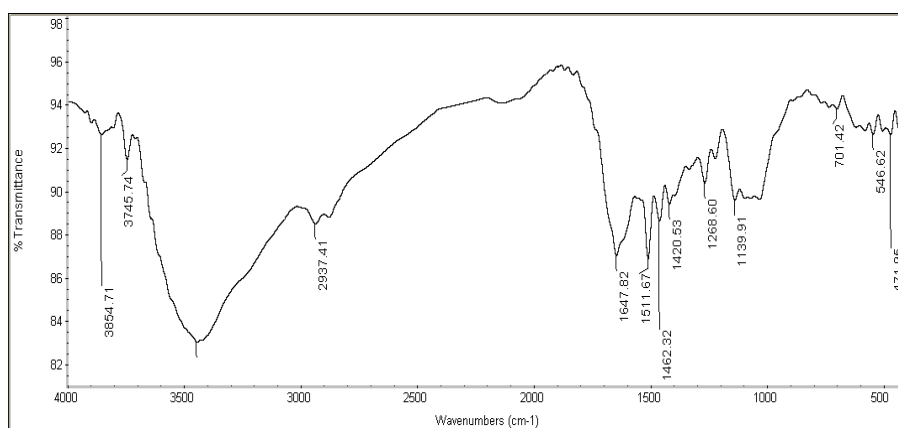
Fig.III.2 (b): FT-IR spectrum of TPH.

Fig.III.2(C): FT-IR spectrum of AV19 adsorbed on TPH.
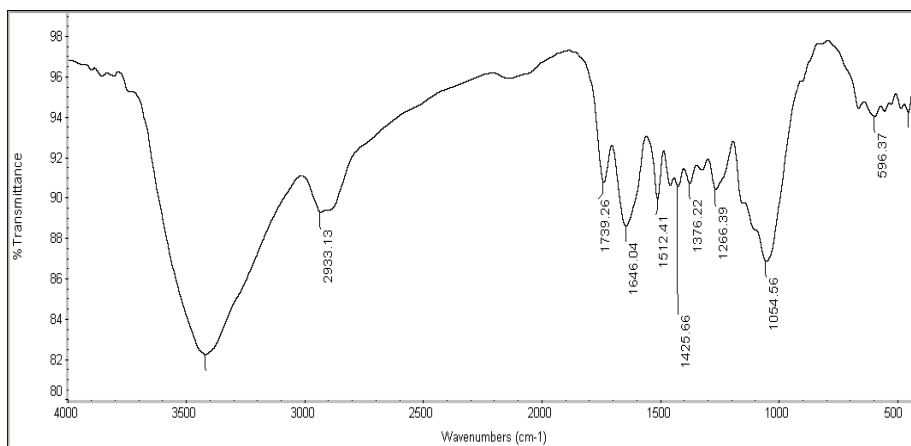
Fig.III.2(d): FT-IR spectrum of BR2 adsorbed on PH.
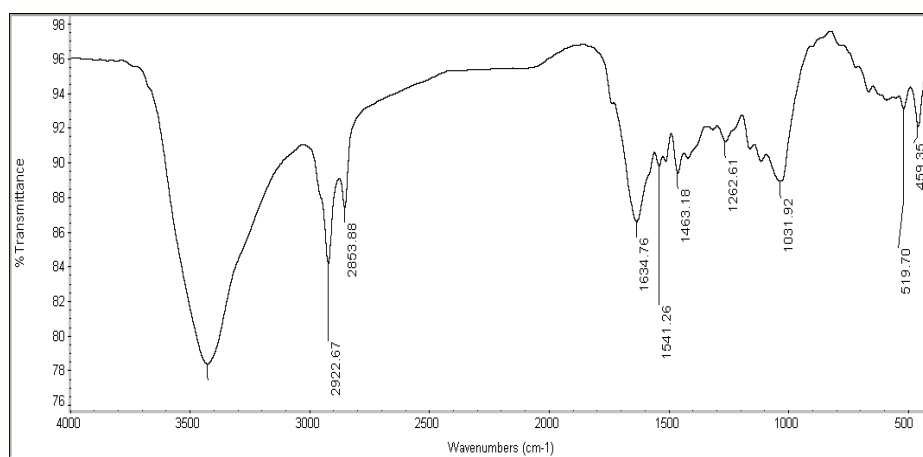
Fig.III.2(e): FT-IR spectrum of binary system adsorbed on TPH.

Fig.(III.2): FTIR spectrum of PH (a) and after treatment (b) and after adsorption of AV19 (c) and BR2 (d) and binary system (e).

1.3 Determination of the point of zero charge of (PH and TPH):-

The point of zero charge (pHpzc) is an important parameter for biosorbent to characterize the sensitivity to the pH and their surface charges, **(Sadaf *et al* .,2013).** The activation of acidic or basic functional groups of adsorbents approaches zero at point of zero charge ,**(Mohamad *et al*.,2012 and Noureddine *et al*.,2016).** The point zero charge of (PH and TPH) was determined and the results are shown in Fig.III.3(a and b). The pHpzc was found to be 5, 8 for (PH and TPH), respectively. Values (5 and 8, respectively) represent pHpzc value, when the sorbent surface was neutral. At values of pH < pHpzc, the sorbent surface is positively charged and susceptible to electrostatic interactions with the polar portions of the anionic dye molecules (dissociated sulphonic groups). At pH > pHpzc, the sorbent surface was negatively charged and was available to bind the cationic dye(dissociated amino groups) **(Daniela *et al*., 2010 and Moawed and El-Shahat,2016).**
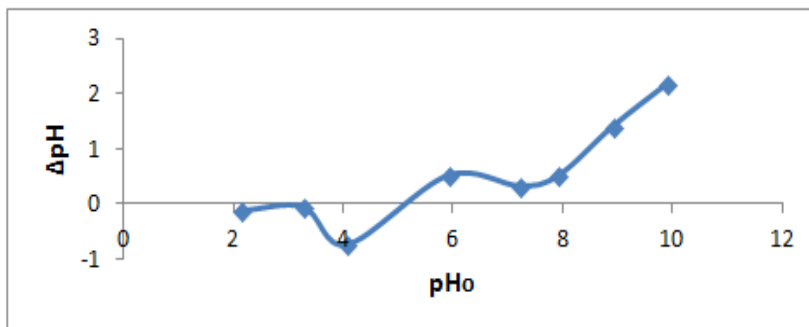
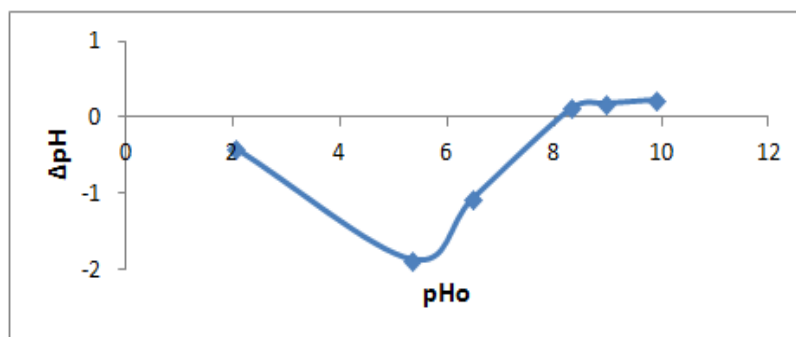**Fig.III.3(a):** The point zero charge of (PH).

Fig.III.3 (b): The point zero charge of (TPH).

2. Effect of some parameters on dye adsorption:-
2.1. Effect of pH on dye adsorption by PH (untreated and treated) in both single and binary dye solutions:-

At low pH solution, the percentage of dye removal will decrease for cationic dye adsorption, while for anionic dyes the percentage of dye removal will increase. In contrast, at a high pH solution the percentage of dye removal will increase for cationic dye adsorption and decrease for anionic dye adsorption **(Ihsan. 2016).** In single system the adsorption of AV19 dye by (PH) is low at pH 0.2. Since the maximum AV19 dye adsorption by (TPH) is at pH 0.5. While the maximum BR2 dye adsorption by(PH) is at pH6. Since BR2 molecules compete with positively charged surface of (TPH), thus a very lower adsorption results expected. However, the adsorptions of AV19 and BR2 by (TPH) in binary system were less than those for the single systems as shown in Table (III.1) and Fig.(III.4). This result indicated that the dye competed with other dye ions for the same sites on adsorbent. For example the sorption of binary dye molecules by (TPH) is based on the electrostatic attraction as postulated
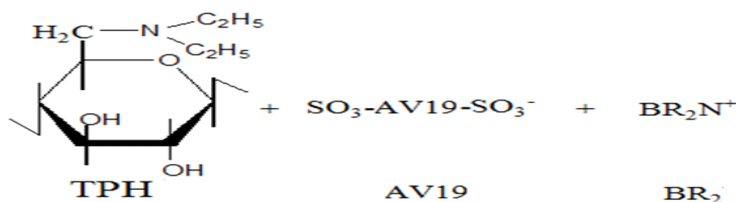
Where $SO_3^- –AV19– SO_3^-$ represents the structure of AV19 and $BR2-N^+$ represents the BR2 dye ion. According to the conversion scheme above, surface group of TPH will bind with each dye. These results reinforce an enhancement of the removal of binary dye molecules by TPH.

Table (III.1): The comparative study of removal percent for AV19 and BR2 by (PH and TPH) in single system and for example between single and binary system by (TPH) ,at (5.85,3.51mg/L) for AV19 and BR2, respectively) and equilibrium time 40 min.

Sorbent	Dye Removal%			
	C.I. Acid violet19 (AV19)**(single)**	C.I. Basic red 2 (BR2)**(single)**	C.I. Acid violet19 (AV19)**(binary)**	C.I. Basic red 2 (BR2)**(binary)**
PH	39.1	89.2	-	-
TPH	97.9	47	59.7	44
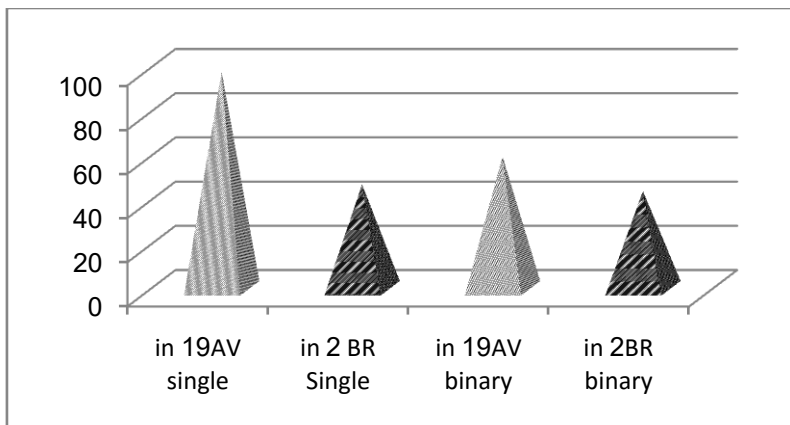
Fig.(III.4): Removal % of (AV19 , BR2) dyes in single and binary system by(TPH) , [dye] 5.85 and 3.51 mg/L, respectively and equilibrium time 40min.

2.2. Effect of initial dye concentration on adsorption by PH (treated and untreated) in both single and binary dye solutions:-

The percentage of dye removal by PH (treated and untreated) decreased with increasing initial AV19 and BR2 dyes concentration. This may be probably as a result of the fact that for a fixed adsorbent dose, the total available adsorption sites remain invariable for all the concentrations checked. With increasing concentration the available adsorption sites become fewer **(Noureddine *et al.*,2016)**. From this study concluded that the less initial dyes concentration (5.85 and 3.51 mg/L) for AV19 and BR2, respectively give the high removal percentage of dye as shown in Fig. (III.5).
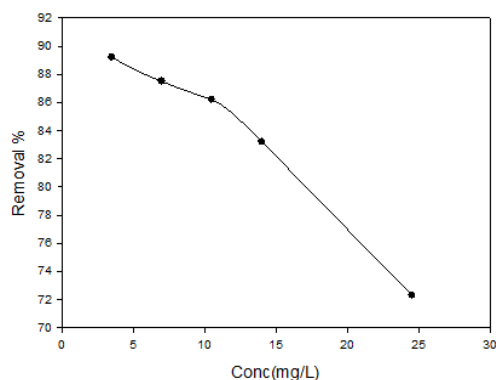
Fig.(III.5): Effect of initial dye concentration on removal percent of BR2 with PH dose 0.75 g of particle size 0.335 mm at pH6, 25°C and 40 min.

2.3. Effect of adsorbent dosage on adsorption dye by PH (treated and untreated) in both single and binary dye solutions:-

The removal percentage of AV19 and BR2 dyes increase with the increasing dosage of PH (treated and untreated) until reached at certain dosage after this dosage take place decrease in removal percentage as shown in Fig.(III.6).Because of the increase in adsorbent dosage lead to increasing in available sorption sites. These results may be due to the overlapping of adsorption sites as a result of adsorbent particle overcrowding **(Garg et al., 2003 and Aseel.2016).** This study show the best dose that give high removal percent is 0.75 g for (PH and TPH) in single system while in binary system the best dose is 1g for TPH.
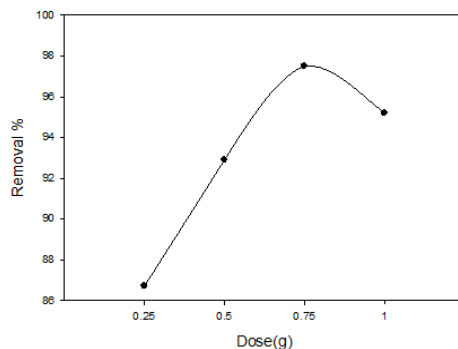
Fig.(III.6): Effect of TPH dose of particle size 0.335 mm on removal
percent of AV19 with initial AV19concentration 5.85 mg/L
at pH5, 25°C and 30 min.

2.4. Effect of temperature on dye sorption by PH (treated and untreated) in both single and binary dye solutions

The adsorption of AV19 and BR2 increases with increasing the temperature as shown in Fig.(III.7) this may be due to increasing the mobility of the dye molecules and an increase in the number of active sites for the adsorption with increasing temperature **(Zohreh and Anita, 2014 and Taha and El-Maghraby,2016).**This study apply at different temperature (30, 50, 70°C) where we concluded that 70°C give the high removal percent.
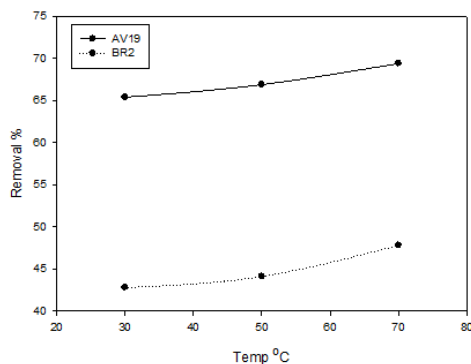
Fig.(III.7): Effect of temperature on removal percent of AV19 and
BR2 with initial concentration 5.85 mg/L and 3.51 mg/L
,respectively and TPH dose 1 g of particle size 0.335 mm
at pH4 and 40 min.

3. Adsorption isotherm:-

3.1. Langmuir adsorption isotherm:-

Assume that the adsorption occurs at specific homogeneous sites within the adsorbent. It also assumes that the adsorption sites on adsorbent have the same affinity for the adsorption of a single molecular layer of dye, with no interaction between the adsorbed molecules of the dye. And from this study the R_L values are between 0 and 1 indicate favorable adsorption and r^2 is 0.99 **(Amir et al., 2016).**

3.2. Freundlich adsorption isotherm:-

Freundlich equation fits in nearly all experimental adsorption – desorption data and is especially useful for data from highly heterogeneous sorbent systems. From the Freundlich isotherm, since the values of $1/n < 1$ in all the sorption processes studied indicate the adsorption was favorable. Where r^2 is lower than that result from Langmuir isotherm. So the data follow Langmuir adsorption isotherm (**Manimekalai *et al*., 2015**).

Table(III.2):Comparison of isotherm parameters obtained for the removal of AV19 on TPH.

The parameters	Langmuir parameters				Freundlich parameters		
	Q_{max} (mg/g)	K_L x10 (cm³/mg)	R_L	r^2	K_F (L/g)	N	r^2
pH	1.08	0.842	0.015	0.996	0.785	4.75	0.990
initial AV19 5.85 Concentration 11.71 17.57(mg/L) 23.42 40.99	9.34	0.085	0.117 0.093 0.057 0.045 0.026	0.997	1.61	2.09	0.995
TPH dose	13.8	0.035	0.06	0.996	3.82	1.31	0.984
Temperature	1.26	0.016	0.0005	0.999	0.807	32.2	0.993

4. Kinetic studies
4.1. Pseudo-first-order model

In this study the correlation coefficients r^2 for the pseudo first-order kinetic model are low indicating a poor pseudo first-order fit to the experimental data. (**Chairat *et al*., 2005; Noureddine *et al*.,2016 ; Davoud   *et al*.,2016**).

4.2. Pseudo-second-order model

The pseudo second-order model is based on the assumption that the rate-determining step may be a chemical sorption involving valence forces through sharing of electrons between adsorbent and adsorbate. The correlation coefficients were all extremely high and all greater than 0.97 indicate that pseudo second-order model is the best model for adsorption and the adsorption process is indicative of a chemisorption mechanism. (**Chiou *et al*., 2004; Chairat *et al*., 2005; Ho. 2006 ;Annadurai *et al*., 2008; Raji and Pakizeh, 2014**).

4.3.The intraparticle diffusion kinetic model

Show two stage the initial stage of the adsorption process within the first minutes indicating also a high affinity between dyes and adsorbent surfaces due to the intraparticle diffusion of dye molecules. Following this phase, the adsorption process slows suggesting a gradual equilibrium, possibly finally, the saturation is reached, and showing the final equilibrium beyond which no adsorption takes place. (**Chairat *et al*., 2008 ; Ejikeme *et al*.,2014and Manimekalai *et al*.,2015**).

Table (III.3): Kinetic parameters obtained for the removal of AV19 on TPH.

The parameters	Pseudo first order model			Pseudo second order model			Intra particle diffusion model	
	q_{e1}(mg/g)	K_1(min⁻¹)	r^2	q_{e2}(mg/g)	K_2(g/mg min)	r^2	K_i(g/mg min⁻¹)	r^2
pH5	1.04	0.201	0.971	1.84	0.311	0.998	0.321	0.835
Initial AV19 concentration 5.85mg/l	1.04	0.201	0.971	1.84	0.311	0.998	0.321	0.835
PH dose 0.75g	1.04	0.201	0.971	1.84	0.311	0.998	0.321	0.835
Temperature 70°c	1.31	0.262	0.996	1.41	0.417	0.998	0.244	0.835

Table (III.4:(Kinetic parameters obtained for the removal of BR2 on PH.

The parameters	Pseudo first order model			Pseudo second order model			Intra particle diffusion model	
	q_{e1}(mg/g)	K_1(min^{-1})	r^2	q_{e2}(mg/g)	K_2(g/mg min)	r^2	K_i(g/mg min^{-1})	r^2
pH6	0.888	0.157	0.966	0.987	0.278	0.999	0.141	0.864
Initial BR2 concentration 3.51mg/l	0.882	0.156	0.967	0.988	0.277	0.999	0.141	0.864
PH dose 0.75g	0.915	0.157	0.966	1.02	0.270	0.999	0.145	0.864
Temperature 70°c	0.821	0.144	0.988	0.995	0.255	0.999	0.141	0.876

5. Thermodynamics of adsorption:-

Evaluated in terms of the thermodynamic parameters, namely, the changes in Gibbs free energy(ΔG^o), enthalpy (ΔH^o), and entropy (ΔS^o) .Where the negative values of Gibbs free energy (ΔG^o) show a spontaneous and favorable adsorption process and standard enthalpy (ΔH^o) for the adsorption process is positive, thus indicating that the process is endothermic in nature and irreversible(**Maher *et al*.,2016**). While the positive value of (ΔS^o) revealed the increased randomness. While the negative value of ΔS^o suggests the formation of ordered activated complex **(Manimekalai *et al*.,2015)** .

Table(III.5):Thermodynamic parameters of BR2, AV19 and binary system adsorbed on PH (untreated and treated) .

Temperature ($^\circ$C)		Thermodynamic parameters		
		ΔG^o (kJ/mol)	ΔH^o (kJ/mol)	ΔS^o (KJ/mol)
Adsorption of BR 2 on PH	30 50 70	-0.317 -0.876 -1.44	8.16	0.028
Adsorption of AV19 on TPH	30 50 70	-3.59 -4.87 -6.16	15.8	0.064
Adsorption of BR2 in binary system on TPH	30 50 70	5.55 5.63 5.71	4.31	-0.004
Adsorption of AV19 in binary system on TPH	30 50 70	3.16 3.11 3.06	3.91	-0.003

Conclusion:-

The present study results showed that the both untreated peanut husk (PH) and treated peanut husk (TPH) have the ability to asorption the dye from the effluent. The pHpzc was found to be 5 for (PH) and 8 for (TPH) .It was found the removal efficiency increased with increase pH until it reached to limited pH then decreased and increase with increase in dose and temperature and decrease with increase in concentration .Where the experimental results fit Langmuir isotherm which indicate to mono layer adsorption and fit also pseudo-second-order which indicate to a chemisorption mechanism and thermodynamic parameters indicated to adsorption process was spontaneous and endothermic in nature. It was also found that the adsorbed species/solute may either block the access to the internal pores or cause particles to aggregate and there by resulting in the availability of active sites for adsorption.

References:-

1. **Alshabanat M ,.Alsenani G. and Almufarij R) .2013 .(**Research Article Removal of Crystal Violet Dye from Aqueous Solutions onto Date Palm Fiber .Chemistry ,.9:1-6.
2. **Arun K., Panmei G. and Uzma N.(2014).** Adsorption Equilibrium and Kinetics of Crystal Violet Dye from Aqueous Media onto Waste Material. Chem. Sci .Rev. and Letters, 3(11): 1-13.
3. **Annadurai G., Ling L.Y. and Lee J.F.(2008).** Adsorption of reactive dye from an aqueous solution by chitosan: isotherm, kinetic and thermodynamic analysis.J. Hazard. Mater., 152(1): 337-346.
4. **Amir H.M., Mehdi V., Mohammad J. M., Anvar A., Bayram H., Amir Z. and Soudabeh P.(2016).** Sodium Dodecyl Sulfate Modified-Zeolite as a Promising Adsorbent for the Removal of Natural Organic Matter From Aqueous Environments. J. health scope.,5(1):1-8.
5. **Arockiaraj I. , Karthikeyan S. and Renuga V.(2014).** Sorption dynamics of acid and basic dyes onto activated carbon derived from ipomoea carnea stem waste. Pelagia Res. Lib., 5(2): 118-123.

6. **Akar E., Altinişik A. and Seki Y. (2013).** Using of activated carbon produced from spent tea leaves for the removal of malachite green from aqueous solution. J. Ecologic. Eng., 52: 19-25.
7. **Aseel M. A.(2016).** Adsorption of crystal violet dye by Fugas Sawdust from aqueous solution. Int. J.Chem.Tech .Res., 9(3): 412-423.
8. **Bharathi K. S. and Ramesh S. T.(2013).** Removal of dyes using agricultural waste as low-cost adsorbents:a review. J.Appl. Water Sci ., 3:773–790.
9. **Bekci Z., Seki Y. and Yurdakoc M.(2006).** Equilibrium Studies for Trimethoprism Adsorption on Montmorillonite KSF. J. Hazard. Mater.,133 :233 – 242.
10. **Babatunde O. O., Adesola B. and Kayode A.(2014).** Adsorption of Malachite Green from Aqueous Solution using Plantain Stalk (Musa paradisiaca).J. Sci. Technol., 15(1):223-231.
11. **Binglu Z ., Wei X., Yu S., Huimin Z., Runping H.(2014).** Adsorption of light green anionic dye using cationic surfactant-modified peanut husk in batch mode. Arab. J. Chem., 10:1-8.
12. **Chairat M., Rattanaphani S., Bremner J.B. and Rattanaphani V. (2005)**. An adsorption and kinetic study of lac dyeing on silk. J. Dyes . Pigm., 64: 231-241.
13. **Chairat M.,Rattanaphani S., Bremner J.B. and Rattanaphani V. (2008).**Adsorption kinetic study of lac dyeing on cotton .J. Dyes . Pigm., 76(2): 435-439.
14. **Chiou M.S., Ho P.Y. and Li H.Y. (2004)**. Adsorption of anionic dyes in acid solutions using chemicallycross-linked chitosan beads. J.Dyes . Pigm., 60: 69-84.
15. **Cao W. , Dang Z., Zhou X., Yi X., Wu P. and Zhu C. (2011).** Removal of sulphate from aqueous solution using modified rice straw: Preparation, characterization and adsorption performance. Carbohydrate polymer.,85:571-577.
16. **Daniela S., Carmen Z. and Marinela B.(2010).** Agriculture wastes used as sorbents for dyes removal from aqueous environments. J. Uni. Agric. Sci . Vet. Medic. Iaşi ., 53 (1):140-145.
17. **Davoud B., Edris B. and Ferdos K. M.(2016).** Equilibrium, Kinetic Studies on the Adsorption of Acid Green 3 (Ag3) Dye Onto Azolla filiculoides as Adosorbent. J. Am. Chem. Sci., 11(1): 1-10.

18. **Dahri M. K., Lim L. B. L. , Priyantha, N. and Chan C. M.(2016).** Removal of Acid blue 25 using Cempedak Durian peel from aqueous medium: Isotherm, kinetics and thermodynamics studies. Int. Food Res. J., 23(3): 1154-1163.
19. **Ejikeme , Ebere M., Ejikeme, Abalu , Benjamin N.(2014).** Equilibrium, Kinetics and Thermodynamic Studies on MB Adsorption Using Hamburger Seed Shell Activated Carbon. Eng. Technol.J., 14(3):74-83.

20. **Eldien I.M., Al-Sarawy A.A., El-Halwany M.M. and El-Msaly F.R.(2016).** Kinetics and Thermodynamics Evaluation of Activated Carbon Derived from peanuts shell as a Sorbent Material. J. Chem. Eng. Process Technol.,7(1):1-7.
21. **Fakir A. S. S., Malak S. A. and Usmani G. A.(2016).** Kinetics Modelling Study: Adsorption of Victoria Blue on Mahaneem Leaf Powder.Int. J. Adv. Sci. Technic. Res.,1(6) :293-302.
22. **Frederick A. , Ufuah. and Maz O. (2014).** Studies on the use of orange peel for adsorption of congo red dye from aqueous solution. Computing, Information Systems, J. Develop. Inform. Allied Res.,5(4):37-44.

23. **Garg V.K., Gupta R., Yadav A.B. and Kumar R. (2003)**. Dye removal from aqueous solution by adsorption on treated sawdust. J.Bioresour Technol., 89:121–124.
24. **Gbekeloluwa O., JamesH. and Dong H.(2014).** Biosorption of Azure Dye with Sunflower Seed Hull: Estimation of Equilibriu, Thermodynamic and Kinetic Parameters. Int. Eng. Res.Develop.,10(6): 26-41.
25. **GuptaV.K. and Suhas.(2009).** Application of low-cost adsorbents for dye removal-a review. Environ. Manag., 90:2313–2342 .
26. **Hamdaoui O. and Chiha M. (2007).** Removal of methylene blue from aqueous solutions by wheat bran. J. Acta Chem. Solv., 54: 407-411.

27. **Han R., Han P., Cai Z., Zhao Z. and Tang M. (2008).** Kinetics and isotherms of neutral red adsorption on peanut husk. J. Environ Sci., 20: 1035-1041.

28. **Ho Y.S. (2006).** Review of Second-Order Models for Adsorption Systems. Hazard. Mater. , 136:681–689.

29. **Ho Y. S. and Mckay G.(2009).** Sorption of dye from aqueous solution by peat. Chem. Eng. Environ. Manag., 90 :710-720.

30. **Hongxiang X., Yongtian W., Gen H., Guixia F., Lihui G. , Xiaobing L.(2016).** Removal of quinoline from aqueous solutions by lignite,coking coal and anthracite. Adsorption kinetics. Physicochem. Probl. Miner. Process. 52(1): 397−408.

31. **Ihsan H. D.(2016).** Acomparative Study for Removal of Dyes from Textile Effluents by Low Cost Adsorbents. J. Mesop. Environ., 1-9.

32. **Li Q., Yue Q., Su Y., Gao B .and Suo H.(2010).** Equilibrium, thermodynamics and process design to minimize adsorbent amount for the adsorption of acid dyes onto cationic polymer-loaded bentonite. Chem. Eng., 158 :489-497.

33. **Lagergren S. (1898).** About the Theory of So-Called Adsorption of Soluble Substances. Kungliga Svenska Vetenskapsakademiens. Handlingar Band., 24(4):1-39.

34. **Maher E. S., Ahmed A. E. and Amal H. M.(2016).** Effectiveness of Sunflower Seed Husk Biochar for Removing Copper Ions from Wastewater: a Comparative Study. J. Soil and Water Res., 11 (1): 53–63.

35. **Mahmudur R. I., Md S. A. and Md W. R.(2014).** Use of Renewable Adsorbent (Peanut Husk) for the Treatments of Textile Waste Water.J .Chem Cheml. Sci., 4 (4): 156-163.

36. **Moaweda E.A. and El-Shahat M.F.(2016).** Equilibrium, kinetic and thermodynamic studies of the removal of triphenyl methane dyes from wastewater using iodo polyurethane powder. J.Taibah Uni. Sci., 10 :46–55.

37. **Mohammad A. H. and Md S. A.(2012).** Adsorption kinetics of Rhodamine-B on used black tea leaves. Environ. Health Sci.Eng.,9(2):1-7.

38. **Mohamad A. M. S., Dalia K. M., Wan A. W. A, Azni I.(2011).** Cationic and anionic dye adsorption by agricultural solid wastes: A comprehensive review. Desali., 280 :1–13.

39. **Mohamad R. M., Salman M. S., Sara K. Y. and Soraya H.(2012).** Equilibrium and Kinetic Studies of Safranine Adsorption on Alkali-Treated Mango Seed Integuments . Chem. Eng . Appl.,3(3):160-166.

40. **Mohammed B. A.(2014).** Removal of Textile Dyes (Maxilon Blue, and Methyl Orange) by Date Stones Activated Carbon. Int. J. Advan. Res. Chem. Sci., 1(1): 48-59.

41. **Mohammed M.A., Shitu A. and Ibrahim A.(2014).** Removal of Methylene Blue Using Low Cost Adsorbent. Chem. Sci., 4(1): 91-102.

42. **Manimekalai T. K., Sivakumar N. and Periyasamy S.(2015).** Real-world mixed plastics waste into activated carbon and its performance in adsorption of basic dye from textile effluent. Digest. J. Nanomater .Biostru.,10(3): 985–1001.

43. **Mohamed M.E.(2013).** Kinetics and Thermodynamics of Activated Sunflowers Seeds Shell Carbon (SSSC) as Sorbent Material. Chromat. Sep.Techniq.,4(5):1-7.

44. **Nahal. and Azza.(2014**).Characterization of peanut hulls and adsorption study on basic dye: iso-therm and kinetic analysis. Int.J. Innov Res. Technol. Sci.,2(2):9-18.

45. **Noureddine B.,Hassiba M., Zahra S. and Mohamed T.(2016).** Biosorption of cationic dye from aqueous solutions onto lignocellulosic biomass (Luffa cylindrica): characterization, equilibrium, kinetic and thermodynamic studies. Int. J. Ind Chem.,1-14.

46. **Oladoja N.A. and Aliu Y.D.(2009).** Snail Shell as Coagulant Aid in the Alum Precipitation of Malachite Green from Aqua System. J.Hazard. Mater.,164: 1496-1502.

47. **Panneerselvam P., Morad N. and Tan K.A.(2011).** Magnetic nanoparticle (Fe 3 O 4) impregnated onto tea waste for the removal of nickel (II) from aqueous solution. J. Hazard Mater., 186:160.

48. **Pragathiswaran C., Anantha K. N., Mahin A. B., Govindhan P. and Syed A. K.A.(2016).** Adsorption of methylene blue dye using activated carbon from the gloriosa superba stem. Int. J. Res. Pharm.Chem., 6(1): 95-103.

49. **Rahulkumar M., Tonmoy G., Chetan P., Anupama S., Kaumeel C., Imran P., Arup G. and Sandhya M.(2014).** Biosorption of Methylene Blue by De-Oiled Algal Biomass: Equilibrium, Kinetics and Artificial Neural Network Modelling. Plos One.,9(10):1-13.

50. **Raji F. and Pakizeh M. (2014).** Kinetic and thermodynamic studies of Hg(II) adsorption onto MCM-41 modified by $ZnCl_2$. J. Appl. Sur. Sci., 301:568-575.

51. **Sadaf S., Bhatti H., Ali S. and Rehman K .(2013).** Removal of Indosol Turquoise FBL dye from aqueous solution by bagasse, a low cost agricultural waste: batch and column study. Desali. Water Treat., 52: 184–198.

52. **Sara D. and Tushar K. S. (2014).** Review on Dye Removal from Its Aqueous Solution into Alternative Cost Effective and Non-Conventional Adsorbents. J. Chem . Proc Eng .,1: 104.

53. **Smitha T. and Santhi T.(2015).** Adsorption of Acid violet-17 from Synthetic aqueous Solution on Two kinds of Cucumissativus L. Peel adsorbent. Res. Chem. Environ.,5(2):35-43.

54. **Sun D., Zhang X. ,Wu Y. and Liu T.(2013).**Kinetic mechanism of competitive adsorption of disperse dye and anionic dye on fly ash. Environ. Sci. Technol., 10:799-808.

55. **Suteu D., Zaharia C. and Malutan T.(2011).**Removal of Orange16 reactive dye from aqueous solutions by Waste sunflower seed shells. Serb. Chem. Soc.,76(4):607-624.

56. **Sohn S. and Kim D.(2005).** Modification of Langmuir isotherm in solution systems definition and utilization of concentration dependent factor. Chemosphere., 58:115–123.

57. **Taha N.A. and El-maghrabyA.(2016).**magnetic peanut hulls for methylene blue dye removal: isotherm and kinetic study. Global Nest J., 18 (1): 25-37.

58. **Xiaoyu. Z., Jia .T., Xinhao. W. and Lijuan .W.(2013).** Removal of Remazol turquoise Blue G-133 from aqueous solution using modified waste newspaper fiber. Carbohydrate Polymers ., 92 : 1497– 1502.

59. **Zamouche M. and Hamdaoui Q. (2012).** Sorption of Rhodamine B by cedar cone: effect of pH and ionic strength. J. Energy Procedia ., 18: 1228-1234

60. **Zhuhong D., Rui Y. , Xin H. and Yijun C.(2014).**Adsorptive removal of Hg (II) ions from a queous solutions using chemical-modified peanut hull powder. Pol. J. Environ. Stud., 23(4):1115-1121.

61. **Zohreh S. and Anita M.(2014).** Equilibrium Modeling and Kinetic Studies on the Adsorption of Basic Dye by a Low Cost Adsorbent**.** J. Phys.Chem . Electrochem.,2(2):10-23.