Studying the use of vegetable waste (pineand cypresscones) as adsorbent in industrial water purification

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Abstract: In this paper, the adsorption of some dyes onto Pine Cones (PC) and cypress Cones (CC) was investigated in aqueous solution ,which was used in natural and carbonized forms as an eco-friendly and low-cost.Physical treatment of Pine and cypress Cones, with cones carbonization process(CPC,CCC) were also tested as alternative adsorbents for the removal of Methylene Blue from aqueous effluents.Surface study of (PC),(CC)was investigated using Fourier transform infrared (FTIR).Various physiochemical parameters were investigated in a batch-adsorption technique where adsorbed amount on the cones increased with an increase in the dye initial concentration and contact time, but the adsorbed amount decreased with increasing the amount of the adsorbent .Equilibrium and isotherms were analyzed using Langmuir andFreundlich adsorption models. The results indicated that isotherm data of Methylene Bluefollowed Freundlich isotherm model for natural and for carbonized Cones .the pseudo-first order and the pseudo-second order were used todescribe the kinetics data. The experimental data for natural and carbonized Cones fitted well to the pseudo-second order kinetics model It can be concluded that (PC), (CC),(CPC) and(CCC)could be effectively employed as an effective adsorbent for the removal of dyes.

Keywords : Pine Cones and cypress Cones, Methylene Blue, adsorption isotherms, Equilibrium kinetics.

1. Introduction

The dye house water residues Constitutebig threat to the environmentwhere sewage, sanitation, soil and groundwater were polluted by metal salts and pigmentary and organic pollutants, which are harm to the environment and there is difficult to get rid of them if not treated from start to flow[1] Dyes have been used as colorants at different industries such astextile, food, paper, cosmetic, etc[2].More than 0.7 million tons ofsynthetic dyes are produced annually worldwide. In addition, over10,000 different dyes and pigments have been applied in thoseindustries. Researches indicate that approximately 15% of producedsynthetic dyes per year have been lost during processing operationsthat involve the production and handling with many organiccompounds hazardous to human health[2]

Wastewaters of dyeproduction and application industries present an environmentalproblem because of the aesthetic nature due to the fact that thecolor is visible even in a low dye concentration[2] Also these dyes may drastically affect photosyntheticphenomenon in aquatic life due to reduced light penetration[3] The textile industry consumes large quantities of water at its different steps of dyeing and finishing, among other processes. The non-biodegradable nature of dyes and their stability toward light and oxidizing agents complicate the selection of a suitable method for their removal[2] In addition, toxicity bioassays have demonstrated that most of them are toxic.

Several methods such as membrane, electrochemical,coagulation/flocculation, biological, etc. have been used for dye removal from wastewater[2]. Among the treatment methods, adsorption is considered to be relatively superior to other techniques because of low cost, simplicity of design, availability and ability to treat dyes inmore concentrated form[2] Many techniques have been used to treatment the dye house water, including: technology adsorption using Rzenat exchange ion because most dyes carry a negative or positive charge, and

technology oxidation where both of the water oxygen and ozone is used alon with ultraviolet rays, chlorine and dichlorobenzene dioxide, which is effective against all dyes and the use of reagent Vuitton (water Aoxgeni existence of iron ц ions) for the treatment of active and direct dyes[1] and The research of the recent years mainly focuses on utilizing agricultural naturalmaterials as lowcost and available adsorbents[2].Activated carbon ,has been widely studied and proved to have high adsorption abilities to remove a large number of organic compounds[3],is composed of a microporous, homogenous structure with high surface area[4] Nowadays, there is a great interest in finding inexpensive and effective alternatives to the existing commercial activated carbon[4]

Studies on porous solid surfaces was conducted in a common way of contaminated water purification. where in the table (1) proved researches on porous surfaces can take advantage of these shells as adsorbent in dye house water purification instead of throw it ,A literature review showed that Pine Cone was not used to remove dyes from colored wastewater,this was to be of interest in these cones because pinetrees most plants in the world. The ratio to the total of other types of trees 19%[5] In this study, used as a natural pine and cypress cones as naturaladsorbent to removeMethylene Blue dye from the solution

The objective of this work was to investigate the potential of using pine and cypress cones as an agricultural waste, that are not utilized and usually threw with waste as a cheap adsorbent as adsorbent in the removal of the basic dye (methylene blue) from aqueous solutions and replacing it by effective coal, inorganic ionic exchangers and others expensive, that by determining the chemical structure of these cones (pine and cypress cones) before carbonization process (PC,CC)and after carbonization process (CPC,CCC) that for to determine the best conditions for the best of dye removal amount for reduce as much as possible from harm on the environment, Where the effective factors such as the amount of adsorbent, the concentration of dye, ph, kinetics of adsorption, adsorption isotherm were studied to evaluate the adsorption ability (capacity) the Cones , the dye removal ratio was compared between carbonized cones and   natural cones then compare features and cost both cases.

Table (1) some of theused wastein theadsorption of Basic dyes

Adsorbentdye Maximum adsorption capacity (mg/g		
Peat	Basic blue 69	184–233 [3]
Flyash Methylene Blue	4.48 [8],[3]	
Pyrophyllite Methylene Blue	70.42 [8]	
Banana peel Methylene Blue 20.8 [3]		
Banana peel	Methyl orange	21.0 [3]
Baggase pith	Basic blue 69	152±5 [3]
Baggase pith	Basic red 22	75±2 [3]
Indian Rosewood sawdust (sulphuric acid treated) Methylene blue	24.3 [3]	

2.   Materials and methods of research

2.1 Preparationof dye (adsorbate):

Basic dye used in this study was methylene blue (MB) purchased from REACHIM company made in USSR methylene blue Dye used in dyeing yarns and fabrics, that is uesing for dyening acrylic , The maximum absorption wavelength of this dye isλmax =660nmusing (UV–Visible spectrophotometer) device within the domain (400-800nm), thePH =7.55,The structure of MB is shown is fig .1$C_{16}H_{18}C_1N_3S.XH_2O$,The MB was chosen in this studybecause of its known strong adsorption onto solids, a series of standard (2-3-4-5 -6) mg / l of dye were prepared, then absorbance was recorded for each concentration, then Calibration curves were plotted between absorbance and concentration of the dye solution, experiments have been conducted on the dye concentration's =2 mg/l to study dye's ability onto two cones adsorption and the results were evaluated by observing the disappearance of solutions color after adsorption
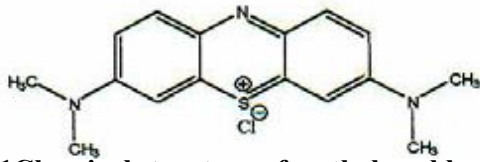
Fig .1Chemical structure of methylene blue.

2.2 Preparation of adsorbent:

The pine and cypresscones used was collected from Syria ,that were washed   thoroughly with distilled water to remove the surface adhered   particles and water-soluble materials,Then the cones were sliced, spread on trays and dried by dryer at 70 ◦C for 24 hours,The dried slices were ground and sieved to obtain a particle size range of 630μmand stored in plastic bottle for use and pine cones were given name for using easyer (PC) and cypress cones (CC).

After the previous work,the department of cones was taken and conducted on it carbonizationprocessby device(030509   3000,w)by placingeachtypeofraw material(cones) separately within closed metal cylinder closed then introduced in the oven400-450◦Cfor 4 hoursafter thewarm uptime thensieved to obtain a particle size range of 630μm and stored in plastic bottle for use, the carbonized pine cones were given name for using easyer (CPC) and cypress cones (CCC) ,asan analysis of theconeswas conductedusingthe infrared deviceto determine thechemicalstructure of theconeswhere the spectra were recorded from 4000 to 400 cm−1**(I R (FT/IR-4200,fourier Transform)** As well as Real density (g/cm3) and Apparent density (g/cm3 were calculated.

2.3 Adsorptionkinetics

The batch adsorption experiments were carried out in 250-mL Erlenmeyer flasks where 1 g of the adsorbent and 100mL of the MB solutions (2 mg/L) were added. The pH of all solutions in contact with adsorbents was found to be in the range 7.55, The Erlenmeyer flasks were subsequently capped at 25 ◦C and taken batch samples after5-10-15-20-30 min the 30 min to achieve equilibration. The concentration of MBin the solution after equilibrium adsorption was measured by a double beam UV–vis spectrophotometer (2120,UV) at 660nm. The amount of adsorption at equilibrium, qe (mg/g), was calculated by

$$qe = \frac{(C_0 - C_e) * V}{W}$$

where C_0 and C_e are the initial and equilibrium dye concentrations in mg/L respectively, V is the volume of solution (L) andW is the mass of the cones adsorbent (g), the amount ofadsorption at time t, qt (mg/g) was calculated by then   repeat the same conditions by adding the agitated in an isothermal shaker at 200 rpm and again without agitated but using ultrasonic waves and finally reiterates previous operations on carbonized cones , the % ratio of dye removal in the three mechanisms was compared between natural and carbonized cones.

To study The effect of adsorbent dosage were mixing different amounts of cones (1,2,3,4) g inErlenmeyer flaskscontaining 100 ml of dye solution (2 mg / l Methylene Blue) at 25 ◦Cand value of pH = 7.55 and wavelength = 660 nm for dye then taken samples after5-10-15-20-30min, as well as repeat this on the carbonized cones.

As well as the adsorption experiments carried out at different concentrations of the dye using 1 g of adsorbent at the PH solution, temperature= 25   and contact time = 30 min , the dye concentration   was determined by using UV / Vis spectrophotometer device , the dye removal % ratio was calculated after periods 5-10-15-20-30min during adsorptionAnd also studied the adsorption at different pH (2-12),The pH of the solution was adjusted using H_2SO_4 or NaOH.,repeated of the carbonized cones.

Kinetic studies of adsorption were also carried out at various concentrations of the MB where in the extent of adsorption was investigated as a function of time. The amount of adsorption at time t, qt (mg/g), was

calculated by

$$qt = \frac{(C0 - Ct) * V}{W}$$

where C_0 and C_t (mg/g) are the liquid phase concentrations of the dye at initial and any time t, respectively. V is the volume of solution (L) and W is the mass of the conesadsorbent (g) [4]

The Adsorption was plotted in constant temperature for describe how the dye is binding on the surface of adsorbent , the four models were applied on obtained results in practice to finding the nearest model , both the Langmuir and Freundlich model and the pseudo-first order and pseudo-second order .therefor the analysis of the results that were applied of these models gives described of the best model can be described adsorption process by the following equations Table (2),(3).

Table (2) adsorptionkineticsmodels

Kinetic adsorption models				
Kinetic model	**Differential equation**	**Integrated equation**	**Non-linear equation**	**Ref.**
Pseudo-first order	dq/dt= kf(qe − qt)	Ln (qe −qt)=Ln (qe)−kft	qt = qe[1−exp (−kft)]	[9]
Pseudo second order	dqt/dt=ks(qe − qt)	$qt = \frac{ks\ qe^2t}{1 + ksqet}$	$qt = \frac{ks\ qe^2t}{1 + ksqet^2}$, ho = ksqe2	[9]

Table (3) adsorption isotherm models

Isotherm model	Equation	Ref.
Langmuir	qe= $\frac{QmaxKLCs}{1 + KLCs}$	[9]
Freundlich	qe= $\frac{KFC}{1/n}$	[9]

3.   Results and Discussion

3.1   Physical and chemicalproperties :

The first step of this work was a preliminary characterization of the adsorbent (pine cones and cypress cones) in order to understand the process of adsorption and the way that they interact with the surrounding medium. four samples of adsorbent PC,.CPC,CC and CCC were used in the experiments

Physical and chemical characterization for the carbonized conesand naturalcones were studied, where Real density calculated by putting 2g from the each cone in the density flask and weighed with its contents then filled with distilled water to the middle and was shaken for a quarter of an hour, and then the density flask was weighed and the density law was applied in the table (4) ,as well as calculating Apparent density by putting 2 g of each cone in the cylinder and was shaken to get rid of the spaces and then read the volume of the cones inside the cylinder then calculated the Apparent

Table (4) physical properties ofPC, **CPC**,**CC and CCC**

Properties	pine		Cypress	
	naturalconesPC	**Carbonized conesCPC.**	**naturalcones CC**	**carbonizedconesCCC**
Real density (g/cm3)	1.07527	1.10497	0.6211	0.8511
Apparent density (g/cm3)	0.32258	0.338983	0.38462	0.43478

Chemical properties of the cones :

Chemical characterization of the adsorbent surface was performed by FTIR analysis. The spectrum (Fig. 1) identifying the chemical composition of the cones (PC.,CPC,CC and CCC) by using FT- IR in the field (450-4000).

(a)   (b)
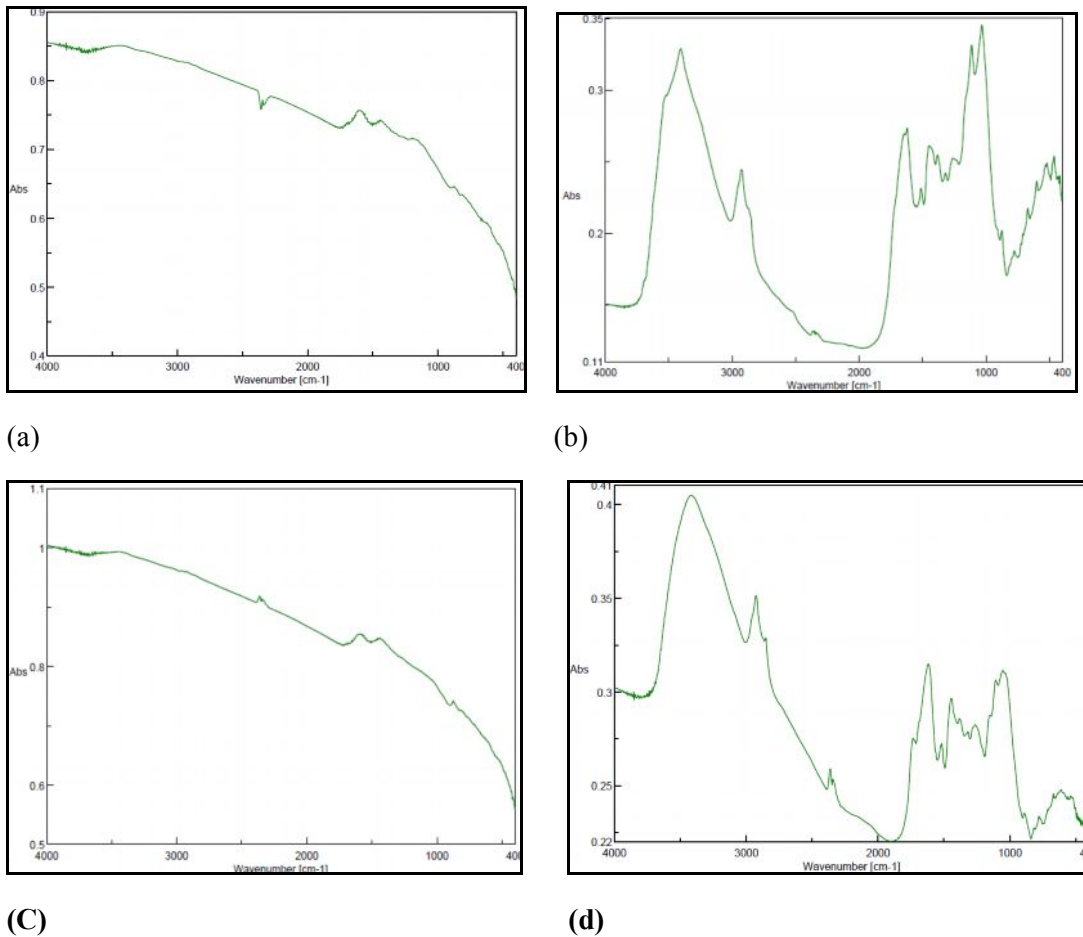
(C)   **(d)**
Fig.**2The FTIR spectrum of PC (a)**,**CPC(b)**,**CC(c)**, **and CCC(d)**

The FTIR spectrum of naturalPine cones (PC) given in Fig. 2 a shows peaks **at**(3406.64, stretching vibrations) O-H[2,9,10,11] The width of this band indicates thepresence of strong hydrogen bonds[12], C-H AL (2927.41, stretching vibrations[9,10,11], C = O [(1626.661 ,stretching vibrations) [10,11] or C = O (Amide)] [2] and N-H (1512.88, bending vibrations)[2] or C = C Ar[9],C-H (1321.71, bending vibrations[2] andC-N (stretching vibrations, 1261.22) [11] orN-H bending[12],AndC-O (stretching vibrations, 1115.62) [2] C-Oacid[10] C-Ophenol[1] ,C-Hn aliphatic or aromatic bonds, (800-900),And The FTIR spectrum of natural Cypress cones (CC) given in Fig. 2 a shows peaks **at** (3413.39, stretching vibrations) O-H, (2926.45, stretching vibrations) C-H AL, C = O (stretching vibrations, 612.288 or Amide C = O; and carbonyl) N-H (1518.67, bending vibrations) or C = C Ar, C-H (1379.82, bending vibrations) and C-N (stretching vibrations, 1261.22) or N-H (bending ,And C-O (stretching vibrations, 1104.05 ,C-O acid ,C-O phenol ,C-Hn aliphatic or aromatic bonds, (800-900[15]

Pine cone is composed of epidermal and sclerenchyma cells which contain cellulose, hemicelluloses, lignin, rosin, and tannins in their cell walls which contains polar functional groups such as alcohols, aldehydes, ketones, carboxylic, such as alcohols, aldehydes, ketones, carboxylic, phenolic and other groups[11,10] the elemental analysis showing aromatic rings that can be potential biosorption sites for interaction with the dyes[9.] this model features a separate Association of C-O in various different phenols, This splitting pattern is characteristic of several different C–O bonding of different phenols, indicating that Brazilian pine-fruit shell is rich on tannins[9],And can be seen in fig .2 there are not peaks due to during carbonization process a lot of elements noncarbonic such as oxygen and hydrogen is exiting shaped aeroplane gases by thermic disintegration way for solid material but the remaining carbonic atoms are arranging self it in sheets and this sheets left distance called pores, this pores making the carbon as excellent porosity material[16]

3.2 Adsorptionkinetics

3.2.1 Effect of different parameters on the dye adsorption processes

The effectiveness of adsorption was compared in three mechanisms the Decantation, the stirring and ultrasound waves (from WhaledentBiosonic) and the best mechanism was chosen for the study where the batches taken from the solution every 5 minutes for a half-hour that concentration = 2 mg/l of Methylene Blue dye, where stirring speed of 200, the mass of adsorbent m = 1g, and temperature T = 25 C, PH =7.55 t=30,and the dye removal ratio % was compared in the three mechanisms for each cone following table (5)

Table (5) the Dye removal (%)of Methylene blue dye in the three mechanisms for PC,.CC,CPC, and CCC

cones	Pine		Cypress	
Dye removal (%)	natural cones PC	carbonized cones C PC	natural cones CC	carbonized cones CCC
stirring	71.27	66.5865	61.627	76.42019838
Decantation	60.99	55.2206	60.8433	61.28644424
ultrasound waves	36.13	60.391566	60.8433	17.25903614

(a)   (b)

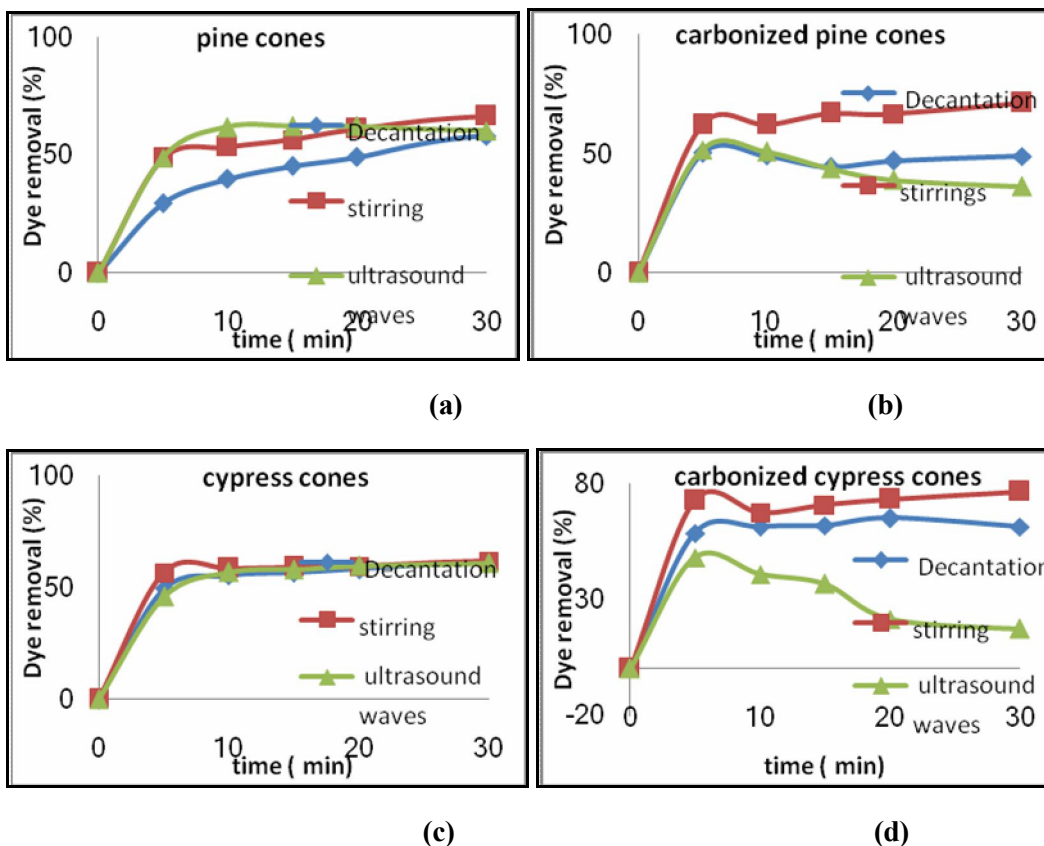(c)   (d)

Fig. 3the Dye removal (%)of Methylene blue dye in the three mechanisms for PC(a),CPC(b),CC(c),and CCC(c)

The Experiments showed by comparing the Methylene Blue removal ratio on the conesbetween the Decantation and the stirring and ultrasound waves , the stirring (200 =rpm)was better than from other mechanisms and the adsorption removal ratio for carbonized cones was high from naturalcones where Dye removal (%) 71.27,76.420 for carbonized pine cones and carbonized cypressrespectively. cones As can be seen from fig(3) and table 5 indicates Fig. 3that while the adsorption of dyes was quite rapid initially, the rate

of adsorption became slower with the time and reached a constant value (equilibrium time). The initial faster rate may be due to the availability of the uncovered surface area of the adsorbents. [4]

3.2.2 Effect of the amount of adsorbent

The effect of PC,CPC,CC,CCCdosage on the amount of dye adsorbed was investigated by contacting 100 mL of dye solution with initial dyeconcentration of 2 mg/L at room temperature (25°C) at pH 7.55 for 30 min. Different amounts of cones (1,2,3,4 g) were applied ,The plots of adsorbed amount (qe) at different adsorbent dosage are shown in Fig. 4.
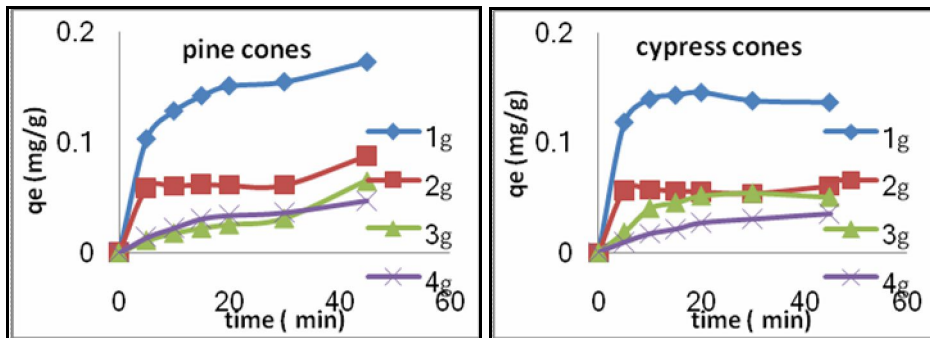

(a)   **(b)**

Fig.4 The effect of adsorbent dosage on dye removal on PC (a) CC, (b)(pH 7.55, T 25 °C and C_0: 2 mg/L).

It was observed that the amount adsorbed, qt (mg /g-1)decreased with an increase in the amount of the adsorbent. The latter trend may be due to the effect of adsorbent mass on porosity of the adsorbent suspension. In general, the trends might have been influenced by changes in a number of physical properties of the solid liquid suspensions including their viscosity[7].A given mass of shell can adsorb only a fixed amount of adsorbate. So the initial dosage of adsorbed solution is very important[2], Thiswasidenticalin[7] whenchangedthe amountofadsorbent(2-10 g / l)for constant dye concentration of 25 mg/L, the adsorbed amount decreased from 11.63 to 2.38 mg g_1 as the adsorbent mass was changed from 2 to 10 g/L[7]

Thus, adsorbed amount on the cones decreased with increasing the amount of the adsorbent that's compatible with dyes (Maxilon blue GRL, direct yellow DY 12) adsorbed on coconut husk[4] and[7]

3.2.3 Effect of the initial concentration of the adsorbate

The effect of initial dye concentration on dye removal was studied. Experiments were done on carbonized cones and naturalcones at different dye concentrations (2 ,3,4 , , 5 mg/L) (adsorbent mass (1 g), pH 7.55and100 mL dye solution). The dye removal increases by increasing the initial dye concentration as shown in Fig.5.
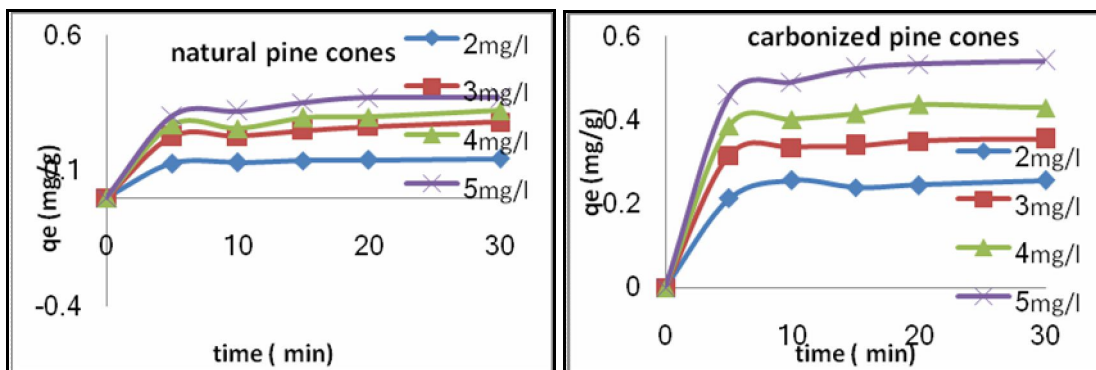
(a)   **(b)**
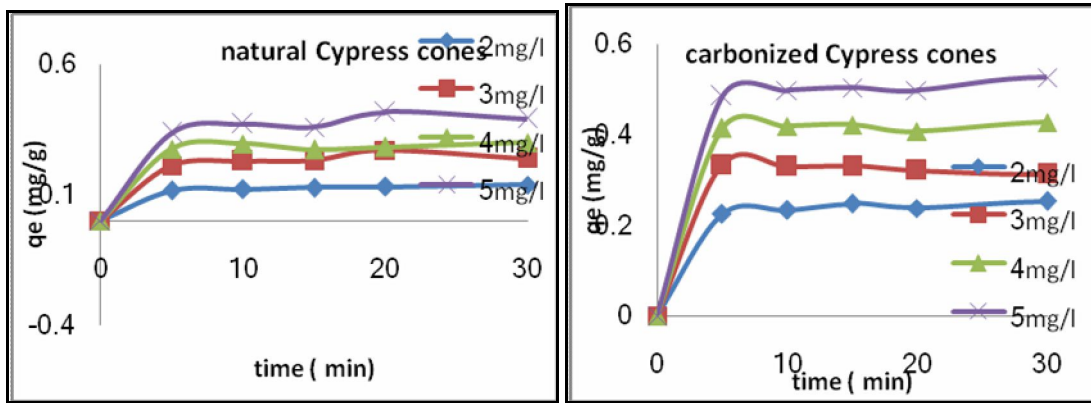
(c) **(d)**

Fig.5 **Effect of initial concentration on removal of MB byPC. (a),CPC(b),CC(c), and CCC(d) (conditions: adsorbent dosage, 1 g; initial pH, 7.55; temperature, 25 °C).**

Results showed that the amount of adsorbed increases with initial concentration that due to decreased the activesites in adsorbent because increase the initial concentration[7] The initial concentration provides an important driving force to overcome all mass transfer resistances of the MB between the aqueous and solid phases. Hence a higher initial concentration of dye will enhance the adsorption process[13] we found that the adsorption in different concentrations be fast in the initial stages and decreases gradually progress adsorption even get to Equilibrium. this corresponds to adsorption Methylene Blue dye on coconut husk at 0.2 g and rpm = 100, and PH = 7 and T = 30[13],Also this is compatible with the[7] When extract 2 g of 25 ml / l in T=300kthe adsorbed amount increased from (11.63 to 30.66 mg / g)when increasing the initial concentration of (25 to 70 mg / l) so   the adsorbed amount increased with increasing concentration[7] also found the adsorbed amount increased the of the   from 30.42-65.55 mg / g when increasing initial methyleneblue concentration of 50-500 mg / l[13]

Thus, adsorbed amount   on the cones increased with an increase in the dye initial concentrationas early reported[7] and   contact time, but the adsorbed amount decreased with increasing the amount of the adsorbent that's compatible with dyes (Maxilon blue GRL, direct yellow DY 12) adsorbed on coconut husk[4] and[7]

3.2.4Effect of solution pH on dye adsorption

The effect of ph on color removal ratio was studied on ph (2 - 6 - 10-12) , The pH of the solution was adjusted using H_2SO_4 or NaOH.using PH METER (SELECTA-2005 from SPAIN .) at 25 °C, 200 = rpm, 2mg / l of Methylene Blue dye concentration and   particles size630μm, The results of blank dye solution studies indicate that change of the initial pH (pH 2–12) of dye solution has negligible effect on the λmax of AB26, AG25 ,AB7,DR80, DR81, AR14 AB92[2-3].

This observation provided proofs that, at this range of pH, there is not any chemical structural change of dye molecules and in all cases no hydrolysis of dyes occurring. Based on this observation and assuming negligible dissociation of adsorbent, the pH of all dye solutions were reported as initial pH and pH control during all experiments was ignored[3].
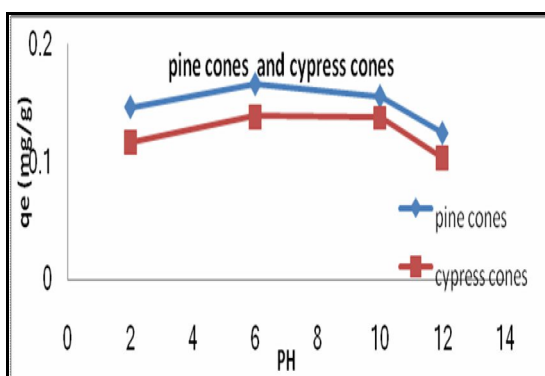
Fig. 6 Effect of the solution pH on the adsorption of methylene blue on pc,CC, (C_0 = 2 mg/L, temperature 25 °C, stirring rate 200 rpm and m= 1 g).

Through Fig (6), the adsorbent amount of Methylene Blueby pine cones and cypress cones increased as pH from 2.0 to 6.0 but decreased as pH increased from 10.0 to 12.0. However, the adsorption remained constant within the range of pH 6.0-10.0 that is similar to[7] that is shown the extent of removal of a basic dye (Basic Red 18) by activated clay decreased rapidly as pH increased from 3.0 to 5.0 and from 8.0 to 10.0. However, the adsorption remained constant within the range of pH 5.0-8.0. It was suggested that the increase in adsorption depended on the properties of the adsorbent surface and the dye structure. At a lower pH, the adsorbent surface might have become negatively charged attracting more of the basic dye molecules. Itis likely that positive charge develops on the surface of an adsorbent in an acidic medium, resulting in a higher adsorption of anionic dyes than in a basic solution. If this is the case, the sorption of the cationic dye should decrease at a lower pH. In addition, the effect of pH may also be explained on the basis of surface hydroxylation, acide base dissociation and surface complex formation.[7]

[7]have reported for the granulated activated carbon (GAC) adsorbent that the chemical nature of the surface is influenced by solution pH, which therefore plays an important role in the adsorption of solutes from aqueous solutions. At a lower pH, the molecular form is the predominantly adsorbed species, while at a higher pH, the ionized form is preferentially adsorbed. The results in the present study may be interpreted if the cones surface had equal preference for molecularly adsorbed Methylene Blue species and dissociated cationic species. from fig .2. These cones contain a number of phenolic- OH groups , COO_ groups. and comprised of various functional groups, such as amine, hydroxyl and carbonyl which could also be affected by the pH of solutions[2-3]. Therefore, the effect of pH on the solid liquid equilibrium can be explained on the basis of three possible mechanisms: (i) chemical interaction between OH groups of cones and the reactive group (Cl_) of Methylene Blue (with elimination of HCl), (ii) chemical interaction between COO_ groups of cones and the dye cations and (iii) weak electrostatic interaction between the cationic dye and electron-rich sites of the surface of the cones particles as giving[7].The pH of the medium would definitely influence the course of the first two mechanisms, but the third mechanism may operate over a large range of pH without being affected much. The amount adsorbed in the present work remained nearly constant in the pH range of 2.0-10.0[7]

In other words, at various pH, the electrostatic attraction[2-3] as well as the organic property[3] and structure of dye molecules and cones could play very important roles in dye adsorption on cones[3] 3.2.5Adsorption isotherm

1.   Langmuir isotherm :This model assumes that the sites obtained by adsorption to be unified in the sense of energy adsorption in an orderly and evenly over the surface occurs, and no transmission Ottpadl sites by adsorbed on the surfaces of materials[14]

This model describes quantitatively about the formation of a monolayer adsorbate on the outer surface of the adsorbent and after that no further adsorption takes place. The Langmuir represents the equilibrium distribution of adsorbate between the solid and liquid phases .The Langmuir adsorption isotherm the most widely used isotherm for the biosportion of pollutants from a liquid solution based on the following hypotheses (1) monolayer adsorption Monolayer (2) Alametzaszew heterogeneous designated ites on the dsorbent material ccurs. (3) When the pollutantoccupya site; notanotheradsorptioncan occurat that location. (4)fixed adsorption energy does not depend onthe degree of concern adsorbent material active centers. (5) the strength of the forces of attraction between particles is believed to disappear Bsrahma distance. (6) adsorbent material has a limited capacity for pollutant (7)all equal and similar sites are actively identical and energetically equivalent) -8 article adsorbent homogeneous structurally (structurally homogeneous) (9there is nointeraction between themolecules ofthe adsorbentadsorbedon neighboringsites[6] based on these assumptions and the linear Langmuir equation is representing by the following equation[14]

$$\frac{C_e}{qe} = \frac{1}{q_{max}K_L} + \frac{1}{q_{max}}C_e$$

where Ce, KL and Q0 are the equilibrium concentration of dye solution (mg/L), the Langmuir constant (L/mg) and the maximum adsorption capacity (mg/g), respectively.RL RL = 1 / (1 + KLC0) RL separation factor[7] value refers to the   adsorption   curvedtypeof isotherm(RL = 0 (appropriate (0 <RL <1)linearRL = 1isa positiveRL> 1[2]

That decreed line between each of the (Ce / qe) and Ce will give a straight line that slope it equal to (1 / q_max) which can be compared with the obtained practically as is evident in the table (6), (7) and the value of q_max obtained through the application of model to four concentrations (2-3-4-5) and the value of Langmuir constant was also extracted[14]

2   Freundlich isotherm: This model assumes that the adsorption sites of unequal energies in obtaining allowing multi-layer adsorption and can be represented by the equation as the following form[14]

$$\ln q_e = \ln K_F + \frac{1}{n} * \ln C_e$$

where KF (L/mg) and 1/n are adsorption capacity at unit concentration and adsorption intensity, respectively.1/n values indicate the type of isotherm to be irreversible (1/n=0), favorable (0b1/nb1), unfavorable (1/nN1)[2]is not appropriate1 / n> 1[2],The model is applicable to the adsorption on heterogeneous   surfaces by a uniform energy distribution and reversible adsorption. The Freundlich equation implies that adsorption energy exponentially decreases on the finishing point of adsorptional centres of an adsorbent[6] as giving table (6)(7) the adsorption data was analyzed by applying Langmuir and Froendlish equationthat is indicated in Fig .7.8

Table (6) Langmuir and Freundlich isotherm model constants and correlation coefficients for adsorption of Methylene Blue onto PC ,CCat 25 C

natural cones	Langmuir isotherm			isotherm Freundlich			
	Q0	KL	r2	kf	n	1/n	r2
Pine cones PC	0.48954815	-1.90461538	0.3253	1.0795	0.57847	1.7287	0.9794
Cypress cones CC	1.24859533	0.490777621	0.2067	1.72375	0.91416	1.0939	0.9958
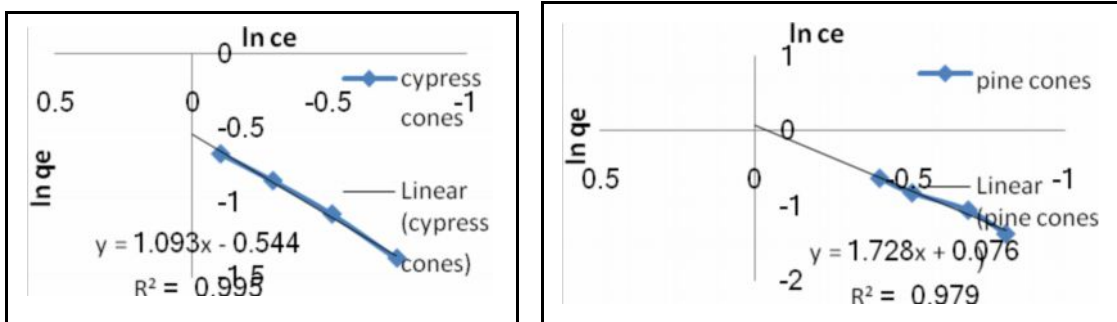
Fig .7Freundlichisotherms for adsorption of Methylene Blue on PC ,CCat 25 C

Table (7) Langmuir and Freundlich isotherm model constants and correlation coefficients for adsorption of Methylene Blue onto CPC , CCC at 25 C with dye concentration of 2 mg/L

carbonized cones	Langmuir			Freundlich			
	Q0	KL	r2	kf	n	1/n	r2
Pine cones CPC	0.88920505	0.707696	0.9155	2.7191	2.076	0.4816	0.9704
Cypress cones CCC	0.55380185	-6.45123	0.0855	1.79158	1.106	0.9041	0.9966
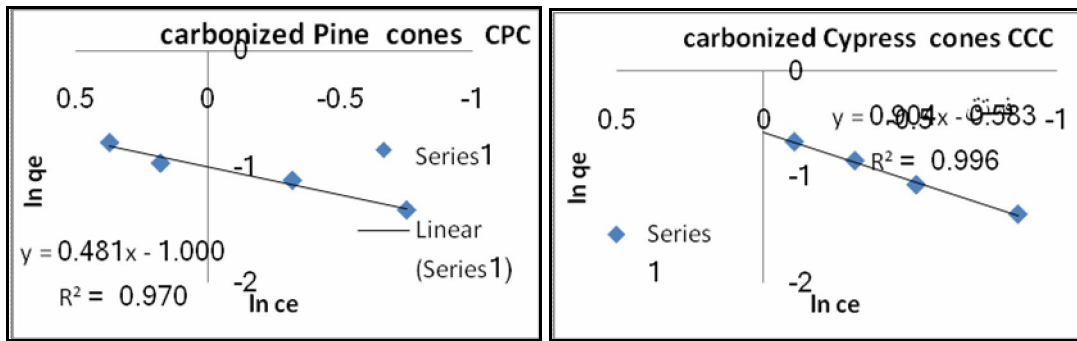
Fig.8 Freundlich isotherms for adsorption of Methylene Blue on CPC, CCCat 25◦C with dye concentration of 2 mg/L

The results indicated that isotherm data of methylene Blue dye followed Freundlich isotherm model for natural cones and for carbonized coneswith correlation coefficient (0.9794,0.9958, 0.9704, 0.9966 Pine cones PC , Cypress cones   CC, Pine cones   CPC , Cypress cones CCC

The Langmuir adsorption   isotherm has been successfully used to explain the adsorption of basic dyes from aqueous solutions using methylene blue on coconut shell[13]and in[7] The Langmuir monolayer adsorption capacity,C1, was large with values between 3.67 and 19.61 mg g1.The Langmuir adsorption intensity,Kd, had values of 0.186e0.729 L mg1. The dimensionless separation factor, RL, had an average value of 0.96 in the range of 0.91e0.98 in concurrence with the suggested values for favourable adsorption[7] The monolayer adsorption capacity according to   this model was 70.92 mg/g at 30 ◦ C. The fact that the Langmuir isotherm fits the experimental data very well may be due to homogeneous distribution of active sites onto CBW surface, since the Langmuir equation assumes that the surface is homogenous.[13],also carried out a study ofthe use ofpalmfiberpulpto remove the blue methylene and crystal violet solution of Almaúa.o studying the adsorption of factors, which include variousinitialconcentrations ofdye(20.40, 80 and160 mg / l),the time of contact contact time,(pH (1.0-11.0) and the amount of adsorbent material (0.4, 2.0, 4.0 and8.0 g / l). and then formulated using data adsorption desorption curve of equal class Langmuir, Freundlich was the data fit the budget process biosorption dynamic adsorption model Freundlich (determine the coefficient=0.997and0.991) blue methylene crystal violet, respectively [13] the pseudo-first order and Pseudo-second order kinetics : A linear form of pseudo-first-order model was described by Lagergren in the form:[13]

$$\ln(qe - qt) = \ln qe - k1/(2.303)t$$

where qe and k1 are the amount of dye adsorbed at equilibrium (mg/g) and the equilibrium rate constant of pseudo-first order kinetics (1/min),   respectively.

Alinear plot of log(qe -qt) against time allows one to obtain the rate constant . If the plot was found to be linear with good correlation coefficient, indicating that Lagergren's equation is appropriate to MB adsorption on cones. So, the adsorption process is a pseudo-first-order process. The Lagergren's first order rate constant (k1) and qe determined from the model are presented in Table along with the corresponding correlation coefficients. It was observed that the pseudo-first-order model did not fit well. It was found that the calculated qe values do not agree with the experimental qe values. This suggests that the adsorption of MB does not follow first-order kinetics[7]. The Pseudo-second order kineticsmay be expressed in a linear form as[11]:

$$t/qt = \left(\frac{1}{k2q2e}\right) + (1/qe)t$$

where the equilibrium adsorption capacity (qe), and the second order constantsk2(g/mg h) can be determined experimentally from the slope and intercept of plott/qtversust[13] (Fig. 910.).

The k2 and qe determined from the model are presented in fig .9 along with the corresponding correlation coefficients and The value of the calculated and experimental qe are represented in Table 8,9 It can be seen from Table 8,9the correlation coefficients for the plots were in the range 0.972-0.99for pine cones and between 0.98-0.99for cypress cones that there is an agreement between qe experimental and qe calculated values for the pseudo-second-order model. Hence, the pseudo-second-order model better represented the adsorption kinetics. Similar phenomenon has been observed in the adsorption of methylene blue by Coconut

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(Cocosnucifera) bunch waste, hazelnut shells and wood sawdust, activated carbon prepared from rattan sawdust and bamboobased activated carbon[13].

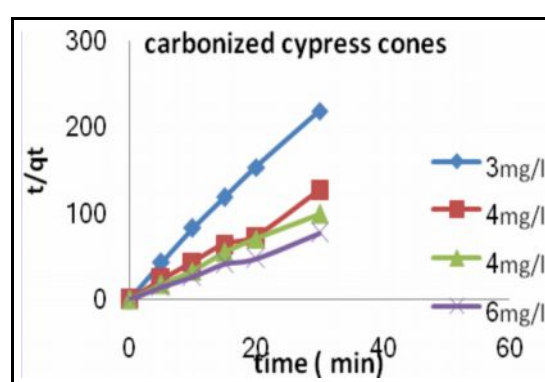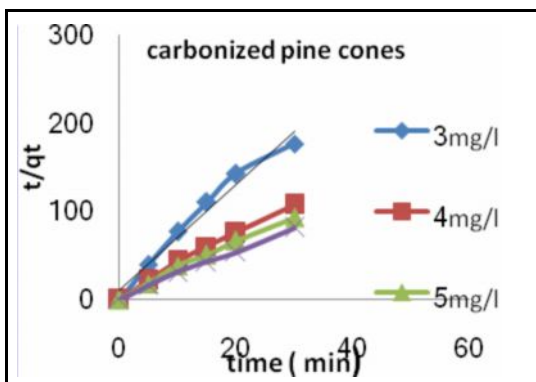**Table (8) Pseudo-second-order adsorption kinetics of MB on of PC,C PC**

pseudo-second order for (pine cones)							
initial dye concentration(mg/l) natural cones	carbonized cones	natural cones			carbonized cones		
(qe)Exp (mg/g)	(qe)Exp (mg/g)	R2	(qe)Cal.(mg/g)	k2(min-1)	R2	(qe)Cal.(mg/g)	k2(min-1)
3	0.255	0.139886	0.9967	0.27035	3.298	0.972	0.16706	3.17032
4	0.3531	0.262579	0.9986	0.34162	156.4	0.9924	0.2814	2.86215
5	0.42937	0.262579	0.9994	0.43954	4.205	0.9915	0.32428	2.59569
6	0.54109	0.368921	0.9994	0.54993	2.685	0.9964	0.37749	2.96069

Table (9) Pseudo-second-order adsorption kinetics of MB on of CC, CCC

pseudo-second order for (cypress cones)							
initial dye concentration (mg/l)	natural cones (qe)Exp (mg/g)	carbonized cones (qe)Exp (mg/g)	natural cones			carbonized cones		
			R2	(qe)Cal.(mg/g)	k2(min-1)	R2	(qe)Cal. (mg/g)	k2(min-1)
3	0.25251	0.130237	0.9991	0.25112	9.009	0.9968	0.13763	8.65223
4	0.31223	0.270334	0.9994	0.31831	19.42	0.9894	0.24617	11.9926
5	0.42691	0.281996	0.9995	0.42755	9.443	0.9961	0.29677	7.68006
6	0.52576	0.41605	0.9987	0.5063	36.77	0.9938	0.39944	4.41903
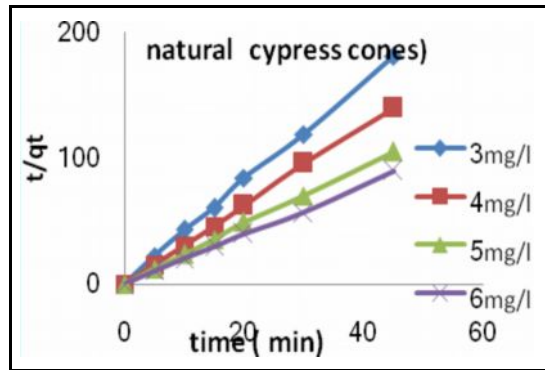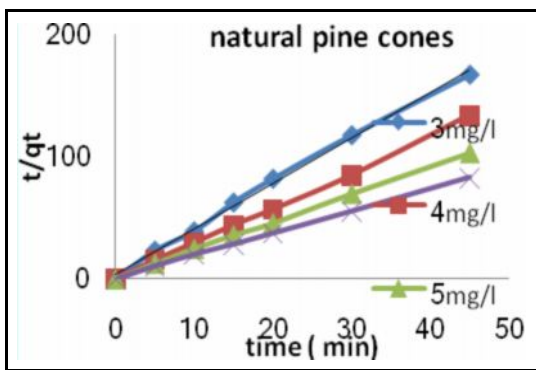
(a)   (b)

Fig. 9 **Pseudo-second order adsorption kinetics of dyeon PC(a) and CC (b) (pH 7.55, T 25 °C and (1 g/L for PC and CC**

(a)   (b)

Fig. 10 **Pseudo-second order adsorption kinetics of dye on CPC(a) and CCC(b)(pH 7.55, T 25 °C and (1 g/L for PC and CC**

4. Conclusion

Kinetic and equilibrium of methylene Blue were done for aqueous solutions onto Pcand CC. Results of adsorption were showed that PC, CPC, CC and CCC can be effectively used as a biosorbent for the removal of anionic dyes. Thus, adsorbed amount on the cones increased with an increase in the dye initial concentration and contact time, but the adsorbed amount decreased with increasing the amount of the adsorbent, kinetics studies of dye on PC,CC,CPC and CCC indicated that the adsorption kinetics of dye on PC,CC,CPC and CCC followed the pseudo-second order at different dye concentration. The equilibrium data have been analyzed and The results showed that the methylene Blue followed Freundlich isotherm ,and the results showed that at alkaline pH values high electrostatic repulsion existed between the negatively charged surface of the adsorbent and cationic dye, Based on the data of present studies , PC and CC is an eco-friendly adsorbent for dye removal from colored textile wastewater

References

1. Bahra.M,Azmeh.H and Rizkalla.A , 2001,Chemical Treatment of the Waste Water of Dyehouse, Damascus University Journal for the basic sciences 17 (2).
2. Mahmoodi. N. M,2011, Adsorption of textile dyes on Pine Cone from colored wastewater: Kinetic,equilibrium and thermodynamic studies.J. Desalination117-125.
3. Arami.M, Limaee.N. Y,Mahmoodi. N. M, Tabrizi.N. S,, 2006Equilibrium and kinetics studies for the adsorption of direct acid dyes from aqueous solution by soy meal hullHazardous Materials B135 ,171–179
4. Aljeboree.A. M, Alshirifi.A. N, Alkaim.A. F ,2014, Kinetics and equilibrium study for the adsorptionof textile dyes on coconut shell activated carbon, Arabian Journal of Chemistry xxx, xxx–xxx
5. www:///encyclopaedia are you learning my school instructional forums .htm(20/10/2014)
6. Rangabhashiyam.S,Anu. N, GiriNandagopal.M.S,Selvaraju. N, 2014,Relevance of isotherm models in biosorption of pollutants by agriculturalByproducts,Journal of Environmental Chemical Engineering 2 ,398–414
7. Bhattacharyya .K. G, Sharma .A, 2005 ,Kinetics and thermodynamics of Methylene Blueadsorption on Neem (Azadirachtaindica) leaf powderDyes and Pigments 65 , 51e59,
8. Ardejani.F. D, Badii.Kh, N.Limaee. Y, Shafaei.S.Z, Mirhabibi.A.R, 2008,Adsorption of Direct Red 80 dye from aqueous solution onto almondshells: Effect of pH, initial concentration and shell type, Hazardous Materials 151 ,730–73
9. Lima.E. C, Royer. B, Vaghetti.J. C.P, Simona.N. M, da Cunhaa.B. M,Pavan.F. A, Benvenutti.E. V, Catalu~na-Veses. R, Airoldi.C , 2008 ,Application of Brazilian pine-fruit shell as a biosorbent to removal ofreactive red 194 textile dye from aqueous solutionKinetics and equilibrium study, Hazardous Materials 155 ,536–550
10. Dawood. S,KantiSen. T,2012,Removal of anionic dye Congo red from aqueouspine and acid-treated pine cone solutionby raw powder as adsorbent:Equilibrium, thermodynamic, kinetics, mechanism andprocess design, water research 46 , 1933 -1946
11. Ofomaja, A.E., Naidoo, E.B., Modise, S.J., 2009. Removal of copper(II) from aqueous solution by pine and base modified pinecone powder as biosorbent. J. Hazard. Mater. 168, 909-917
12. Bla´zquez.G, Martı´n-Lara .M.A, . Dionisio-Ruiz. E,Tenorio. G,Calero. M, 2012 , Copper biosorption by pine cone shell and thermal decomposition study of the exhausted biosorbent, Industrial and Engineering Chemistry, xxx–xxx
13. Hameed.B.H, Mahmoud .D.K, Ahmad .A.L,2008 , Equilibrium modeling and kinetic studies on the adsorption of basicdye by a low-cost adsorbent: Coconut (Cocosnucifera) bunch waste, Journal of Hazardous Materials 158 , 65–72
14. Ibraheem .M.A , 2012,sorption   study of AlPHA-CYPERMFTHRINE by spent tea leave ,Diyala Journal for the agricultural sciences 4(2):166-176.
15. kodsi.Y ,Hakee.W,2007, organic spectroscope and chemical synthesis, Damascus University (6)
16. Fatih.R,2004 , activating carbonic that is   preparing local and studying effect method of activation on surface properties and adsorption effect in various mediums .

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