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Removal of Congo red dye from aqueous solution using a new adsorbent surface developed from aquatic plant (*Phragmites australis*)

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Abstract: The present study aimed to evaluate the removal activity of aquatic plant *Phragmites australis* for removal of the carcinogenic dye (cango red) from aqueous solution . The aquatic plant was collected from local aquatic system (Hilla River) in Babylon provinus, middle of Iraq as low cost materials, eco-friendly adsorbents and highly removal efficiency.
Bach adsorption studies are carried out by observing the effect of experimental parameters such as amount of adsorbents (1-3gm/L), contact time, pH(4-9), mesh size(45-150µm), and concentration of dye as optimum removal conditions of congo red dye from its aqueous solution. The results showed that the removal percentage of dye was 98%, and the removal processes raised with increasing of p H, adsorbent dosage, and mesh size.

Introduction:

Industry play Major role in the providing human need and improving their life style however the negative consequence of industrial activities such as paper, printing, textile, and pharmaceutical manufacturing due to existence hazardous chemical and dyes in their effluents cannot be ignored[1]. however The world now is use large amount of dyes in the Textile, leather, food, agro industries for colored their productions. So The world now is facing many Problems regarding water pollution that resulting from industrial use for these dyes, The big problem is come from effluent from textile industries, which has created environmental problems around all the world areas[2]. especially These dyes are chemical aromatic compounds have very complex structures which become a serious environmental problem, such as the colour is aesthetically objectionable[3-7]. It reduces the photosynthetic activity by rguably dyes have adverse effect on water bodies as they are visible pollutants, the presence of color in the water bodies reduce light penetration which in turn upsets the biological metabolism process, disposal of dye wastewater without proper treatment destructes the aquatic communities present in the ecosystem and some dyes are reported to cause allergic dermatitis, skin irritation, cancer and mutation in humans if they are discharged as wastewater without any treatment[8-13].

There are many Various conventional techniques have been employed to eliminate dyes from wastewaters, like adsorption, photocatalytic degradation, reverse osmosis, coagulation, flocculation, membrane technology, and biological treatments[2,14-32] . Adsorption technique is by far the most versatile and widely used Moreover, this process become economic if the adsorbent material used is available and cheap in cost. Common adsorbents materials are: activated carbon, activated alumina, silica gel, metal hydroxides, alumina silicates (molecular sieves) and activated carbon[33]. In this work study the ability to remove of cango red from aqueous solutions by low cost, neutral materials, eco-friendly, highly efficient as aquatic plant *Phragmites australis* under various experimental conditions, such as effect of contact time, effect of adsorbent dose, and effect of concentration of dye, additionaly experiment by FTIR. This work an ideal alternative to the current expensive methods of removing the dye from waste water.

Material and Methods

Preparation of Adsorbent

The aquatic plant were used as adsorbent were collected from Hilla river near Hilla city middle of Iraq. The unwanted materials (suspended impurities) like soils, dust etc were removed by extensively washed in running tap water for 2-3 hours for removing. It was followed by washing with distilled water. The washed material was dried under sun light for ten days, It was ground in pulverized mill. This ground powder was treated with water till the colour leached out and the powder was oven dried at 25 ^{o}C for 24 hours.

FTIR spectroscopy

FTIR spectra were obtained using a PerkinElmer Tensor 27 Fourier transform infrared spectrometer (Germany). The spectral region between 4000 and 500 cm^{-1} was scanned. Specimens prepared as KBr pellets were used. Dried, Phragmites australis powder (2 mg) was mixed thoroughly with KBr (300 mg) and then pressed in vacuo to homogeneous disc with a thickness of about 0.9 mm.

Preparation Adsorbate Solution

The dye congo red (Chemical formula=$C_{23}H_{22}N_6O_6S_2Na_2$, Formula weight=696.65g.mol^{-1}) supplied by BHD chemicals. The solution of congo red were prepared by dissolving appropriate amounts (accurate weighed) of dry powdered dye in double distilled water to prepare Stock solution (1000 mg L^{-1}). The experimental solution was obtained by dilutions were made to obtain the working solution at desired concentrations.

Adsorption study

0.5g of powder of adsorbent material (aquatic plant) was weighted each into 250ml conical flasks. 100ml of the solution congo red dye was measured and added to the content in each conical flask. The content was shaken rigorously and continuously for 30, 60, 90, 120, 150, 180, 210, 240, 270, and 300 min respectively. The particles of the adsorbent was separation by centrifuged from solution to obtain the equilibrium concentration. The final concentration of congo red dye was estimated for each sample spectrophometrically at the wavelength corresponding to maximum absorbance for congo red (λ_{max}=497nm) using a spectrophotometer (UV/VIS-JENWAY,1600, Germany). A graph of removal congo read percentage (g/L) versus time (hour) was plotted for Congo red. Generally the amount of dye removal was calculated from following equation:

$$removal\% = (A^{\circ} - A)\, A^{\circ} \times 100 \qquad (1)$$

A^{o} and A are the absorption of concentration of congo red dye before and after adsorption respectively.

Results and discussion

A washing adsorbent was play an important roles in this study: first to remove impurities from the adsorbent, and second to release the color of material and avoided interfere spectrophotometrically with wave length of cango red, this case recognized by analyzed washing solution spectrophotometrically after each one washing time. After second washing time the absorbance was negligible at 663nm. So the per-treatment of two washing cycles were adequate[34].

Spectroscopic studies

Fourier Transform Infrared Spectrometry (FTIR) is another active tool for identifying types of functional groups of adsorbent that are responsible for entrapping the molecules of dye. The IR spectrum of *P. australis* powder in the form of KBr pallet is shown in Figure 1. and the typical functional groups and their corresponding IR signals are listed in Table 1. The spectra of *P. australis* powder Appears of many weak and strong peaks(Fig. 2, and 3) indicating the complex nature of *P. australis* powder.

The O–H stretching vibrations between 3300 and 3400 cm^{-1} indicating the presence of alcohols and phenols are present in the structure. The bands at 2923 and 2957 cm^{-1} are indicative of the presence of aliphatic structure in the *P. australis* powder. The bands at 2855 and 2915 cm^{-1} is due to the C-H symmetrical and asymmetrical stretching of saturated (sp3) carbon, respectively. The band at 1635.6 cm^{-1} is assigned to the bending mode of absorbed water since fibers with hemicellulose component are known to have a strong affinity for water[34]. The 1265 cm^{-1} band refers to the stretching vibration of ethers. The bands at 700–900 cm^{-1}. The C=O stretching vibrations at 1732 cm^{-1} denoting the presence of the carbonyl groups refer to ketones, phenols, carboxyl acids and aldehydes[35].

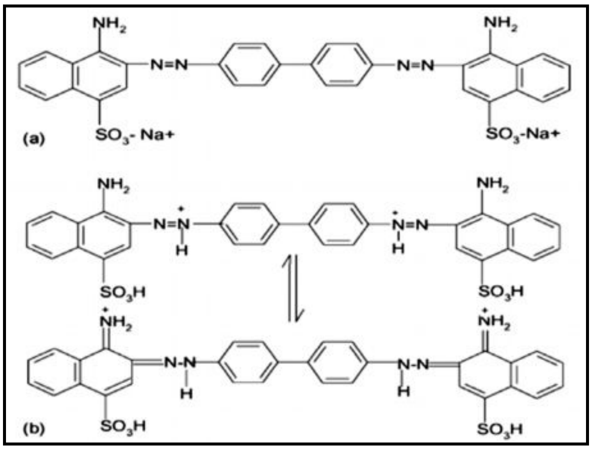

Fig.1.Structure for Congo red dye at (a) basic medium, (b) acidic medium.

Table 1: Infrared spectrum data of *P. australis* powder

No	Frequency cm^{-1}	Assignment	Suggested peak
1	3390.86	O-H	Alcohol
2	2960 2922.16		aliphatic structure
3	1732.08	C=O	stretching vibrations
	1635.64	O-H	bending (of H_2O)
4	1371.39	O-H	bending
5	1250.22	C-O	stretching
6	1161.15	C-OH	bending
7	1103.28	C-O-H	(OH association)
8	1060.85	C-OH	bending
9	1045.42	C-O-C	stretching (pyranose ring skeletal)

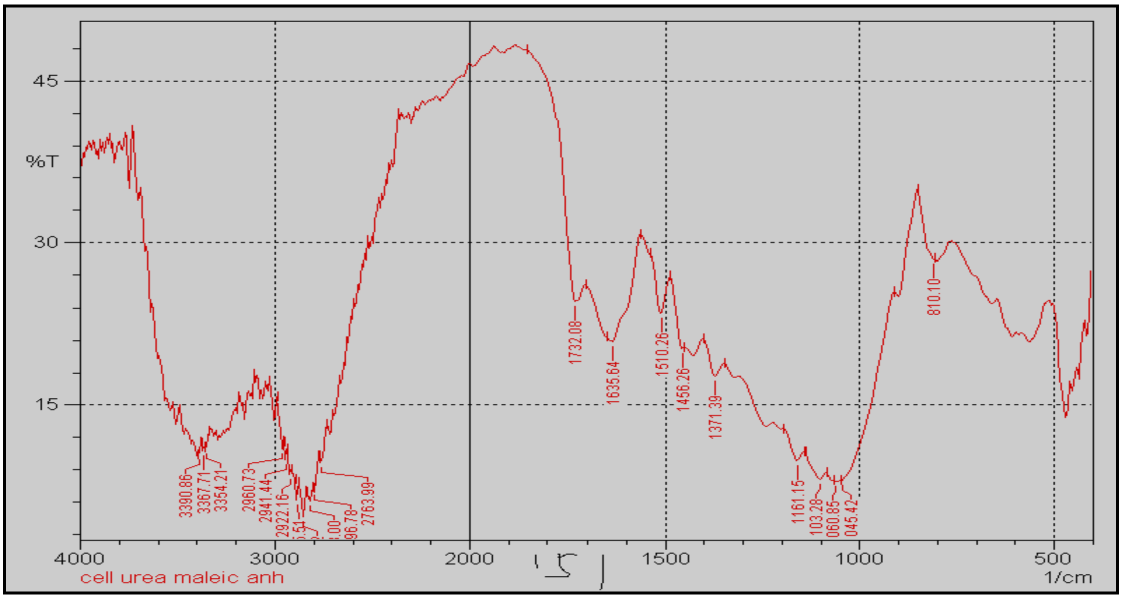

Fig. 2. FTIR spectrum of Phragmites australis powder befor adsorption.

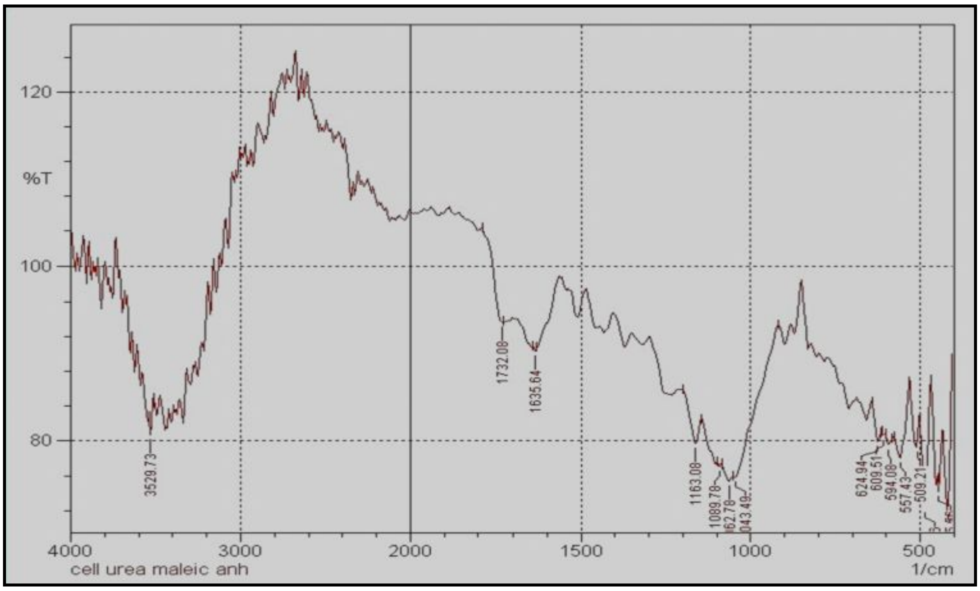

Fig. 3. FTIR spectrum of Phragmites australis powder after adsorption.

After adsorption the, some of bandes change the orginal position as result of the interaction between the dye and the adsorbent of were observed in the spectra as a result of the interaction between the dye and the adsorbent. The O–H stretching vibrations have band in the 3390.6 cm^{-1}befor adsorption, that appeared at higher frequencies in comparison to the position before the sorption process at 3529.73 cm^{-1}, Another band not appeared after adsorption comparison befor adsorption.

Effect of contact time

The influence of contact time on removal efficiency of Congo red dye was studies with different contact time (10-120 min) and The experiment was achieves with initial dye concentration 10mg/L at pH-6.0, room temperature (22±2^{o}C) and adsorbent dose-2g/L Lemna minor for the adsorption of dye (Congo Red) dye. The results which are obtained at these conditions are shown in Fig.(1), it was observed that the removal efficiency increased with the contact time increased. At the initial stage, there was a rapid adsorption of the dyes. It was found that 91% of the dye concentrations was removed in the first 30mins, and thereafter the removal on the *P.australis* was gradual till it became constant at 25 min as shown in Fig. 4.

The rapid adsorption at the initial contact is attributed to the highly active sites available on the surface of the Lemna minor powder, so there strong attraction between active site available on the surface of the adsorbent and basic cationic adsorbate[36]. The gradual rate of adsorption is probably due to the electrostatic hindrance or repulsion between the adsorbed positively charged adsorbate species onto the surface of the *P.austalis* and the available basic cationic adsorbate species in the solution, as well as the slow pore diffusion of the solute ions into the bulk of the adsorbent (i.e saturation of the active site which do not allow further adsorption to take place). The equilibrium was achieved at 80mins when the maximum dye adsorption on to *P.austalis* powder was reached[37].

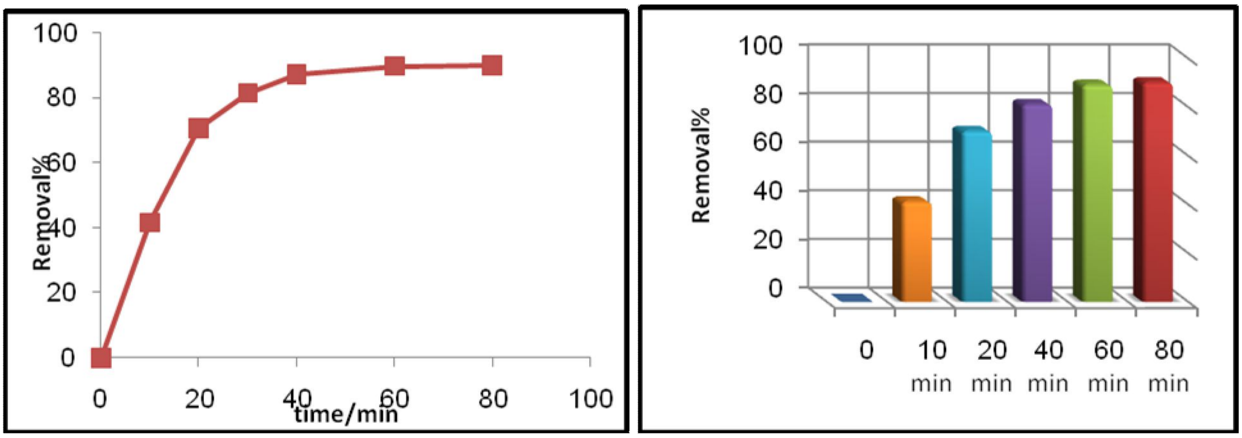

Fig.(4) Effect of contact time on removal efficiency. Exp. Conditions: (initial dye concentration of 10 mg/l, adsorbent dose of 2g/L and neutral pH).

Effect of Initial Dye Concentration

Fig.(5) shows the effect of initial Congo red dye concentration on removal efficiency at constant adsorbent dose 4 gm/L, neutral pH and optimum contact time at 80 min. It was also found that the removal efficiency of Congo red dye decreased from (98.1% - 87% - 69%), as the initial Congo red dye concentration increased from (20 – 40 - 60) mg/L respectively, as shows in fig.5 with increase initial dye concentration the adsorption of dye is increased but the removal percentage is decreased due to reduced surface area and saturated the active sites[37].

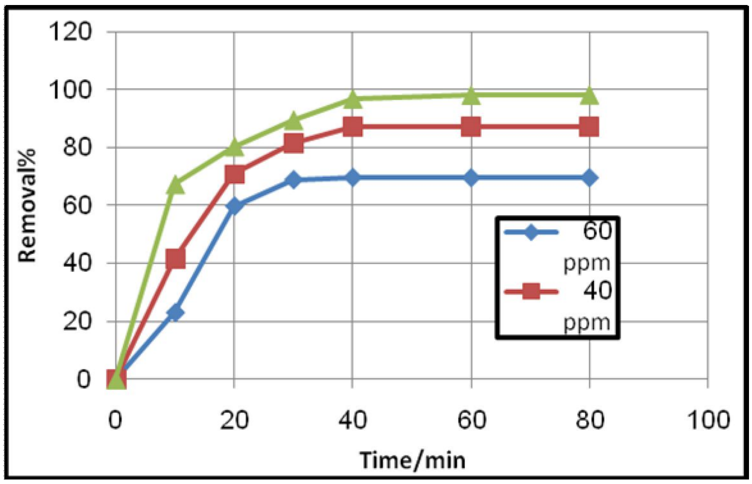

Fig.(5) Effect of initial dye concentration on removal efficiency. Exp. Conditions: (adsorbent dose of 4 g/L, neutral pH and contact time of 80 min).

Effect adsorbent dose

The effect of adsorption dosage was studies for adsorbent dose (2, 4, 6g/L) at contact time of 90 min with initial concentration of dye 10mg/L at room temperature (22±2^{o}C) and pH-6.0. and the obtained data are shown in Fig.6. The figure show that the removal dye percentage increases with increasing adsorbent dose and then it remains constant. An increase in adsorption with increase adsorbent dose due to increased surface area and the availability of more adsorption sites, but the amount adsorbed for unit mass of the adsorbent decreases considerably. The decrease in unit adsorption with increasing dose of adsorbent is due to the adsorption sites remaining unsaturated during the adsorption process[36,37].

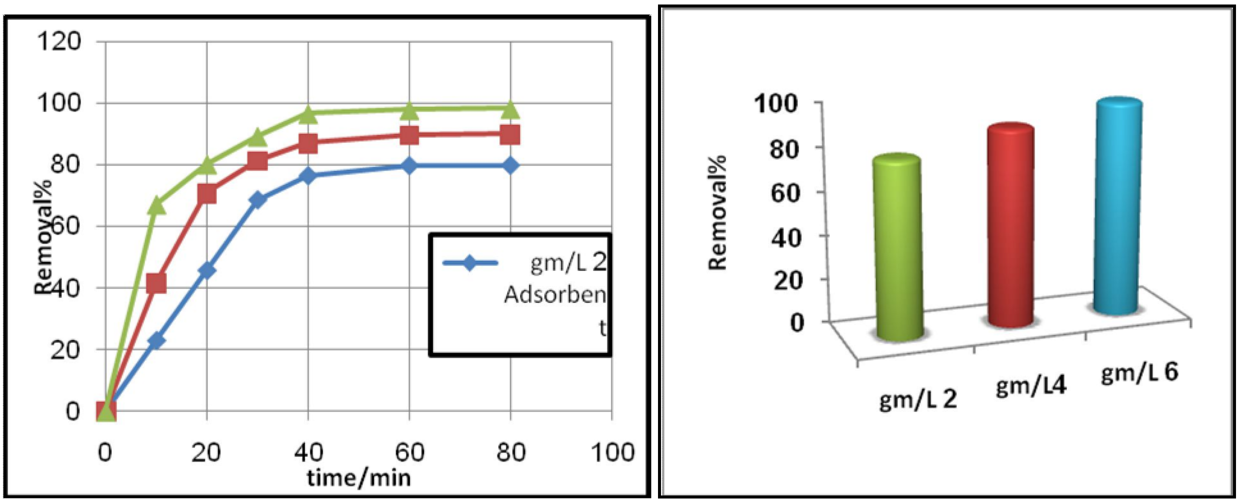

Fig.(6) Effect of adsorbent dosage on percentage removal of dye . Exp. Conditions: (initial dye concentration of 10 mg/l, neutral pH and contact time of 80 min).

Zero of point charge

The Zero of point charge (pH_{ZPC}) of adsorbent was measured to be 6.5, and the surface of Congo red dye was anionic in nature in Fig. (7) . The (pH_{ZPC}) of the adsorbent revealed that the surface of adsorbent is positively charge at pH less than 6.5 a competition exists between the protons of protonated amine or sulpher groups[38,39]. In addition when the pH greater than (pH_{ZPC}), the presence of negatively charged surface in the pineapple peel surface, expetite electrostatic attraction between the negatively charged surface and positive charged cationic dye[38,39].

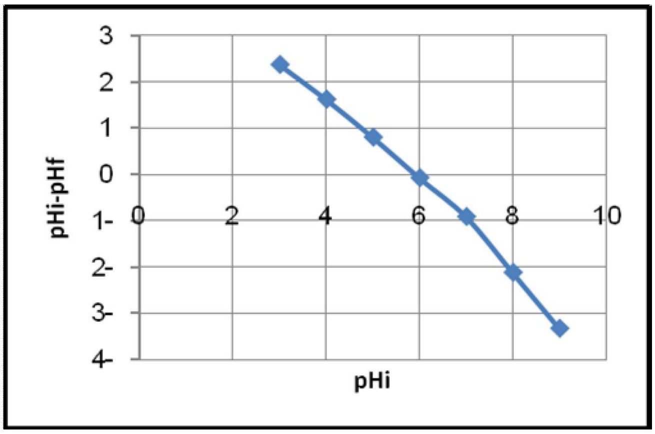

Fig.(7). Zero of point charge (pH_{ZPC}) of adsorbent using (0.01N) KCL.

Effect of pH

The effect of pH on Congo red dye removal has been studies by varying the pH over a range of (4-9) at constant initial dye concentration of 10 mg/l. optimum adsorbent dose of 4 gm and contact time of 80 min, the results are shown in Fig. (8). The initial pH of dye solution play an important role for adsorption process because the initial pH have direct influence on the dye and adsorbent in aqueous solution[36]. The effect of pH is studied between 4 and 9 because reported that at strong acidic medium, the solution of Congored changes its color from red to dark blue and the original red colour is different above pH 10. pH values as shown in Fig.8, the removal Cogo red percentage the maximum removal efficiency is achieved in the acidic medium and gradually reduced to the basic medium. In the acidic medium, the solution of Congo red exists as cationic form[40,41] , and du to the adsorption of cation favorite at pH > pHzpc[36]. The reduced of negative site may be du to of surface absorbent when transfer from acidic to basic medium, therefore , the removal efficiency is reduced from 90% to 77.7% gradually, especially the solution of Congo red exists as anionic form in basic pH (pH=10-12)[37] ,also in the basic medium there are competing between anionic dye and –OH exists in the basic medium to attraction with adsorption site[15,42].

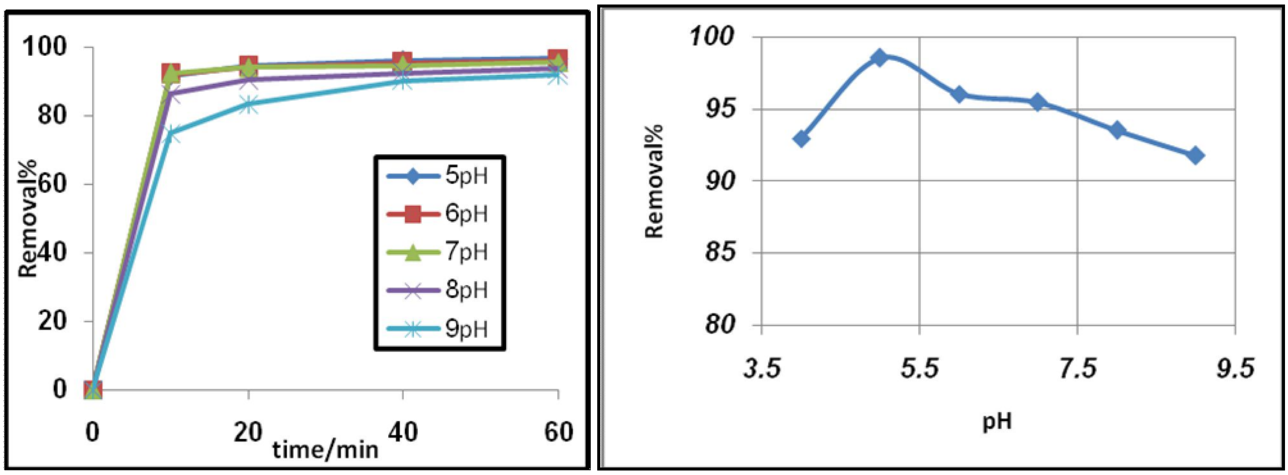

Fig.(8) Effect of pH on percentage removal of dye. Exp. Conditions: (initial dye concentration of 10 mg/l, optimum dosage of 0.6 gm/L and contact time of 80 min).

Conclusion

The ability of aquatic plant (*P.australis*) low cost adsorbents to adsorb Congo red dye has been investigated, This study has shown that *P.australis* have a high adsorption ability to absorb Congo red dye. The optimum operating condition were 10 mg/l initial dye concentration, 6 gm/L adsorbent dosage, pH 5.5 and 80 min contact time.

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References

1. Salman J.M., Amrin A.R., Ali A.L., and Jouda S.A., 2016. Use of aquatic plant (Lemna minor) as adsorbent materials to removal of methylene blue dye from aqueouse solution, Journal of advance chemical scinces, 2: 192-194.
2. Alrobayi E. M., Algubili A.M., Aljeboree A. M., Alkaim A. F., and Hussein F. H., DOI: 10.1080/02726351.2015.1120836. Investigation of Photocatalytic Removal and Photonic Efficiency of Maxilon Blue Dye GRL in the Presence of TiO2 Nanoparticles, Particulate Science and Technology.
3. Maneerung, T., Liew, J., Dai, Y., Kawi, S., Chong, C., & Wang, C., 2016. Activated carbon derived from carbon residue from biomass gasification and its application for dye adsorption: Kinetics, isotherms and thermodynamic studies, Bioresource Technology, 200: 350-359.
4. Kaur, P., Singh, A. P., Prince, A. K. & Kushwaha, J. P., 2015. Optimization and evaluation of CBSOL LE red wool dye adsorption from aqueous solution onto commercial activated carbon, International Journal of Environmental Science and Technology, 12: 3755-3766.
5. Fil, B. A., 2015. Isotherm, Kinetic and Thermodynamic Studies on the Adsorption Behavior of Malachite Green Dye onto Montmorillonite Clay, Particulate Science and Technology: An International Journal: DOI:10.1080/02726351.02722015.01052122.

6. Djilani C., Zaghdoudi R., Djazi F., Bouchekima B., Lallam A., Modarressi A., and Rogalski M., 2015. Adsorption of dyes on activated carbon prepared from apricot stones and commercial activated carbon, Journal of the Taiwan Institute of Chemical Engineers, 53: 112-121.
7. Gong J., Feng J., Liu J., Jiang Z., Chen X., Mijowska E., Wen X., and Tang T., 2014. Catalytic carbonization of polypropylene into cup-stacked carbon nanotubes with high performances in adsorption of heavy metallic ions and organic dyes, Chem. Eng. J., 248: 27-40.
8. Matloob, M. H., „ 2011. Fluoride concentration of drinking water in Babil-Iraq, Journal of Applied Sciences, 11: 3315-3321.
9. Wang, Q.; Chen, C.; Zhao, D.; Ma, W.; Zhao, J., 2008. Change of Adsorption Modes of Dyes on Fluorinated TiO2 and Its Effect on Photocatalytic Degradation of Dyes under Visible Irradiation, Langmuir, 24: 7338-7345.
10. Wang, S.; Zhu, Z. H., 2007. Effects of acidic treatment of activated carbons on dye adsorption, Dyes and Pigments, 75: 306-314.
11. Tahir, S. S.; Rauf, N., 2006. Removal of a cationic dye from aqueous solutions by adsorption onto bentonite clay, Chemosphere, 63: 1842-1848.
12. Gupta, V. K.; Mittal, A.; Kurup, L.; Mittal, J., 2006. Adsorption of a hazardous dye, erythrosine, over hen feathers, Journal of Colloid and Interface Science, 304: 52-57.
13. Chiou, M.; , C., G., 2006. Competitive adsorption of dye metanil yellow and RB15 in acid solutions on chemically cross-linked chitosan beads, Chemosphere, 62: 731-740.
14. Salman J.M., Amrin A.R., and Jouda S.A., 2015. Aquatic crusteans shell as adsorpents for paraquate pesticide removal from its aqueous solution by thermal activation, Mesop environ J., 1: 75-83.
15. Salman J.M., Amrin A.R., and Jouda S.A., 2015. Aquatic crusteans shell as adsorpents for paraquate pesticide removal from its aqueous solution by thermal activation, Mesop environ J., 1: 75-83.
16. Saleh, J. M., , and Matloob, M.H. , 1974. Oxidation of titanium, tantalum, and niobium films by oxygen and nitrous oxide, Journal of Physical Chemistry, 78: 2486-2489.
17. Avlonitis S. A., Poulios I., Sotiriou D., Pappas M., and Moutesidis K., 2008. Simulated cotton dye effluents treatment and reuse by nanofiltration, Desalination, 221: 259-267.
18. Chakraborty S., Purkait M. K., Das S., Gupta S., De S., and Basu J. K., 2003. Nanofiltration of textile plant effluent for color removal and reduction in COD, Sep. Purif. Technol., 31: 141-151.
19. Gheju M., and Balcu I., 2011. Removal of chromium from Cr(VI) polluted wastewaters by reduction with scrap iron and subsequent precipitation of resulted cations, Journal of Hazardous Materials, 196: 131-138.
20. Vergili I., Kaya Y., Sen U., Gönder Z. B., and Aydiner C., 2012. Techno-economic analysis of textile dye bath wastewater treatment by integrated membrane processes under the zero liquid discharge approach, Resources, Conservation and Recycling, 58: 25- 35.
21. Hsu, H., , Chen, S., Tang, Y., and Hsi, H., 2013. Enhanced photocatalytic activity of chromium(VI) reduction and EDTA oxidization by photoelectrocatalysis combining cationic exchange membrane processes, Journal of Hazardous Materials, 248-249: 97-106.
22. Alqaragully M.B., AL-Gubury H. Y, Aljeboree A.M., Karam F.F., and Alkaim A. F., 2015. Monoethanolamine :Production Plant, Research Journal of Pharmaceutical, Biological and Chemical Sciences, 6: 1287-1296.
23. Alkaim A. F., Sadik Z., Mahdi D. K., Alshrefi S. M., Al-Sammarraie A. M., Alamgir F. M., Singh P. M., and Aljeboree A. M., 2015. Preparation, structure and adsorption properties of synthesized multiwall carbon nanotubes for highly effective removal of maxilon blue dye, Korean J. Chem. Eng., 32: 2456-2462.
24. Aljeboree A. M., Alkaim A. F., and Al-Dujaili A. H., 2015. Adsorption isotherm, kinetic modeling and thermodynamics of crystal violet dye on coconut husk-based activated carbon, Desalin. Water Treat., 53: 3656-3667.
25. Aljeboree A. M., 2015. Adsorption of methylene blue dye by using modified Fe/Attapulgite clay., Research Journal of Pharmaceutical, Biological and Chemical Sciences 6: 778-788.
26. Al-Gubury H. Y., Fairooz N. Y., Aljeboree A. M., Alqaraguly M. B., and Alkaim A. F., 2015. Photcatalytic Degradation n-Undecane using Coupled ZnO-Co2O3, Int. J. Chem. Sci., 13: 863-874.
27. Hadi Z. A., Aljeboree A. M. and Alkaim A. F., 2014. Adsorption of a cationic dye from aqueous solutions by using waste glass materials: isotherm and thermodynamic studies, Int. J. Chem. Sci., 12: 1273-1288.

28. Alkaim A. F., Aljeboree A. M., Alrazaq N. A., Baqir S. J., Hussein F. H., and Lilo A. J., 2014. Effect of pH on Adsorption and Photocatalytic Degradation Efficiency of Different Catalysts on Removal of Methylene Blue, Asian Journal of Chemistry, 26: 8445-8448.
29. Aljeboree A. M., Radi N., Ahmed Z., and Alkaim A. F., 2014. The use of sawdust as by product adsorbent of organic pollutant from wastewater: adsorption of maxilon blue dye, Int. J. Chem. Sci., 12: 1239-1252.
30. Aljeboree A. M., Alshirifi A. N., and Alkaim A. F., 2014. Kinetics and equilibrium study for the adsorption of textile dyes on coconut shell activated carbon, Arabian J. Chem., 10.1016/j.arabjc.2014.01.020.
31. Karam F. F., Kadhim M. I., and Alkaim A. F., 2015. Optimal conditions for synthesis of 1, 4-naphthaquinone by photocatalytic oxidation of naphthalene in closed system reactor, Int. J. Chem. Sci., 13: 650-660.
32. Alkaim, A. F., Dillert, R., and Bahnemann, D. W., 2015. Effect of polar and movable (OH or NH2 groups) on the photocatalytic H2 production of alkyl-alkanolamine: a comparative study, Environ. Technol., 36: 2190–2197.
33. Zonoozi M.H., Moghaddam M.R., and Arami M., 2009. Coagulation/Flocculation of dye containing solutions using Polyaluminium chloride and alum, Water Sci. Technol., 59: 1343-1351.
34. Bulut, Y., , and Aydın H., 2006. A kinetics and thermodynamics study of methylene blue adsorption on wheat shells, Desalination, 194: 259-267.
35. Aljeboree, A. M., , Alkaim, A. F., and Al-Dujaili, A. H., 2015. Adsorption isotherm, kinetic modeling and thermodynamics of crystal violet dye on coconut husk-based activated carbon, Desalin. Water Treat., 53: 3656-3667.
36. Han, R., , Zou, W., Yu, W., Cheng, S., Wang Y., and Shi J., 2007. Biosorption of methylene blue from aqueous solution by fallen phoenix trees leaves, J. Hazard Mater., 141: 156-162.
37. Malik P.K., and Saha S.K., 2003. Oxidation of direct dyes with hydrogen peroxide using ferrous ion as catalyst, Sep. Purif. Technol, 31: 241-250.
38. Sharma, Y. C.; Uma, 2009. Optimization of Parameters for Adsorption of Methylene Blue on a Low-Cost Activated Carbon, Journal of Chemical & Engineering Data, 55: 435-439.
39. Dogan, M., , Abak, H., and Alkan, M., 2009. Adsorption of methylene blue onto hazelnut shell: Kinetics, mechanism and activation parameters, Journal of Hazardous Materials, 164: 172-181.
40. Hassan, A. F.; Abdel-Mohsen, A. M.; Fouda, M. M. G., 2014. Comparative study of calcium alginate, activated carbon, and their composite beads on methylene blue adsorption, Carbohydrate Polymers, 102: 192-198.
41. AlOthman, Z. A.,, Habila, M. A., Ali, R., Abdel Ghafar, A., and El-din Hassouna, M. S., 2013. Valorization of two waste streams into activated carbon and studying its adsorption kinetics, equilibrium isotherms and thermodynamics for methylene blue removal, Arabian Journal of Chemistry, http://dx.doi.org/10.1016/j.arabjc.2013.05.007.
42. Salman J.M., Amrin A.R., Hassan F.M., and Jouda S.A., 2015. Removal of congo red dye from aqueous solution by using natural materials, Mesop. environ. J. , 1: 82-89.

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