**Removal of congo red dye from aqueous solution by using natural materials**

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**Abstract**

The present work aims to investigate the removal of dye and Congo red dye from aqueous solutions by low cost neutral adsorbents, eco-friendly, highly efficient such as barnacle shells under various experimental conditions, as an ideal alternative to the current expensive methods of removing dyes from waste water The operating variables such as The effect of dye concentrations, contact time, pH of solution and adsorbent dose on the removal of dyes were optimized.

**Key words*:*** Congo red, Adsorption , barnacle shell*.*

**Introduction**

Dyes and pigments widely utilize in the textiles, paper, plastics, leather, foodstuff, cosmetic industries as well as natural and artificial fibers to color products[1].The Azo dyes one of the important classes of synthetic organic pigments utilize in manufactured coloured productions Worldwide for this reason the Organic dyes appear in many industrial effluents[2].Use of these dyes along with lots of water in textile industries has resulted in the production of polluted and coloured waters being discharged into the environment ( nearby land or rivers) without any treatment because the conventional treatment methods are not Effective[2,3]. These coloured compounds are aesthetically objectionable and inhibiting sunlight penetration into these waters (e.g. streams, rivers etc)[4]. Ground-water are also affected by these pollutants because of leaching from the soil .The major constituents of textile effluent are dyes, Some dyes are reported to cause allergic dermatitis, skin irritation, cancer and mutation in humans[3,5]. The toxicity and carcinogenic nature of these dyes and their precursors pose a threat to the environment Moreover, their degradation often leads to the formation of highly carcinogenic aromatic amines[6], for recycling coloured wastewaters must be there are proper treatment for this polluted water. Congo red one of important dye that found in the wastwater have higher solubility in the water about 1 g/30 mL[7]. There are many Various physical and chemical techniques have been employed to eliminate dyes from wastewaters, like adsorption[4,7],reverse osmosis[7,8], coagulation[8], flocculation[9],, membrane technology[7,8,9], and biological treatments. but in developing countries, these methods are still too expensive to be used widely. but adsorption Among these methods Various is the utilize most in the waste water treatment (purification, decolorization and the removal of toxic organics and heavy metal ions)[10], because efficient and economical. In present study, Barnacles shells were powdered, and characterized by XRD spectroscopy, and it's using as adsorbents under optimum conditions, for the removal of Congo red dye from aqueous solution.

**Materials and methods**

**Preparation of Adsorbent**

The Barnacles shells were used as adsorbent were collected from the Shomalley Water dine station in the Babylon city (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 oven dried at 50 oC for 24 hours. It was ground in pulverized mill. This ground powder was treated with water till the colour leached out and the powder was over dried at 50 oC for 24 hours.The powder prepared were characterized by X-ray diffraction analysis (XRD with Cu- Kα radiation, λ=1.5406 oA) Shimadzu,1800, Japan.

**Preparation Adsorbate Solution**

The dye Congo red (Chemical formula=C23H22N6O6S2Na2, 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.

**Experimental**

**Effect of Contact Time**

1g of Barnacle shells powder (i.e. adsorbent) was weighed each into 250ml conical flasks. 100ml of the solution congo read 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 read was estimated for each sample spectrophometrically at the wavelength corresponding to maximum absorbance for Congo red (λmax=497nm) using a spectrophotometer (UV/VIS-Shimadzu,1800, Japan). 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:

Ao and A is the absorption of concentration of dye before and after adsorption respectively.

**Effect of Adsorbent Dose**

100ml of the Congo read was measured and added to0.5,1, 1.5,2.5 and 3g into different conical flasks. The content were shaken rigorously and The particles of the adsorbent (powder of barnacle shells) was separationby centrifuged from solution to obtain the equilibrium concentration. The process was conducted at room temperature. The final concentration was measured using the UV-Spectrophotometer. The relation between the removal of Congo red, and reaction time was studied at pH 6.50 with increase of contact time.

**Effect of Initial Dye Concentration**

The adsorption of CR on adsorbent (barnacle sells) was studied at different CR concentrations (1,2,3,4mg L−1). Fig. 5 shows the result of effect of initial concentration on adsorption of CR onto adsorbent (barnacle sells) at 20±2 ◦C.

**Effect of pH**

100ml of the Congo red dye was measured and added to 2g of the activated carbon in 4-250ml conical flasks. The pH of the solution was adjusted using dilute 0.1M HCl and 0.1M NaOH solution to vary the pH of each content from 4-9 and was checked using a pH meter. The content of each flask was shaken rigorously for 30mins at room temperature. The particles of the adsorbent (powder of barnacle shells) was separation by centrifuged from solution to obtain the equilibrium concentration, A plot of removal dye% versus time(hour) for each solution.

**Results and discussion**

XRD scanning: The Fig:1 show XRD pattern for The powder prepared (barnacle shells), the results of XRD show sharp beak which indicated the well-define nanocrystalline material. The size of the crystallite shurrer[11] formula

Where the K is Sharpe factor, λ is the X-ray wavelength, β is the line broadening at the half maximum intensity (FMWH) in the radian, and is Bragg angle. generally the practical size at maximum intensity was found 40.8nm.

Fig. 1. XRD pattern of powder of barnacle shells**.**

**Effect of Contact Time:**

The value of optimum contact time was varied in the range of 1-4 hour in a series of experiments in which the initial Congo red dye concentration 100 ppm, the temperature 20OC and adsorbent amount 1g.100ml. The effect of contact time on the removal of CR by the adsorbent is illustrated in Table 2. It is observed that dye is rapid adsorption at the first time (first hour) and then the process gradually it becomes slowly and finally the process continuous to becomes almost constant, this effect result from coverage the surface of adsorbents by the molecules of Congo red dye[5,12].

**Table.1** Effect of contact time

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Contact time (hour) | 1 | 2 | 3 | 4 |
| Congo Red dye removal % | 81.4 | 91.9 | 94.8 | 95.8 |

**Effect of NLP Dose**

The effect of adsorbent (barnacle sells) dose on the removal of CR from the aqueous solution is shown in Fig. 2.The figure show that the removal 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[12,13].

**Fig. 2**: Effect of dose of the barnacle shell powder on the adsorption of CR. Conditions: V=100ml; temp. = 20±2 °C; C0=50 mgL-1; pH 7.29**.**

**Effect of Initial Dye Concentration**

The adsorption of Congo Red on barnacle shell powder was experimented at different Congo Red concentrations (100,200,300,400 mg L-1), The experimental data is measured at 4 hours that is the time required to complete equilibrium is attained. the Effect of Initial Dye Concentration on the adsorption Congo red illustrated in fig.5. 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[14,15].

**Fig. 3**: Effect of initial concentration and contact time on CR adsorption. Conditions: V=100ml; temp. = 20±2 °C; speed of; Dose on powder of barnacle shells = 10 g L-1; pH 7.29.

**Effect of pH**

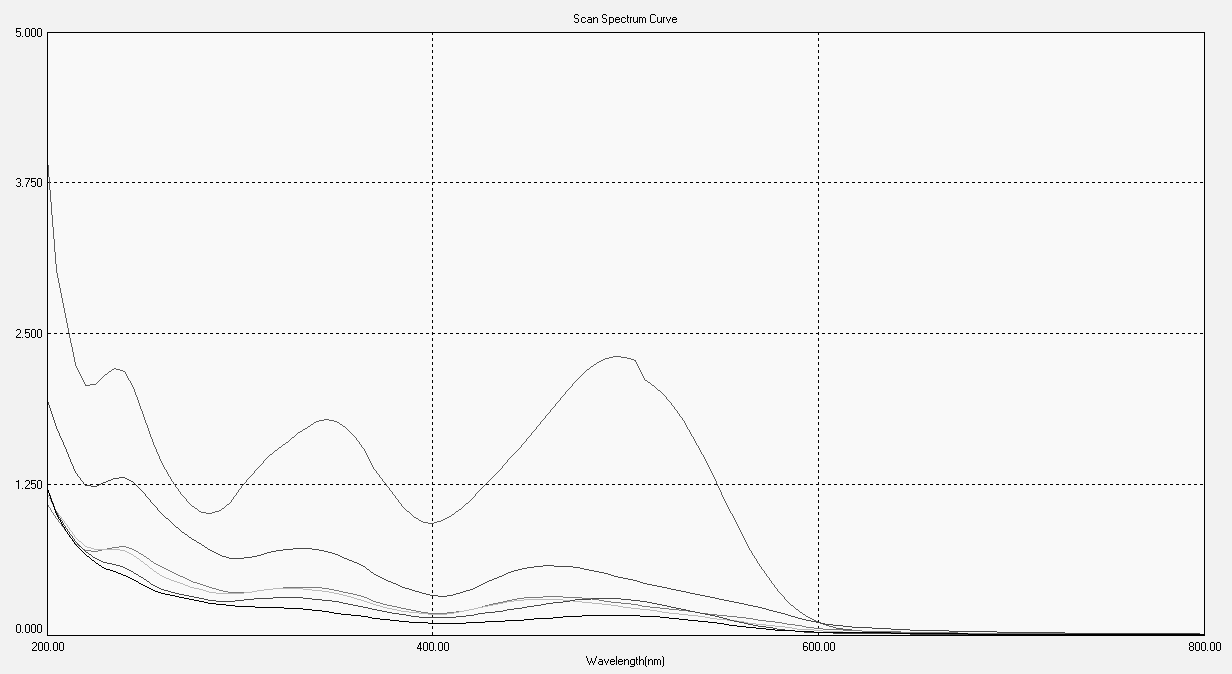
The initial pH of dye solution play an important role for adsorption process because The initial pH have direct influence on the dye and adsorbent in aqueous solution[16]. the effect of pH is studied between 4 and 9because reported that at strong acidic medium, the solution of CongoRed changes its color from red to dark blue and the original red colour is different above pH 10. pH values as shown in Fig. 3, the removal Cogo red percentage the maximum removal efficiency is achieved in the acidic medium and gradually reduced to the basic medium. In the acidicmedium, the solution of Congo Red exists as cationic form (asFig 3)[17,18], and the adsorption of cation favorite at pH >pHzp[19] this result indicated that the surface of barnacle shell powder have negative charge in acidic medium. Due to reduced negative site 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)[20] (as Fig.3). Also in the basic medium there are competing between anionic dye and –OH exists in the basic medium to attraction with adsorption site[18,20].

**Fig. 4**: Effect of pH on adsorption of CR on powder of barnacle shells. Conditions: V=100ml; temp. = 20±2 °C; C0=50 mgL-1; Dose of powder of barnacle shells = 10 g L-1.

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**Fig.5**.[18]Structure for Congo red dye at (a) basic medium, (b) acidic medium.

After the optimum conditions were limited the absorption of Congo red dye onto powder of the barnacle shell was illustrated in the fig.6.



The adsorption of Congo Red on powder of barnacle shells. Conditions: V=100ml; temp. = 20±2 °C; C0=50 mgL-1; Dose of barnacle shells powder = 10 g L-1.

**Conclusions**

In this study, batch adsorption experiments for the removal of and Congo Red dyes from aqueous solutions had been carried out using barnacle shell powder as adsorbents. This adsorbent may be viewed as useful natural material while considering the economic aspects of wastewater treatment. The obtained results can be summarized as follows:

* The optimum dye concentration for the both dye was found to be 30 mg/L for MAC.
* the removal percentage Increase with Increasing of adsorbent dosage due to Increasing of adsorption sites.
* The equilibrium time for the adsorption of Congo Red dye from aqueous solution was 30 min. The optimum time removal was found to be 3 hour.
* The acidic mediums favor for adsorption Congo red on the powder barnacle shells.
* adsorption Congo red dye on powder of barnacle shells in The acidic mediums more favorite then the basic mediums.

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