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Aquatic Crustean shells as adsorbents for paraquate pesticide removal from its aqueous solution by thermal activation

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Abstract

The present work aims to investigate the removal of Paraquat dichloride Pesticide from aqueous solutions by low cost ,neutral adsorbents, eco-friendly, highly efficient such as aquatic crustean shells under various activation experimental conditions, as an ideal alternative to the current expensive methods of removing pesticide from waste water. Preliminary studies showed that paraquate attained equilibrium at 2 hours in barnacle shell powder indicating to the relative adsorption increased with increasing solution concentration. The results were showed the removal percentage increase with increasing of heat treatment of the adsorbent media (barnacle shell powder).

Key words*:* Paraquate dichloride pesticide, Adsorption, Aquatic crustean shells, thermal activation, X-Ray.

Introduction

Paraquate (1, 1'-dimethyl-4, 4'-bipyridilium dichloride) was invented in England in 1956 and due to its good herbicidal effects (a quick acting, non-selective herbicide [1], and destroys green plant tissue on contact and by translocation within the plant) has been continuously used in agriculture since early 1960s[1], Paraquate is sold in about 130 countries for use producing large economic gains. herbicides that give rise to serious health problems[2],Paraquate is one of the most hazardous compounds for health[3]. The repeated exposures and especially when not use properly may cause skin irritation, sensitization, or ulcerations on contact [4, 5]. Paraquate banned in some country such as Germany and Japan and other urban country, due to its toxicity [6]. Paraquate have been classified as

restricted pesticides [1]. Herbicide and Pesticides have been observed in different kinds of samples such as waters samples, soil, liver samples of birds and agrochemicals [7, 8, and 9]. Paraquate has a high solubility (about 620g/l at 25°C) in water for this reason this herbicide considered real contaminate for water [10].

Therefore it must be eliminate these dangerous compounds from water for improving water environment. Adsorption is one of the most an important removal methods[11,12,13] especially ,if the adsorbet neutral material such as activated carbon product from neutral material. In this paper we investigate the removal of Paraquate dichloride Pesticide from aqueous solutions by low cost neutral adsorbents, eco-friendly, highly efficient barnacle shells under various activation experimental conditions, as an ideal alternative to the current expensive methods of removing pesticide from waste waterThe present study aimed to use the neutral material from local environmental as adsorbent material to treatment water of water from paraquate pesticide.

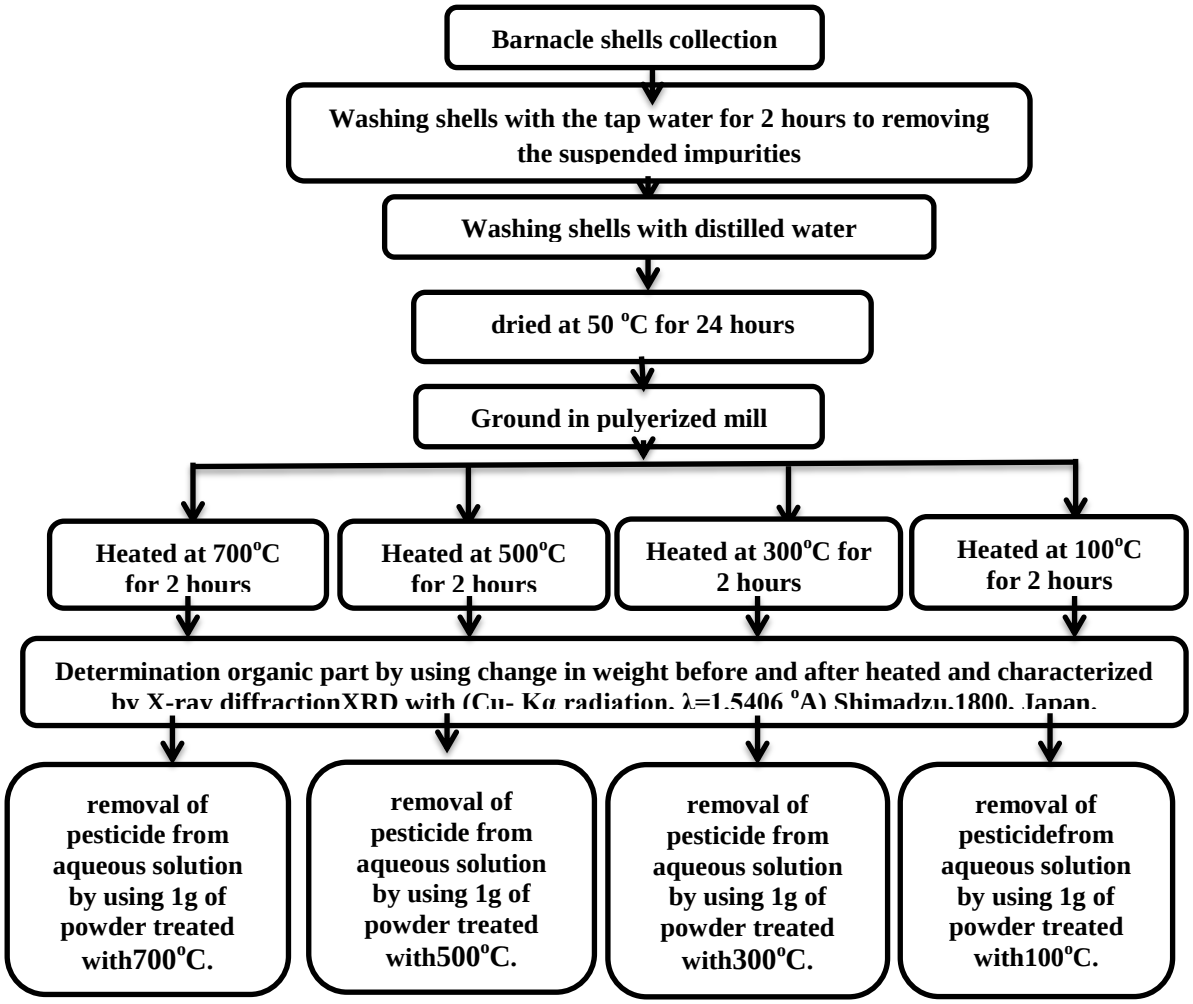
Materials and Methods

Preparation of Adsorbent

The crustean shells were used as adsorbent ,that were collected from the Shomalley Water drainage station in the Babylon city (middle of Iraq) Plate:1 , this animals come from salts water systems in southern of Iraq and recorded in first time in this environment.

Plate.1: Barnacles shells in the Shomalley Water drainage station, and team work that collected of barnacle shells from the study station.

Experimental design:



Preparation Adsorbate Solution

The paraquate dichloride pesticide (Chemical formula=$C_{12}H_{14}N_2]CL_2$, Formula weight=257.2g.mol^{-1}) supplied by BHD company . The solution of pesticide 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.

Removal pesticide

One gm of Barnacle shells powder (i.e. adsorbent) was weighed each into 250ml conical flasks. 100ml of the solution pesticide 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 were separation by centrifuged from solution to obtain the equilibrium concentration. The final concentration of paraquate dichloride was estimated for each sample spectrophometrically at the wavelength corresponding to maximum absorbance for paraquate dichloride using a spectrophotometer (UV/VIS-JENWAY,1600, German). A graph of removal pesticide percentage (g/L) versus time (hour) was plotted for Congo red. Generally the amount of pesticide removal was calculated from following equation: $removal\% = (A° - A)\ /A° \times 100\ldots$

A^o and A is the absorption of concentration of pesticide before and after adsorption respectively.

Results and discussion

The color of Barnacle shells after washing and grounded in pulverized mill become colorless as in the pleat.1.As show in the figure 1 the Wight loss percentages is directly proportionally with the temperature, the loss wight increase with increasing temperature.

Determination of organic material and Structure of barnacle shell

XRD scanning: the Fig:1 show XRD pattern for the powder prepared (barnacle shells), the results of XRD show sharp beak in bird which indicated the well-define nanocrystalline material. The size of the crystallite calculated by Shurrer [14] formula

$$D=K\lambda/\beta\cos\theta$$

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 θ is Bragg angle. Generally the practical size at maximum intensity was found 40.8nm.The literature review indicated that organic material are specific proteins, comprising the shell organic matrix, this proteins play major role in controlling the polymorph type, size and morphology of precipitating crystals. The organic matrix is a high degree of control on the precipitation (of calcium carbonate) process by different components of the organic matrix[15].Barnacle shell organic matrix contains similar to those found in avian eggshell and mollusk shell[16], which are very active in controlling the precipitation of calcium carbonate during the formation of these bio mineral structures.

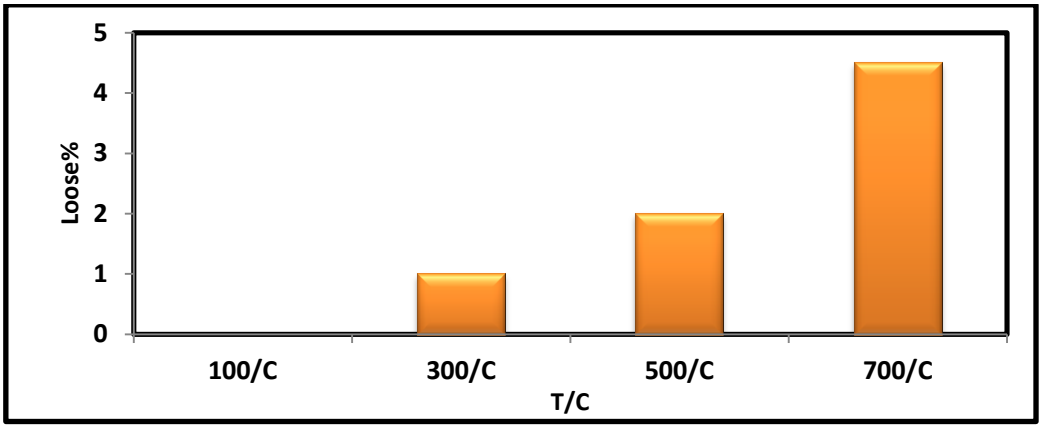


Fig.1: The organic matter contents of different structural parts of the crustean shells.

Table 1: The crystallite size of crustean shells and change its with temperature.

Sample No	Temperature C°	crystallite size(nm)
1	100	27.4
2	300	27.4
3	500	27.9
4	700	27.9

Generally the organic matter percentage was 1.3% when barnacle shell powder treated with 300-350°C(Fig.1) , this results agree with that found by previous studies [17]. The organic matter content was 1.2% when barnacle shell powder treated with 300 to 350°C (Table, 1 ; Fig.2)

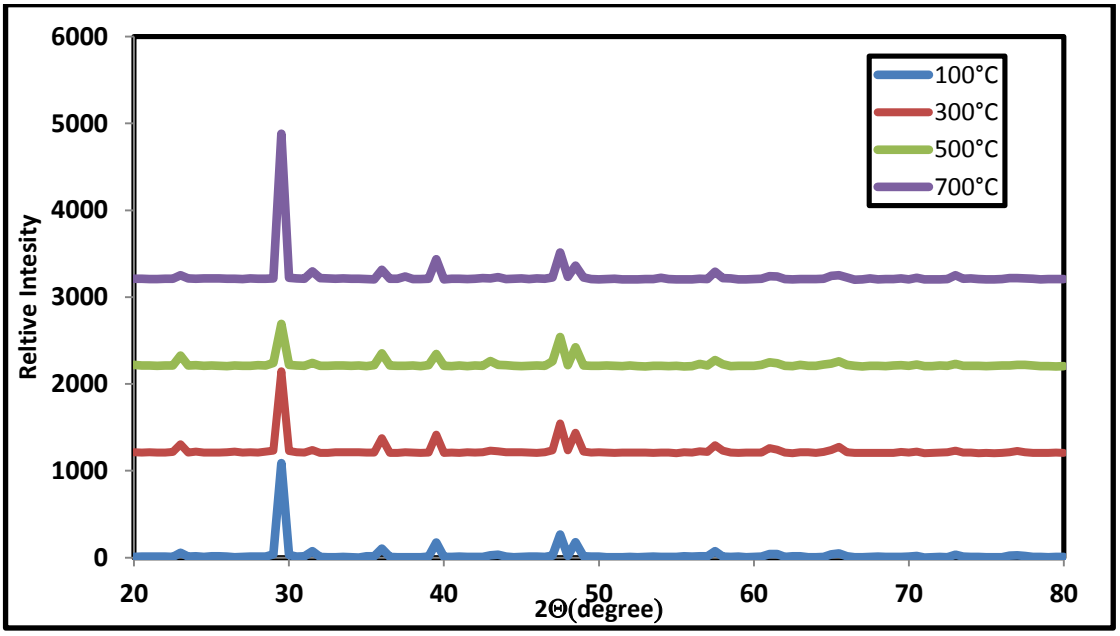


Fig.2: effect temperature on the structure powder of the crustean shells.

Removal pesticide activity

crustean shells powder, as efficient natural adsorbents, are one of the main components that found in soils of agricultural earth and possess a negative charge that is compensated for by exchange

cations, on their surfaces, such as Na^{+} and Ca^{+2}. When paraquat molecules bind to sites on crustean shells powder and penetrate the inter-lattice regions of the expanding clay particles, the herbicide persists for some time because it is no longer available for exchange with other cations. When paraquate enters the soil environment, it is rapidly and strongly bound to clay minerals and organic matter, this nature become it biologically inactive [18, 19].

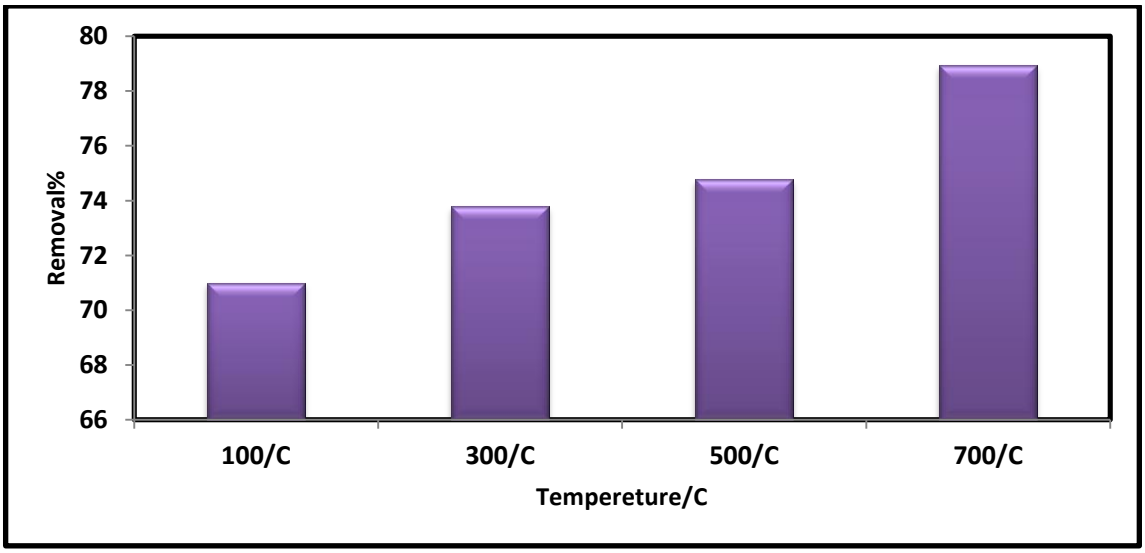


Fig.3: Effect the temperature of crustean shells treatment on the removal paraquate pesticide.

Same say for the barnacle shell powder with the paraquate dichloride. Generally Preliminary studies showed that paraquate attained equilibrium at 2 hours in barnacle shell powder (Fig.3). indicating to the relative adsorption increased with increasing solution concentration(Fig.4). This indicates high adsorption of paraquate to barnacle shell powder, as reported in previous adsorption paraquate on the clays studies. Paraquate adsorbs easily to predominantly negatively charged barnacle shell powder. The mechanism of adsorption of paraquate involves ionic and charge transfer bonds.

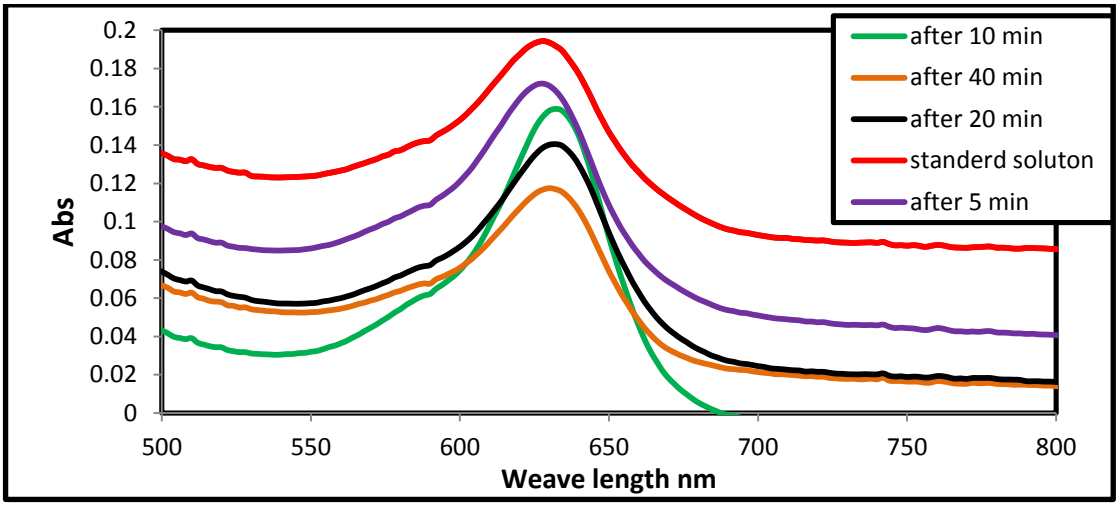


Fig.4: Effect temperature of crustean shells treatment on the removal paraquate pesticide spectrophotometer study.

Conclusions

In this study, batch adsorption experiments for the removal of paraquate dicloride 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: .

- Barnacle shell composite from 1.3-1.6% organic materials.
- The mineral part has higher thermal stability.
- the removal percentage Increase with increasing of heat treatment of the adsorbent (barnacle shell powder).

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