International Journal of Research in Engineering and Science (IJRES)
ISSN (Online): 2320-9364, ISSN (Print): 2320-9356
www.ijres.org Volume 9 Issue 3 ǁ 2021 ǁ PP. 01-18

Using Novel Low Cost Adsorbents to Remove Some Organic Dye from Waste Water

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ABSTRACT
Our study concentrated on studying the kinetics, thermodynamics and the equilibrium of adsorption of Cresol Red (CR) dye on the animal bone and egg shell as a new cheap adsorbent. Ideal adsorption conditions had been examined by changing the solution pH , adsorbent initial dye concentrations, adsorbent sizes, and different temperatures. The data of equilibrium have been found to fit with Langmuir model than Freundlich isotherm model, and a pseudo second order kinetic is the best model to explain the kinetics . Thermodynamic study concluded the spontaneous and endothermic nature of the adsorption of cresol red on animal bone and exothermic nature of adsorption of cresol red on egg shell. The adsorption cresol red on animal bone and egg shell shows their ability in degradation of dyes from aqueous solutions.

KEYWORDS: *Animal bone , Egg shell, degradation , Cresol red, Kinetics.*

Date of Submission: 09-03-2021 Date of acceptance: 23-03-2021

I. INTRODUCTION

Water is an important reason that keep life and energy on the earth, while millions of people in all the world are facing problems of the lack of fresh and clean drinking water. Industrial development has led to major problems of environmental pollution level. Great quantities of contaminants are released into bodies of water such as metal ions, and a large amount of phenol and its derivatives, amongst others. Water pollution and its negative effect on environmental health are some of the important challenges for scientists. The presence of dyes in plastics, cosmetics, pharmaceuticals, food, and other industries generates a huge volume of wastewater every year[**1**]. Some dyes that checked in wastewater even decay to form cancer-causing aromatic amines under anaerobic circumstances, which will origin serious health harms to humans and animals **[2].**

Current days there are many kinds of industrial dyes are developed with the production of over nine million tons yearly.

So, the development of a maintainable technique for wastewater management and for the dye industry became a challenge for observing the dyes in the environment. In particular, many efforts have been created to produce adsorbents that could destroy dyes from drinking water [3,4].

Remediation of industrial wastewater is more essential in the upcoming days because of global rules which required the reduction of different compounds in the cleaned water **[5].**

Artificial dyes are commonly used in numerous fields of modern technology, e.g., in a lot of textile industry branches, the tanning of leather industry, in the paper tanning industry, in food processing technology, in the research of agricultural fields, in light-harvesting arrays, in photoelectrochemical cells, and hair dying tools. Furthermore, artificial dyes have been applied to control the efficiency of sewage and wastewater treatment, and to determine the specific surface area of activated mud for groundwater tracing, etc **[6].**

The degradation of dyes from wastewater became so urgent to protect the ecosystem and human health. using of these aromatic artificial dyes increases daily in different industries mainly in the fabric industries, the pollution of water in these dyes can be the reason for serious problems to the aquatic life and all living organisms.**[7].**

Dye adsorption from aqueous solutions is of considerable practical interest in the context of wastewater treatment and purification because these compounds are considered as priority pollutants due to their stability, low biodegradability, and toxicological profile. Performance of water decolorization processes can vary significantly depending on the adsorbent, dye chemical structure, and operating conditions. sure, Physico-chemical properties of dyes have a significant role in the molecular interactions that present in aqueous phase

adsorption **[8].** Various methods such as biosorption, adsorption, coagulation/ flocculation, advanced chemical oxidation methods, membrane filtration, treatment by Ozon, and photocatalysis are used for the removal of these pollutants. Among these, biosorption appears quite interesting both from an economical and an environmental point of view, in light of its performances and reduced environmental impact **[8,9].**

Adsorption is an important unit operation in several natural and industrial systems such as fundamental biological studies, separation and purification processes, recovery of chemical compounds, and waste treatment processes. It can replace with other separation processes and contribute efficiently to the removal of contaminants from an aqueous solution **[10].** Adsorption technique is a physicochemical wastewater remediation process in which the dissolved molecules are attracted to the adsorbent surface by physical-chemical forces**,** describing the development of an adsorbate molecule from the bulk to the location of adsorption**.**

In the previous recent years, producing cheap adsorbents to degrade dyes that present in wastewater became of a great importance. Use of cheap adsorbents for dye degradation has been examined, and many, cheap adsorbents have been suggested. In our study, we concentrated on creating new different techniques to treat the wastewater from organic dyes by the use of cheap and effective adsorbents **[11].**

Animal bone is used as an efficient adsorbent because it is inexpensive and available. A lot of animals have a great number of bones that can be used as feedstock or fuel for the generation of energy after the slaughterhouse industry. On the other hand, functional groups on the surface of bone show an ideal adsorption capacity for polar or polarizable molecules after suitable modification. Increasing attention has been paid to modified adsorbents for the removal and recovery of different pollutants such as metal ions, organic dyes, and immobilization of enzymes or proteins. These applications could be related to the functional groups of the adsorbent's surface, which can be modified appropriately **[12].**

Eggs are one of the most important Food incomes in the framework of world-wide Feeding, they are important as a source of vital nutrients to human food such as Proteins, fat-soluble vitamins (A, D, E and K) and trace-minerals like iron and zinc **[13,14].** The eggshell of the Hen usually formed from ceramic constituents that have three-layered structure, namely the cuticle on the outer surface, a spongy (calcareous) layer and an inner mammillary layer **[15,16].**

The calcareous and mammillary layers form a matrix consists of protein fibers attached to calcite (calcium carbonate) crystal. Moreover, These two layers are arranged in such a way that contains numerous rounded openings (holes). This arrangement allows the exchanging of gases through the shell. The outer surface of the eggshell is covered with a Mucin protein which acts as a soluble plug for the holes in the shell. The cuticle is also permeable to gas transmission. The percentage of the chemical components (by weight) of the eggshell by-product has been stated as Calcium Carbonate (94%), Magnesium Carbonate (1%), Calcium Phosphate (1%), and Organic Material (4%) **[16].**

The eggshell by-product is about 11% of the whole weight (60 g) of the egg **[16].** It was also stated that about 28% of all eggs produced were directed to commercial breaking operations for the formation of egg products **[17,18].**

II. EXPERIMENTAL

Cresol Red was used as a pH sensitive indicator dye in Nano-engineered optical urea biosensors films and hetero-core structured fibre optic pH sensor. Cresol red obtained from El- Gomhoria company, Egypt having molecular formula C21H18O5S (mol. wt. 382.43 g/L) is chosen as adsorbate scheme.

Cresol red can be used in many common molecular biology reactions in place of other loading dyes as it does not inhibit *Taq polymerase* to the same extent as other common dyes.

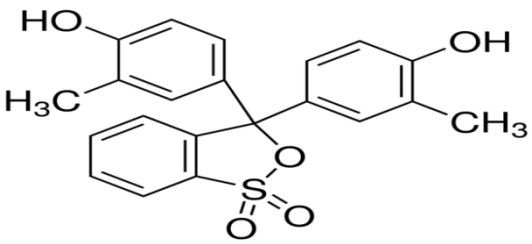


Fig (1): chemical structure of Cresol red

Five solutions of cresol red were prepared with concentrations from 1.0 x10-5 M to 5.0 x 10-5 M. Each solution was then analyzed in a UV-9200 UV-VIS spectrophotometer. A plot of absorbance versus λ for each concentration was obtained and λmax of 367 nm cresol red was experimentally obtained.
By applying Beer-Lambert law (eq.1)

$$A = \varepsilon.C.L \quad (1)$$

Where A is the absorbance of the solution, L is the cell length (1 cm), ε is the molar extinction coefficient (O.D.mole-1cm-1) and C is the molar concentration (M) of dye in solution **[19].**

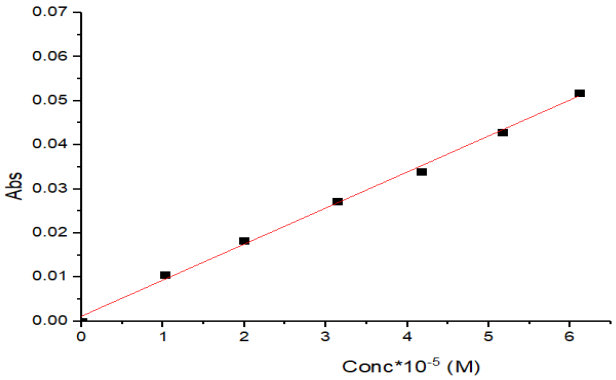


Fig (2): The molar extinction coefficient of cresol red.

It was found that for cresol red is 0.618 x 10^4 $mole^{-1}$ cm^{-1} and r^2 is 0.9993.

Animal bones were bought from butcher shops, and cleaned from any involved meat and fat. then they were washed sometimes using water and kept in air some days in order to eliminate any smells, then they were put in an oven adjusted at temperature 80 °C for complete drying. Then we applied crushing and milling on the dried bones to produce particles have size range of (3.2, 2.36, and 0.85 mm) then calcined for 2 hr at 800 °C. The deposit was cleaned using tap water then dried all night at 100 °C in an oven, and then calcined at a rate of heating 2 °C/min to 400 °C and reservd at this temperature for 4 h until obtaining a constant weight. The resultant matter was referred to as calcined bones designated by (CB). **[20].**

Eggshells were collected from local restaurants. To prevent decomposition, eggshells were first washed in tap water, then boiled in distilled water, and finally dried at 105 °C in a hot air oven for 2 h. The dried eggshell was crushed into a powder crusher and sieved to different sizes (0.850 , 0.355 and 0.180 mm)and then preserved in the desiccators for use**. [21].**

III. RESULTS AND DISCUSSION

3.1. Characterization

FTIR spectrum of animal bone **Fig.3(a)** shows the characteristic bands of hydroxyapatit (547.84, 625.73 and 988.80 cm^{-1} (shoulder), 1176.15 (shoulder) cm^{-1}due to phosphate vibrations and collagen (C,O stretching vibration at 1650 cm -1, N–H in plane bending at 1459 cm^{-1}, C–H and N–H stretching modes in 2962.35 –3459 cm^{-1} region) **[22,23,24] .**

Additionally, the typical bands of carbonate substituting for phosphate site (type B) in the apatite lattice are also observed: band at 746.28 cm -1 and double bands at 1287.20 /1459 cm^{-1} **[25,26].**

The diffractogram of animal bone presents the hydroxyapatite pattern. These outcomes prove that the amorphous component was released after calcinations as found in the literature **[27].** After adsorption of cresol red **Fig. 3(b)**, there is a strong shift in positions and new peaks appear and some peaks disappeared. The analysis of the FT-IR spectrum of eggshell **Fig. 3(c)** discovered the carbonate group presence and proved by the characteristic-peak at 1523 also at 659.39, and 1795.96 cm^{-1}. Furthermore, the observed peaks take place in the area between 3400–3500 and 2516 cm^{-1}, that might be related to amino-groups. The bands between 2875 and 2982 cm^{-1} characterize carbon bonded hydrogen vibration, signifying the presence of an organic layers, formed from amino acids that are involved in the eggshells. The same opinion was stated by **[28].** It was obvious that after the biosorption of dye **Fig. 3(d)** all the previous mentioned peaks indistinguishably change their positions and the greatest change noticed at the peaks of the carbonate group .

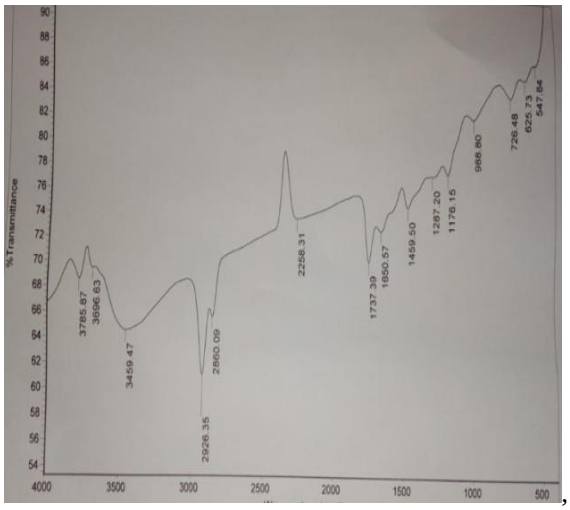


Fig. 3 (a): FT-IR spectrum of red adsorbed on animal bone.

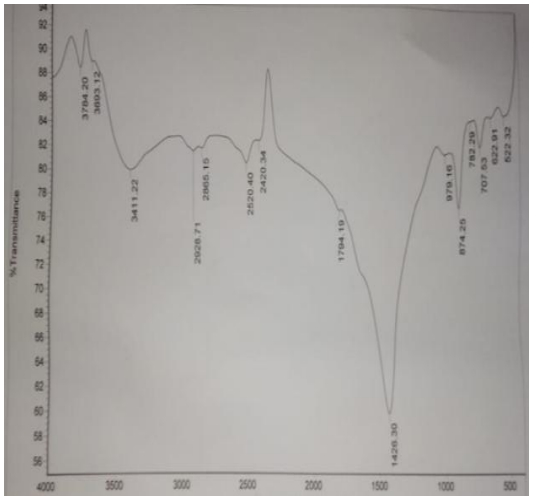


Fig. 3 (b): FT-IR spectrum of cresol animal bone.

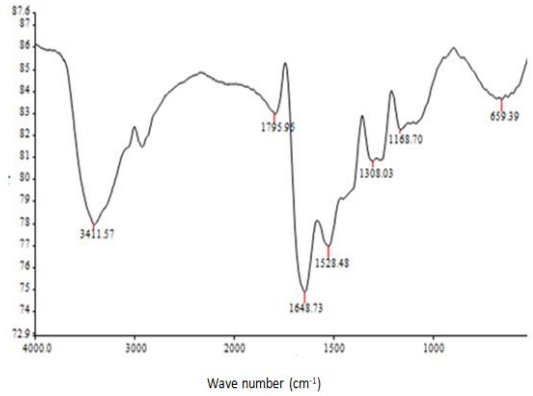


Fig.3 (c): FT-IR spectrum of egg shell.

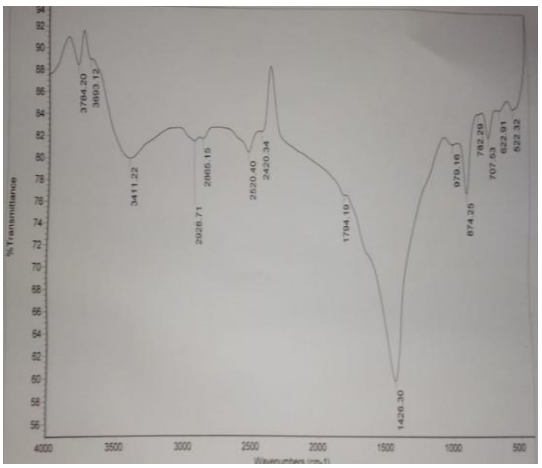


Fig. 3 (d): FT-IR spectrum of cresol red. adsorbed on egg shell.

The technique of scanning electron microscope (SEM) is a primary device for studying the changes of surface morphology, distribution, and fundamental physical properties of the adsorbents after adsorption. The SEM analysis presented in Fig. 4(a)shows that the animal bone has an accumulation of fine particles of irregular form and size with a quite small ravines**[29].** Fig. 4(b) Images after adsorption of cresol red on animal bone shows that more particles are present on the animal surface which becomes rough contains protuberances and thin cylindrical shapes. These particles of cresol red. The negatively charged dye molecules will be electrostatically attracted to the adsorbents animal bone and eggshell. **[30].** Figure 4(c) indicates an irregular pore canals for eggshell adsorbent particles, columns, and crescent-shaped mammillary layers. We see also that the surface after adsorption Fig. 4(d)shows clear pro tubes due to a good chance for dyes to be trapped and adsorbed into these pores **[31].**

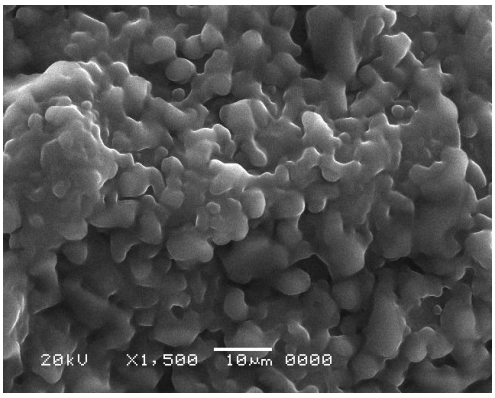


Fig.4(a) animal bone

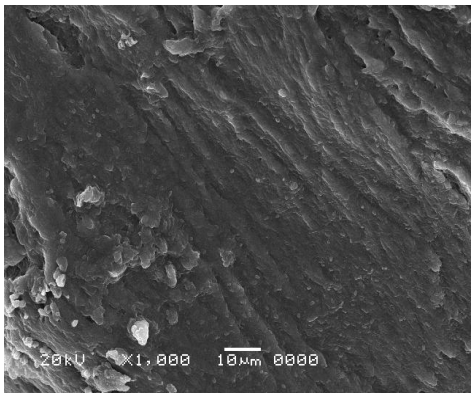


Fig. 4(b) cresol red adsorbed On animal bone

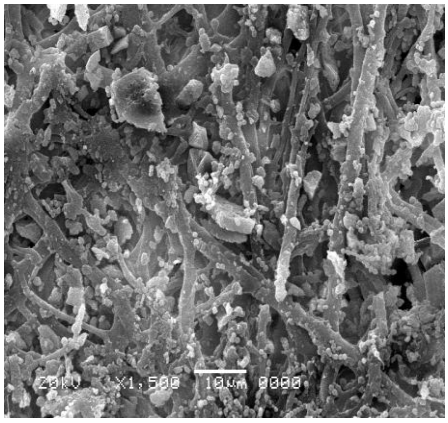


Fig. 4(c) egg shell

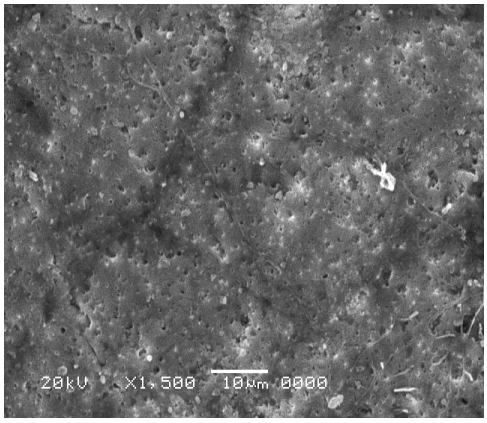


Fig. 4(d) cresol red adsorbed On egg shell

3.2. Effect of pH

The pH values of the solution are an important parameter during the adsorption processes. The adsorption of cresol red dye by animal bone and eggshell was % 45.8 and % 90.3 at pH2 which increase to 81.5 % and 91.5 % at pH7 and pH4, respectively for both adsorbents and at 60 min Fig (5 and 6).

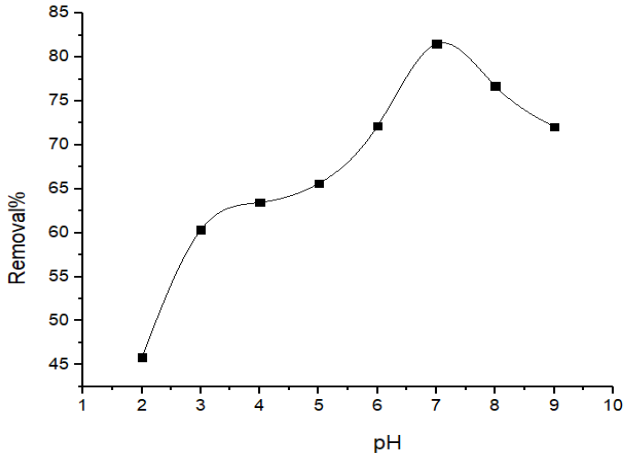


Fig (5) : Effect of pH on removal percent of cersol red at different contact time with initial crsol red concentration 3.82mg/L and animal bone dose 0.75 g of particle size 2.36 mm at 30 °C and 60 min.

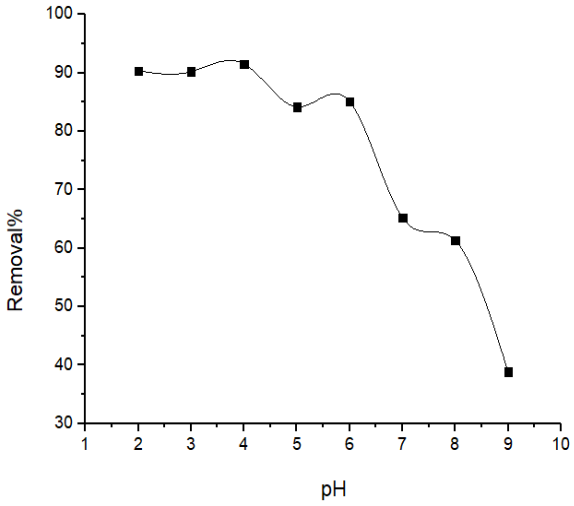


Fig (6) : Effect of pH on removal percent of cersol red at different contact time with initial crsol red concentration 3.82mg/L and egg shell dose 0.75 g of particle size 0.850 mm at 30 °C and 60 min.

The zero charge point (pHpzc) is an important parameter for biosorbent to characterize the sensitivity to pH and their surface charges, **[32].** The point zero charge of adsorbent was estimated by the solid addition method. The batch equilibrium technique was used to calculate variables such as zero charge point, the effect of pH, and surface chemistry. The activation of acidic or basic functional groups of adsorbents approaches zero at the zero charge point, **[33,34].** The pHpzc was found to be 8.1, 8 for ((animal bone and eggshell) samples, respectively meaning that the surface was positively charged Fig (7 and 8).

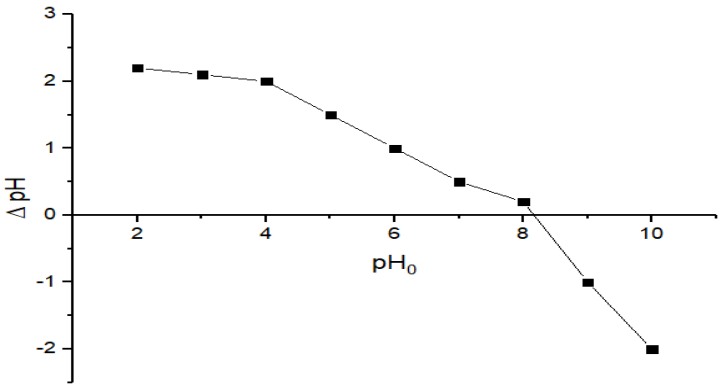


Fig (7) : The point zero charge of animal bone.

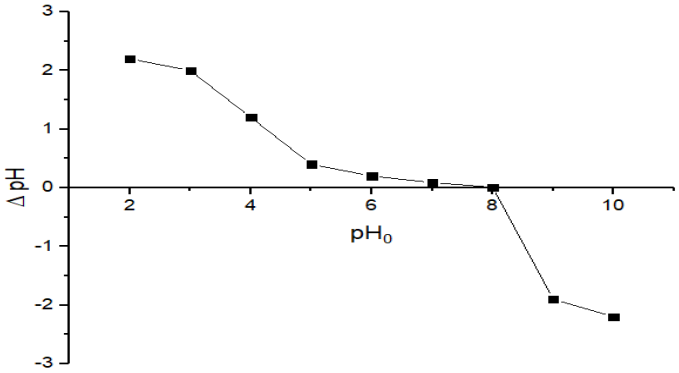


Fig (8) : The point zero charge of egg shell.

3.3. Effect of initial dye concentration

The initial adsorbate concentration in solution and the equilibrium time play important roles during the uptake of dyes from solution by adsorption. Time consumed to reach equilibrium is an important factor to

expect the effectiveness and viability of an adsorbent when it is used for controlling water pollution,**[35,36].** The results show the adsorption capacity is concentration-dependent and decrease with increasing the concentration of the dye. The dye concentration affected the diffusion of dye molecules through the solution to the adsorbent's surface. The increase in concentration resulted in an increase in driving force to the concentration gradient, which helps in advance the diffusion of the dye from the solution into the adsorbent **[37,38,34].**

By increasing dye concentration from (3.81 to 26.74 mg/L) for cerasol red The removal percent of cresol red by (animal bone and eggshell) decreased from 83% to 69 % for (animal bone) and from 86.2 % to 74.5% for (eggshell), Fig (9 and 10).

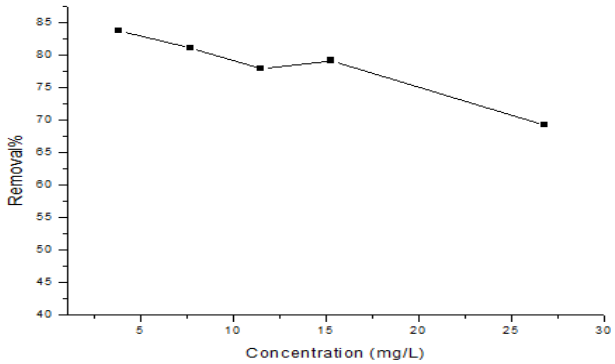


Fig (9) : Effect of initial dye concentration on removal percent of cersol red at different contact time with animal bone dose 0.75 g of particle size 2.36mm at pH 7and 30 °C and at 60 min.

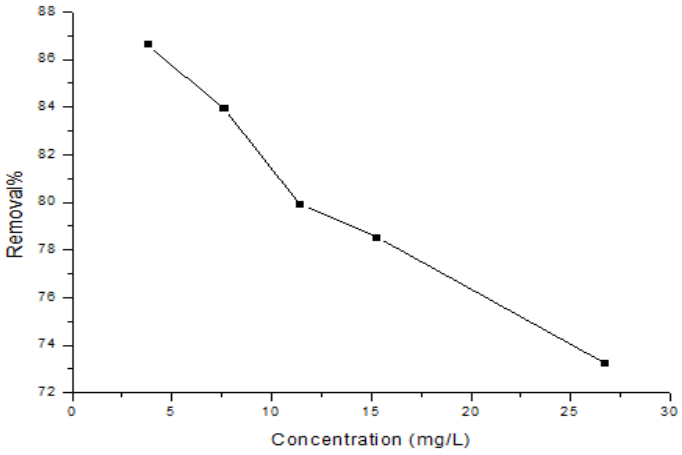


Fig (10) : Effect of initial dye concentration on removal percent of cersol red at different contact time with egg shell dose 0.75 g of particle size 0.850 mm at PH 4 and 30 °C at 60 min.

3.4. Effect of adsorbent dose

The fixed quantity of adsorbent is very important for the degradation of particular concentration of dyes ion from solution and it determined the capacity of adsorbent for the given concentration of adsorbate.

It is clear from these results that the increase in the concentration of adsorbents led to a rise in the removal of dyes because of the increasing in sites number that became more available on the adsorbent for the adsorption of dye **[39].**It is clear that the surface area and the number of empty adsorption sites increase by increasing the concentration of the adsorbent, and this results in increasing the amount of adsorbed dye. After equilibrium, it was noticed a drop in the adsorption amount. This may attributed to the aggregation or overlapping of adsorption sites that results in a decreasing in available adsorbent surface area for dyes and increasing in the length of the path of diffusion**[40].**

The experiment carried by taking different doses (0.25 – 1.25 g) in order to find the effect of different doses of animal bone and egg shell on the removal of cresol red. The efficiency of removal of cresol red by (animal bone and egg shell) increased from 65.13 % to 85.5 % and from 64.2 % to 85.7 %, respectively when the dose increase from (0.25- 0.75 g) then decrease to 84 % of dose 1.25g for animal bone and egg shell

respectively. It was found that the surface area increased by increasing the concentration of the adsorbent which result in a high dye removal, Fig (11 and 12)**[41].**

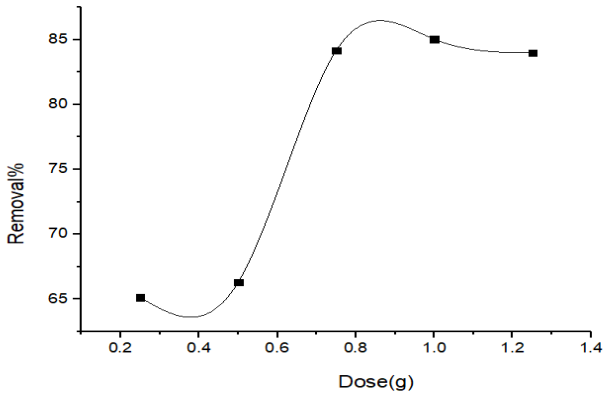


Fig (11) : Effect of different dose of animal bone on removal percent of cersol red at different contact time with initial crsol red concentration 3.82 mg/L and animal bone of particle size 2.36 mm at pH 7and 30 °C

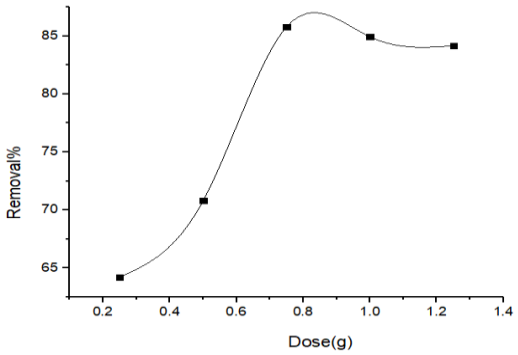


Fig (12) : Effect of different dose on removal percent of cersol red at different contact time with egg shell of particle size 0.850mm at PH 4 and 30 °C at 60 min.

3.5. Effect of adsorbent size

The contact surface between the sorbent and the liquid phase is a great factor that affect the adsorption processes. The effect of particle size of animal bone and egg shell on cresol red removal was studied using three particle sizes (3.2 mm , 2.36mm and 0.85mm)for animal bone and (0.85mm , 0.355mm and 0.180 mm)for egg shell.

Results show that the removal efficiency of cresol red on (animal bone and egg shell) increased from 82 % to 88.3 % and from 81.2 % to 91.4% when the adsorbent particle size was decrease from (3.2 mm to 0.85mm) for animal bone and from(0.850 mm to 0.180mm) for egg shell after 60 min , respectively Fig (13 and 14) .

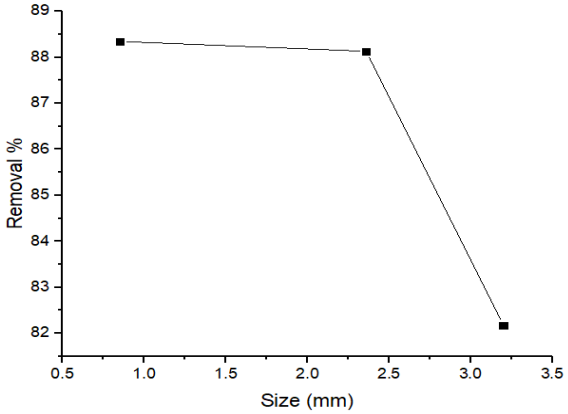


Fig (13) : Effect of different size on removal percent of cersol red with concentration 3.82 mg/L at different contact time with animal bone dose 0.75 g at pH 7 and 30 °C at 60 min.

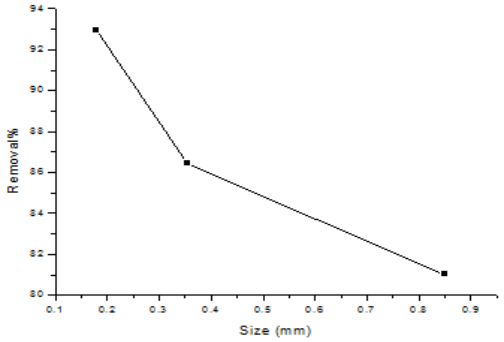


Fig (14) : Effect of initial size on removal percent of cersol red with concentration 3.82 mg/L of at different contact time with egg shell dose 0.75g at pH 4 and at 30 °C at 60 min.

3.6. Effect of temperature

A parameter with great significance in the process of sorption is the temperature. A study of the dependence of the temperature on adsorption reactions gives valuable knowledge about the enthalpy and entropy changes during adsorption **[42].**

The results indicate that adsorption of cresol red on animal bone increases with increasing the temperature , but adsorption of cresol red on egg shell decrease with increasing temperature. The removal efficiency of cresol red using animal bone increase from 82.3% to88.7 % and by egg shell decrease from 82.6 % to 56.2% Fig (15 and 16).

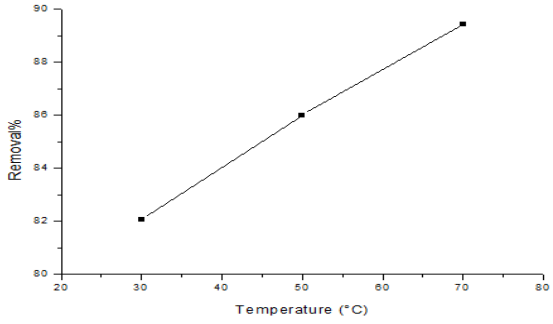


Fig (15) : Effect of different Temperature on removal percent of cersol red with concentration 3.82 mg/L at different contact time with pH 7 and animal bone 0 .75 g of particle size 0.850mm at 60 min.

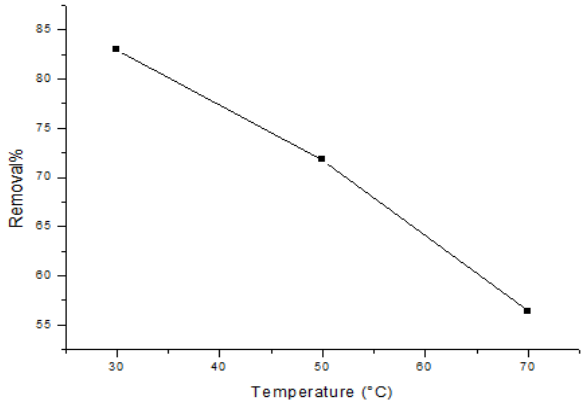


Fig (16) : Effect of different Temperature on removal percent of cersol red with concentration 3.82 mg/L e with egg shell dose 0.75 g and of particle size 0.850mm at PH 4 at 60 min.

3.6 Adsorption kinetics

The kinetic behavior of the process of adsorption is studied for cresol red under different pH values, concentrations, dose sizes and temperatures. The adsorption process was rapid in the initial 60 min indicating a high affinity between dyes molecules and adsorbents [animal bone and egg shell surface due to the intraparticle diffusion of dye molecules **[43-47] .**Following this phase, the adsorption process slows suggesting a gradual

equilibrium, possibly finally, the saturation is reached, showing the final equilibrium at approximately (60–120 min) for acid dye, beyond which no further adsorption takes place Fig (17-26).

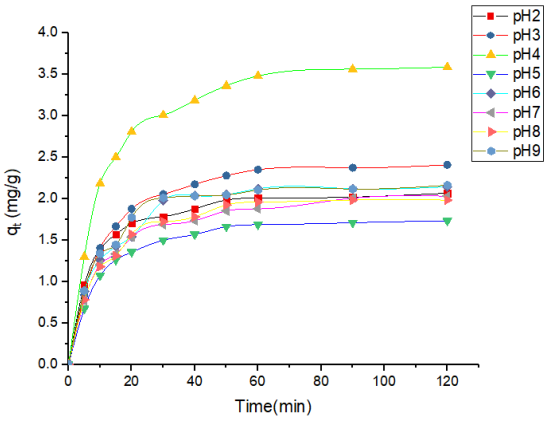


Fig (17) : Plot of cresol red sorption versus contact time at different pH values with initial cresol red concentration 3.82 mg/L and animal bone dose 0.75 g of particle 0.320 mm at 30 °C.

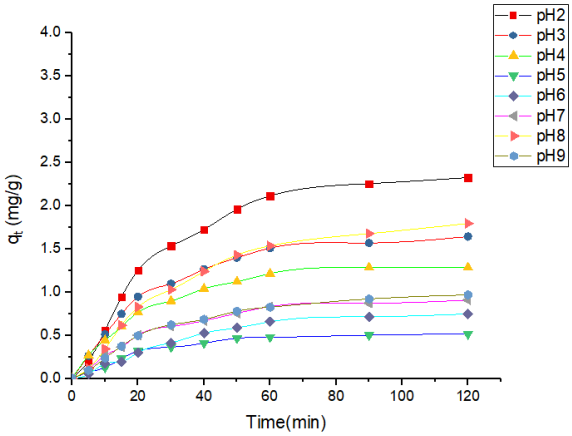


Fig (18) : Plot of cresol red sorption versus contact time at different pH values with initial cresol red concentration 3.82 mg/L and egg shell dose 0.75 g of particle 0.850 mm at 30 °C.

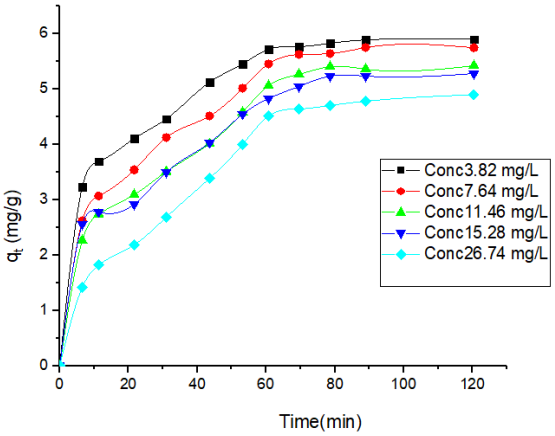


Fig (19) : Plot of cresol red sorption versus contact time at different initial cresol red concentration values with animal bone dose 0.75 g of particle 3.20 mm at pH 7 and 30 °C.

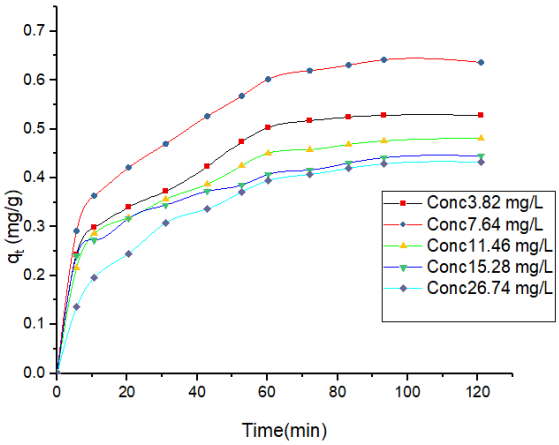


Fig (20) : Plot of cersol red sorption versus contact time at different initial cresol red concentration values with egg shell dose 0.75 g of particle 0.850 mm at pH 4 and 30 °C.

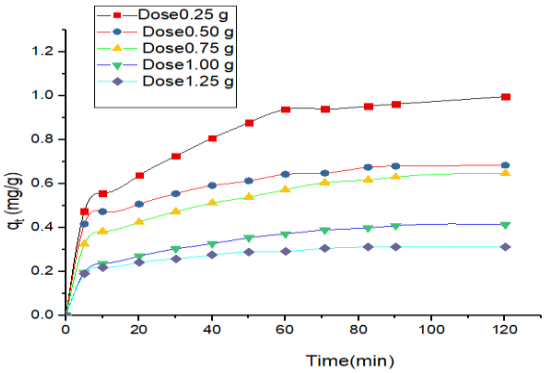


Fig (21) : Plot of cersol red sorption versus contact time at different animal bone dose values of particle size 3.20 mm with initial cersol red concentration 3.82 mg/L at pH 7 and 30 °C.

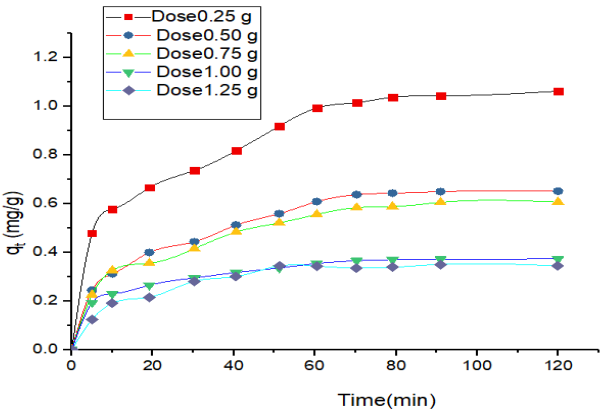


Fig (22) : Plot of cersol red sorption versus contact time at different egg shell dose values of particle size 0.850 mm with initial cersol red concentration 3.82 mg/L at pH 4 and 30 °C.

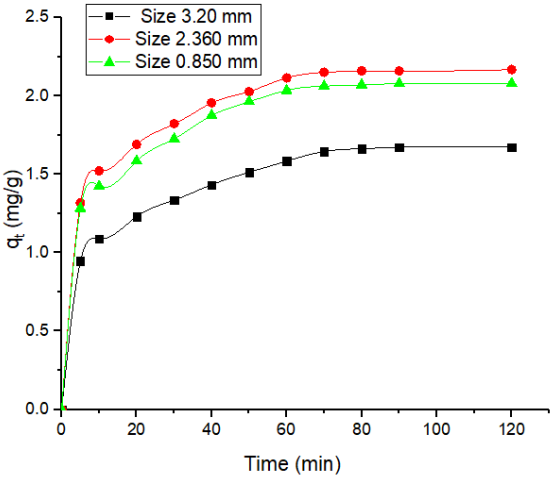
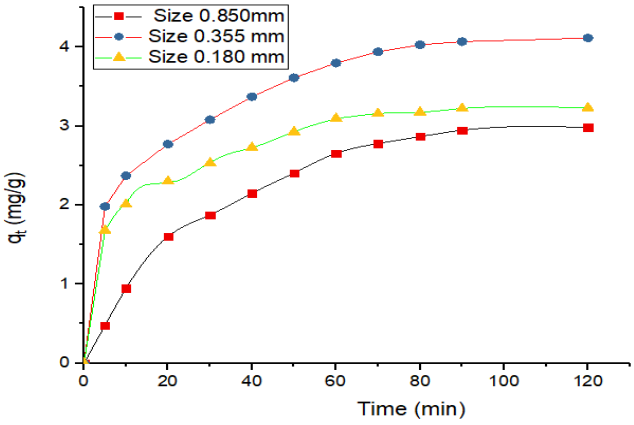


Fig (23) : Plot of cersol red sorption versus contact time at different size values with initial cersol red concentration 3.82 mg/L , animal bone dose 0.75 g at pH 7 and 30° C.



Fig(24): Plot of cersol red sorption versus contact time at different size values with initial cersol red concentration 3.82 mg/L ,egg shell dose 0.75 g at pH 4 and 30° C

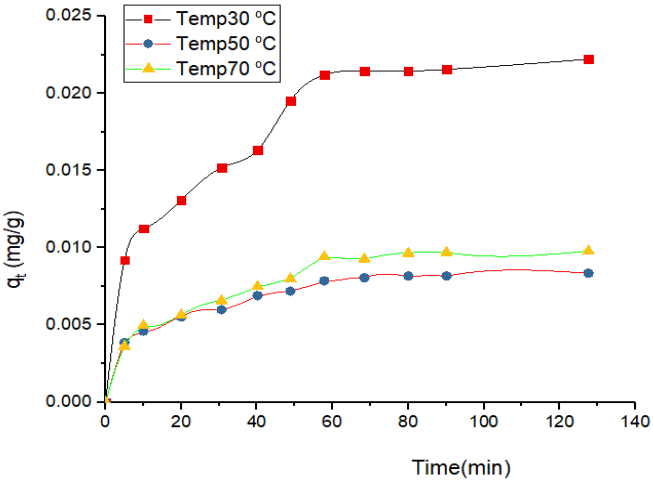


Fig (25) : Plot of cersol red sorption versus contact time at different temperature values with initial cersol red concentration 3.82 mg/L of particle size 0.850 mm and animal bone dose 0.75 g at pH 7.

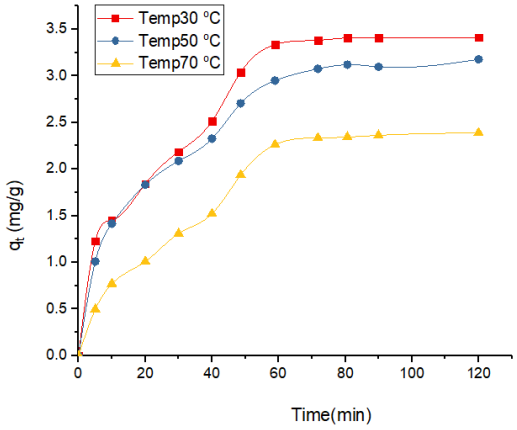


Fig (26) : Plot of cersol red sorption versus contact time at different temperature values with initial cersol red concentration 3.82 mg/L of particle size 0.180 mm and egg shell dose 0.75 g at pH 4.

3.7 Adsorption isotherms

The equilibrium adsorption models is necessary for describing the behavior of the interaction between solutes and adsorbents and is important in the scheme of an adsorption system.

- ***Langmuir assumption isotherm:***

Langmuir assumption isotherm considers that the monolayer-adsorption take place at the bindings sites with homogenous levels of energy, without interactions among the adsorbed particles and there is no migration of adsorbed particles on the surface of adsorption.

- ***Freundlich isotherm*:**

The Freundlich model is an equation based on the sorption on a heterogeneous surface.

The linear correlation coefficients i.e. regression factor for Langmuir and Freundlich models are represented in Tables (1and 2) . These coefficients are having values always greater than 0.931 except for Langmuir model which has a value of 0.983. The Langmuir model have a correlation coefficient of 0.983 that fit the experimental data than the Freundlich isotherm.

Table (1): Comparison of isotherm parameters obtained for the removal of cresol red on animal bone .

The Parameters	Langmuir Parameters				Freundlich Parameters		
	q_{max} (mg/g)	K_L x10 (L/mg)	R_L	r^2	K_F (L/g)	N	r^2
PH	2.058	0.465	0.360	0.996	2.908	2.460	0.953
Initial conc 3.82 (mg/L) 7.64 (mg/L) 11.46 (mg/L) 15.28 (mg/L) 26.74 (mg/L)	3.263	0.003	0.988 0.976 0.965 0.953 0.921	0.997	3.405	3.067	0.947
Size (mm)	0.992	0.001	0.996	0.986	9.160	3.951	0.991
Dose (g)	2.289	2.152	0.109	0.988	2.893	1.189	0.931
Temperature ^oC	5.456	3.889	0.063	0.983	1.184	6.885	0.999

Table (2) Comparison of isotherm parameters obtained for the removal of cresol red on egg shell

The Parameters	Langmuir Parameters				Freundlich Parameters		
	q_{max} (mg/g)	K_L x10 (L/mg)	R_L	r^2	K_F (L/g)	n	r^2
PH	0.952	0.266	0.496	0.994	1.988	2.424	0.936
Initial conc 3.82 (mg/L) 7.64 (mg/L) 11.46 (mg/L)	0.002	0.556	0.320 0.190 0.136	0.997	1.562	2.266	0.948

15.28 (mg/L)			0.105				
26.74 (mg/L)			0.063				
Size (mm)	2.769	0.001	0.998	0.983	9.490	2.993	0.994
Dose (g)	0.896	0.410	0.399	0.993	3.017	1.148	0.992
Temperature ^{o}C	1.867	2.707	0.088	0.988	1.703	1.103	0.985

3.8. Kinetics and isotherm studies

The kinetic parameters, which are needed to determine the adsorption rate, give important information for design and modeling of the adsorption operation. Several kinetic models have been used to study the kinetics of the adsorption process: pseudo first, pseudo second order kinetic and the model of intra-particle diffusion were applied for the experimental data with different pH, different initial dye concentrations, different doses, different particle sizes and different temperatures **[48,49,44,50,51,52,34]**.

The pseudo of the first , the second order kinetic and intra-particle diffusion models were used for the experimental data with different pH values, initial dye concentrations, different doses, different sizes and different temperatures for acid cresol dye indicated that for different dyes that the pseudo of the second-order equation better represented the adsorption kinetics, suggesting that the adsorption process is indicative of a chemisorptions mechanism, which show better fit with the experimental data better than the pseudo of the first-order model. Or we can say that the adsorptions of different dyes were similar to pseudo of the second-order model. As reported in previous theories, the pseudo of the second order model is depend on the theory that the rate of the determining step may be a chemical sorption including valence forces via distribution of electrons between adsorbent and adsorbate **[53-59].**

Table (3) : Kinetic parameters for the adsorption of cresol red on animal bone

The Parameters	Pscudo first order model			Pscudo 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
PH2	1.889	0.063	0.930	1.837	0.18	0.99	0.19	0.858
PH3	2.2876	0.0565	0.945	2.198	0.379	0.99	0.234	0.916
PH4	2.971666	0.0466	0.963	3.261	0.223	0.99	0.37	0.959
PH5	1.510393	0.0552	0.963	1.568	0.327	0.99	0.175	0.928
PH6	1.911393	0.0576	0.943	1.96	0.319	0.99	0.214	0.907
PH7	1.483303	0.1193	0.966	1.825	0.519	0.98	0.203	0.943
PH8	1.9067	0.0561	0.947	1.817	0.379	0.99	0.202	0.931
PH9	1.9503	0.0654	0.951	1.951	0.224	0.99	0.214	0.891
Initial concentration 3.82 mg/L	3.9388	0.0405	0.941	6.137	0.022	0.99	0.378	0.873
7.64 mg/L	4.2531	0.0383	0.946	6.036	0.015	0.98	0.491	0.915
11.46 mg/L	3.7815	0.0357	0.961	5.469	0.016	0.98	0.492	0.947
15.28 mg/L	4.4583	0.0403	0.955	6.217	0.015	0.98	0.495	0.911
26.74mg/L	3.7425	0.0294	0.948	5.302	0.008	0.98	0.500	0.947
Dose 0.25g	0.8517	0.0344	0.955	1.213	0.062	0.99	0.094	0.931
Dose 0.50g	0.4044	0.0402	0.938	0.705	0.271	0.99	0.050	0.743
Dose 0.75 g	0.4848	0.0436	0.912	0.673	0.179	0.99	0.050	0.843
Dose 1.00g	0.3225	0.0439	0.943	0.434	0.269	0.99	0.034	0.875
Dose 1.25g	0.1978	0.0457	0.930	0.321	0.677	0.99	0.024	0.756
Size 3.20 mm	1.304	0.651	0.909	1.740	0.099	0.994	0.088	0.917
2.36 mm	1.750	0.064	0.914	2.240	0.104	0.997	0.102	0.885
0.850 mm	1.743	0.066	0.931	1.610	0.104	0.996	0.101	0.891
Temperature 30 ˚C	2.0279	0.0413	0.939	2.28	0.050	0.99	0.118	0.9298
Temperature 50 ˚C	1.542	0.0451	0.933	3.181	0.063	0.99	0.154	0.915
Temperature 70 ˚C	2.01122	0.0413	0.955	3.240	0.050	0.99	0.161	0.938

Table (4) : Kinetic parameters for the adsorption of cresol red on egg shell

The Parameters	Pscudo first order model			Pscudo 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
PH2	2.615	0.036	0.952	2.750	0.0149	0.998	0.282	0.964
PH3	1.803	0.041	0.93	1.66	0.0560	0.999	0.166	0.951
PH4	1.37	0.037	0.956	1.283	0.099	0.998	0.141	0.961
PH5	0.591	0.042	0.962	0.556	0.123	0.099	0.063	0.97
PH6	0.867	0.033	0.918	1.018	0.022	0.997	0.086	0.953
PH7	1.015	0.038	0.92	0.974	0.063	0.999	0.107	0.967
PH8	1.973	0.033	0.955	2.377	0.0105	0.998	0.21	0.968
PH9	0.991	0.031	0.984	1.083	0.042	0.999	0.108	0.975
Initial Concentration 3.82mg/L	0.333	0.039	0.951	1.21	0.062	0.996	0.027	0.918
7.64mg/L	0.530	0.036	0.950	0.705	0.271	0.996	0.039	0.892
11.46mg/L	0.389	0.041	0.946	0.673	0.179	0.983	0.041	0.899
15.28mg/L	0.332	0.052	0.93	0.434	0.269	0.998	0.045	0.909
26.74mg/L	0.473	0.062	0.977	0.321	0.677	0.996	0.058	0.898 06
Dose 0.25g	0.169	0.034	0.955	1.148	0.082	0.999	0.073	0.951
0.50g	0.544	0.040	0.938	0.7047	0.1090	0.998	0.047	0.941
0.75 g	0.524	0.043	0.912	0.6551	0.1338	0.986	0.045	0.936
1.00g	0.312	0.044	0.943	0.3918	0.398	0.993	0.027	0.913
1.25g	0.355	0.045	0.932	0.372	0.341	0.989	0.025	0.803
Size 0.850 mm	3.274	0.045	0.954	3.557	0.012	0.996	0.234	0.906
0.355 mm	3.300	0.046	0.954	4.337	0.029	0.999	0.250	0.932
0.180 mm	3.058	0.063	0.879	3.389	0.024	0.993	0.187	0.914
Temperature 30 ˚C	3.250	0.044	0.922	3.7468	0.0190	0.999	0.272	0.921
50 ˚C	2.824	0.039	0.966	3.4626	0.0215	0.995	0.268	0.945
70 ˚C	2.212	0.028	0.992	2.868	0.0134	0.999	0.251	0.918

3.9 Adsorption thermodynamic

The thermodynamic parameters offer a great information of the inherent energetic associated with adsorption. The parameter namely, the changes in Gibbs free energy (ΔG°), entropy (ΔS°) **,** and enthalpy (ΔH°) were calculated

The results are shown in Table (5) show a spontaneous and favorable adsorption process over the whole temperature range ($\Delta G^o < 0$) in adsorption of cresol red on animal bone , the positive value of ΔH^o obtained indicated that the dye adsorption process is an endothermic **[60].** The positive value of ΔS^o proposes an increase in the randomness at the solid/solution interface take place at the inner structure of the adsorption of dyes onto adsorbents **[61,62,59].** The value of ΔG^o found in this work suggested that the adsorption of cresol red on animal bone was a chemisorption process.

On other hand $\Delta G^o > 0$ in adsorption of cresol red on egg shell suggested that the adsorption was physisorption ,the negative value of ΔH^o obtained showed that the dye adsorption process in an exothermic. The

negative ΔS^o value suggests the formation of order activated complex and associated mechanism for the adsorption **[62,61,63,64].**

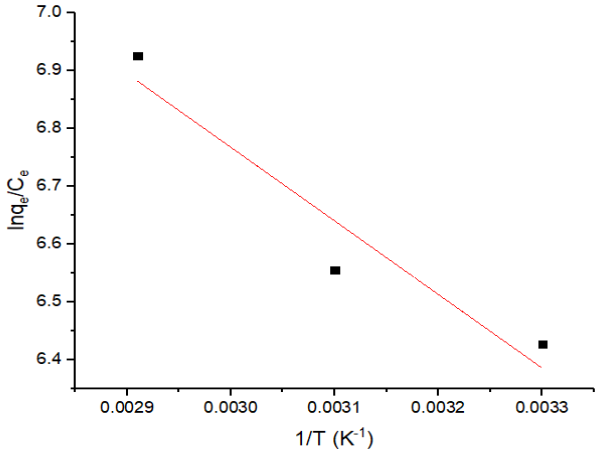


Fig (27) : The parameters for the removal of cresol dye at different range of temperature with initial cresol red concentration 3.82 mg/L and animal bone dose 0.75 g of particle 0.850 mm at pH 7 and 60 min.

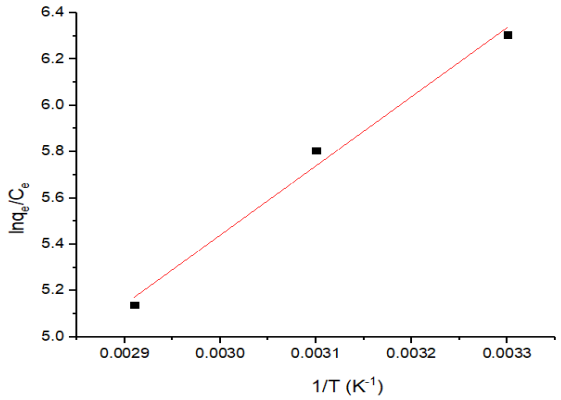


Fig (28) : Thermodynamic parameters for the removal of cresol dye at different temperature values with initial cresol red concentration 3.82 mg/L and egg shell dose 0.75 g of particle 0.180 mm at pH 4 and 60 min.

Table(5):Thermodynamic Parameters of Cresol red O adsorbed on animal bone and egg shell

Temperature (C˚)		Thermodynamic Parameters		
		ΔG˚ (KJ/mol)	ΔH˚ (KJ/mol)	ΔS˚ (KJ/mol)
	30˚C	-1.9378	1.274	0.0106
Adsorption of cresol red on animal bone	50˚C	-2.1498		
	70˚C	-2.3618		
Adsorption of cresol red on egg shell	30˚C	26.466	-3.531	-0.099
	50˚C	28.446		
	70˚C	30.426		

IV. CONCLUSION

The ability of animal bone and egg shell as an adsorbents to remove cresol red from solutions was examined. Some parameters as pH values, initial dye concentrations, adsorbent doses, adsorbent sizes, and temperatures were found to affect the adsorption efficiency of animal bone and egg shell. The kinetic data show that the adsorption process follows the pseudo of second order kinetic, indicating chemisorptions. The adsorption data present the best fit to the Langmuir model, suggesting that adsorption occurs by the formation of a monolayer. The thermodynamic parameters show that adsorption is spontaneous and endothermic in nature in case of animal bone and exo thermic for egg shell. This study proved that animal bone and egg shell could be used as a unique and cheap adsorbents for dye removal treatment.

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