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Removal of (Crystal Violet, Janus Green) dyes by poly acrylic acid hydrogel beads

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***Abstract*— Removal of Crystal Violet (C.V) and Janus Green (J.G) dyes was studied using poly acrylic acid hydrogel beads . The adsorption Isotherm of the process was examined in addition to correlated factors such as Temperature, ionic strength, effect of dry beads and mixing dyes. has been found that the adsorption isotherms of both dyes follows Freundlich equation more than Temkin and Langmuir equations. A relation was noticed between adsorption of dyes and temperature especially at the presence of salt at temperature (20 ^{0}C). Regarding wet beads of poly acrylic acid hydrogel beads no changes were detected. The adsorption is also increased at shaking. Thermodynamic function increased when the temperature increases. The adsorption increased in investigated (Δ H, Δ G, Δ S) to explain that the process are emitter or absorbent and spontaneous and the random of the process . a kinetic parameter has been studied Lagergren equation (first order) and by (second order) equations, depending to the results of the experimental, data shown us that the adsorption obeys the pseudo-second order furthermore the first-order equation .**

***Keywords*— poly acrylic acid, Janus Green, Crystal Violet, Removal, adsorption .**

I. INTRODUCTION

Dyes are one of the many organic substances that pollute water [1] supplies. This is due to their importance and widespread use in various industries of the textile industry[2], printing, photographic color[3], and the petroleum industry, additive and has many applications in a wide range of other fields[4]. The synthesis of many different compounds which environmental behavior is largely unknown has been carried out. About 10-15% of these dyes are discharged into the water as industrial wastewater[5] entering supplies water or soil, it is causing great problems for plants, animals and humans. Began to study the behavior of environmental dyes after news about toxic dyes and the potential danger of these materials, .The main contributor of the carcinogen. These facts have increased the interest in the raw materials used in the preparation of these dyes. And to solve this problem , the scientific proposed biological, chemical and physical treatment methods to degrading polluted effluents. The most useful methods that used are coagulation , flocculation[6], Biodegradation[7], Membrane filtration[8], Chemical Oxidation[8], Ozonation[9, 10] ,Photocatalysis[11, 12], Electrochemical/ion exchange[13] and Adsorption[14] . Adsorption technique has an effective dye removal in which dyes particles are attached into the surface of the adsorbent materials. And for that, there is an interest in using surfaces which are inexpensive and available in public shops to remove or adsorb the dyes [15].

Adsorption approach is common process because it is flexibile in operation and its design, in addition, because of his easier desorption of the adsorbent . the surface used is Polyacrylic acid (PAA) beads ,its character that it is flexible polymer chain that are a quick to solute particles with water to penetrate the hydrogel [16], PAA is colorless [16], and were used as a surface for adsorption Janus Green (J.G) and Crystal Violet. PAA can absorb more than five to ten hundreds of times of their weight in the water [17]. (J G) is a cationic, basic (which contains both azo and azine chromophore) dye and vital stain used in histology. In 1900, it was introduced by Leonor Michaelis and used to stain mitochondria supravitally. This dye changes color according to the amount of oxygen present [18, 19]. Crystal Violet (CV), the chemical structure { N-[4-[bis [4-dimethyl-amino)-phenyl]-methylene]-2, 5-cyclohexadien-1-ylidine]-N-methyl methanaminium chloride} is a triarylmethane based dye, that is basic in nature but is considered more toxic from anionic dyes [20, 21].

In this search the aim is used a Polyacrylic acid hydrogel beads to remove janus green and Crystal Violet from its aqeous solution and study thermodynaic and kinetic of the removal process .

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II. EXPARIMENTAL PART

A. *MATERIALS*

polyacrylic acid (figure 3), Crystal Violet dye (C.V)(figure 1,B), Janus Green dye(J.G)(figure 1,A) (J.G) and NaCl are used ,deionized water.

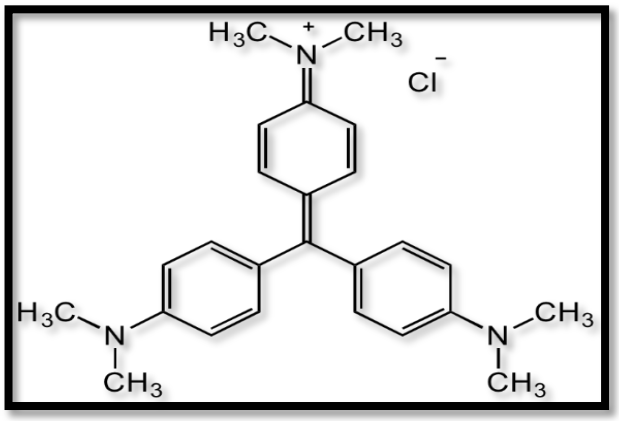
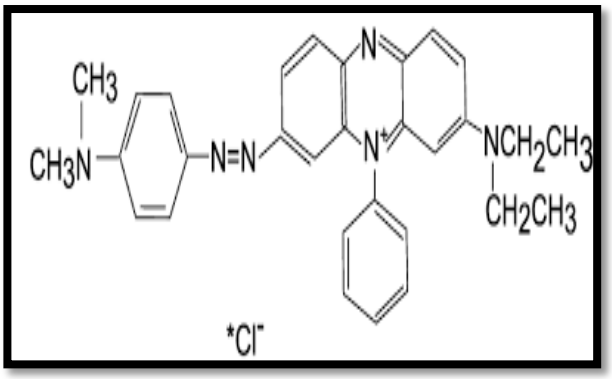


Figure (1) A: The structure of Crystal Violet [22]



B ; the structure of Janus Green [23]

Figure (2) poly acrylic beads before and after swelling in water [24]

B. *Methods*

1) U.V. spectroscopy technique*:*

Is used to determine the concentration of dyes. The wavelength of absorption of Crystal Violet is (590 nm) while the wave length of absorption of Janus Green is (611nm).

contact time was determined to find the equilibrium time between the dyes and surface, there was blending between poly acrylic acid beads (0.025 g) and the solutions of dyes, they were putting in the water bath at (20C0), we measured the absorption in sequence at a different time to notes the change of concentration through time. The contact time of C.V was (200min) while the J.G was (90min)

2) Adsorption isotherm:

Determinate the adsorption isotherm of a dyes solution, mixing (0.025 gm) of PPA in several flasks with (50 ml) of the dyes (C.V , J.G) in each flask, then putting the flasks in a bath shaker at a (20 C0), the quantity of adsorption was measured by the equation [25] :

Qe = ((Co-Ce) Vs)/m ……(1)

Qe= quantity of adsorbed material (mg/g).

Co= initial concentration (mg/L).

Vs= volume of solution (L).

m= the mass of surfaces (g)

Ce= the equilibrium concentration (mg/L).

III. RESULTS AND DISCUSSION

A. *Adsorption Isotherms:*

The equilibrium time for Crystal Violet is (200 min),while the Janus Green is (90min) . as a function of time the adsorption is elevating respectively and figures (4 and 5) shows the rise in adsorption with effect of contact time.

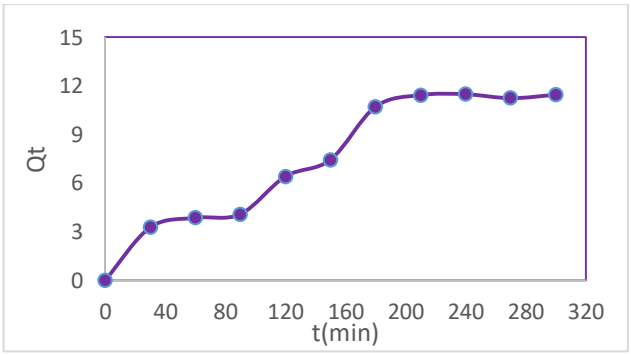
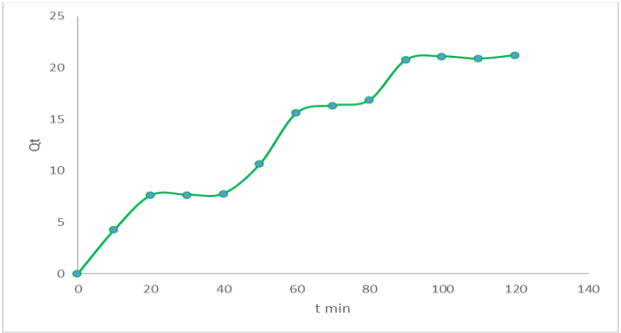


Figure (3) contact time of CV



Figure(4) contact time of JG

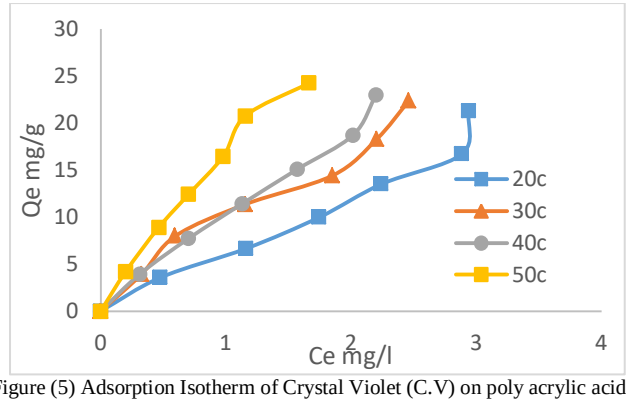


Figure (5) Adsorption Isotherm of Crystal Violet (C.V) on poly acrylic acid at different temperatures.

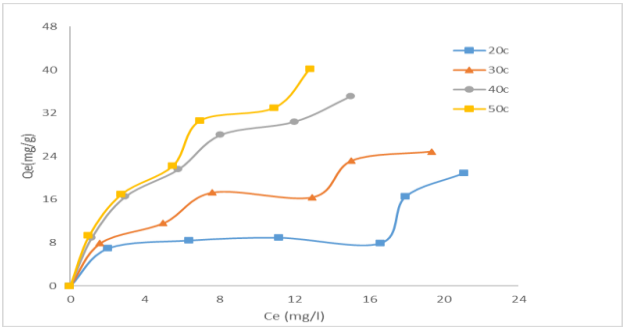


Figure (6) Adsorption Isotherm of Janus Green (J.G) on poly acrylic acid at different temperature.

The main planner in adsorption isotherm of (J.G) , (C.V) on poly acrylic acid (PAA) refers to (S3) and classify according to Giles classification, the particles of adsorption is vertical [26].The format of (Langmuir, Tempkin, Freundlich) equation prove that . the results of experimental found that it is more identical to Freundlich and not identical to Langmuir and Tempkin, and figures below show this in figures (7.8.9):

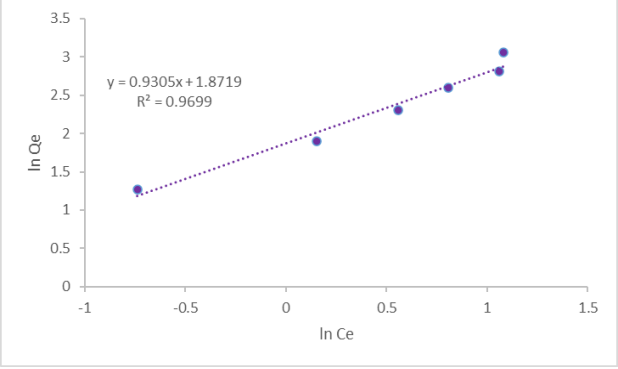


Figure (7) a :application of friendlisch of CV

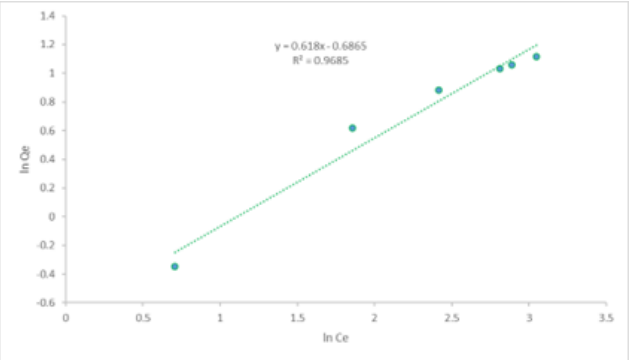
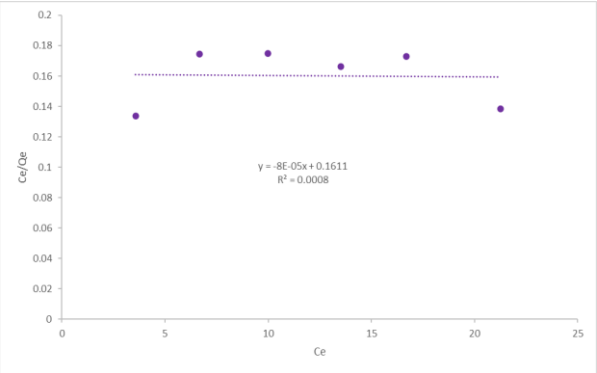


Figure (7) b: application of friendlisch of JG



Figure(8)a: application of Langmuir of CV

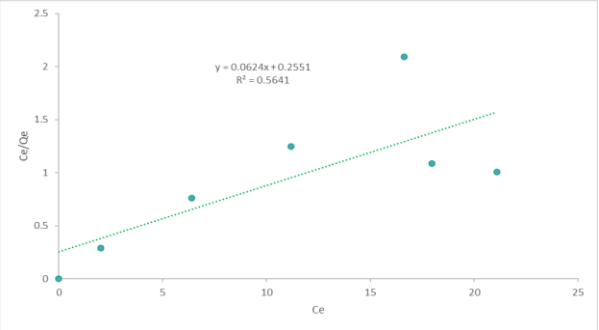


Figure (8) b:application of Langmuir of JG

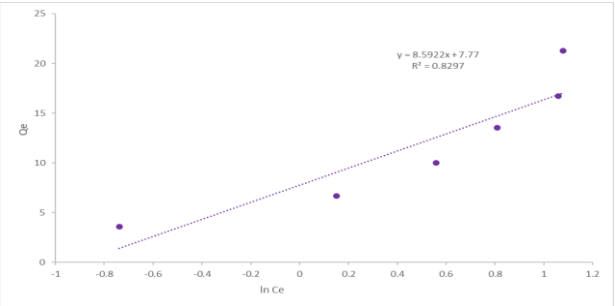


Figure (9)a: application of Temkin of CV

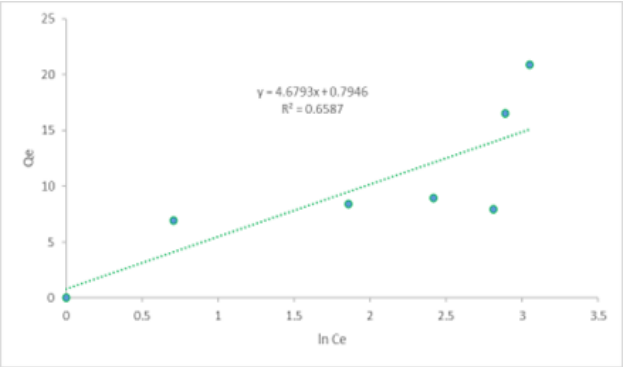


Figure (9) b: application of Temkin of JG

A. *Thermodynamic Studies*

A positive relationship between the quantity of adsorption and the temperature because when the temperature increase the adsorption increases too. The equation of Vant Hoff used to measure (ΔH) as shown:-

Ln Qmax = $\frac{-\Delta H}{R\,T}$ + Constant ……

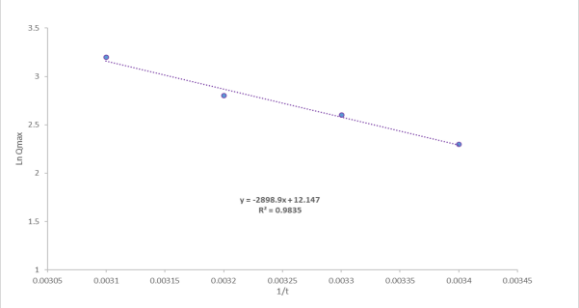
Where:-

Qmax: quantity of adsorbed molecule

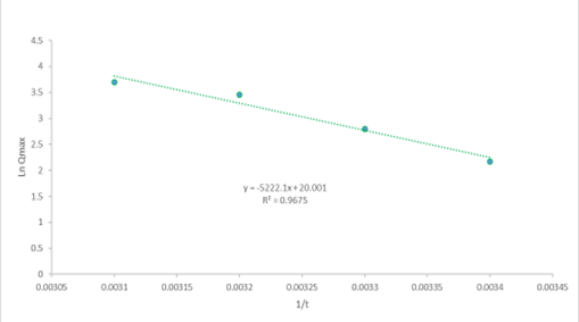
R:Constant of gases (0.0082).

T:the temperature of adsorption

And to find ΔH a plot between Ln Qmax and (1/T) and the figure below shown as:



Figure(10)a: application of Vant Hoff of CV



Figure(10)b:application of Vant Hoff of JG

The equation shows us the value of ΔH and through this ΔG and ΔS will be measured by :-

ΔG = -nRT Ln Qmax ……..

ΔG = ΔH- TΔS ……

The table below shown us the values of (ΔH,ΔG,ΔS):-

Table(1) thermodynamic function of Crystal Violet

T(K)	ΔH(KJ/mole)	ΔG(Jmole)	ΔS(J/mole)
293	24.1	-5.6	101.36
303		-6.765	101.86
313		-7.2	100.25
323		-8.59	101.2

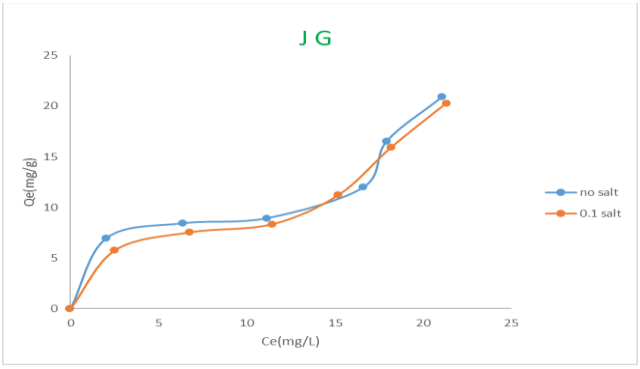
Table (2) thermodynamic function of Janus Green

T(K)	ΔH(KJ/mole)	ΔG(KJ/mole)	ΔS(J/mole)
293	0.6278	-5.29	-20.2
303		-7.05	-25.33
313		-8.98	-30.7
323		-9.92	-32.65

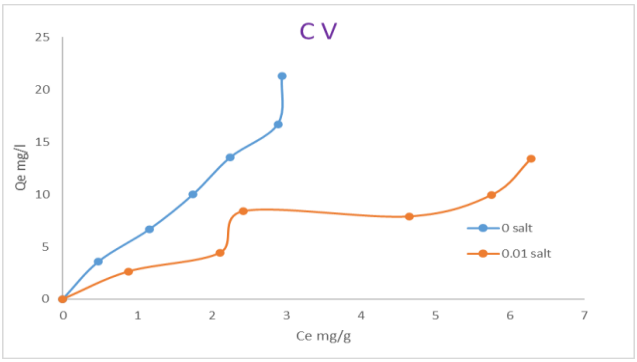
Results in tables 1 and 2 show us that the process of the dyes is Endothermic, the minus values of (ΔG^0) of both dyes refer that the processes are spontaneous. In the Crystal Violet (ΔS) is positive which means that the arrangement of particles in solution is more than on surface, while in case of Janus Green the minus values of (ΔS) mean that the arrangement of particles in surface more than solution [17].

B. *Ion strength effect*

Sodium Chloride (0.01 gm) has been added to the process to check the different or the effect of salt at adsorbed particles of removing , the process under condition (contact time:200 min , temperature : 20 C^0 , rotation per minute:180 rpm) for Crystal Violet , while the Janus Green (Contact time :90 min , temperature :20 C^0 , rotation per minute: 180 rpm) and the two dyes at different concentrations .the results show us that the effect of salt is the adsorption is less when not added salt and that in the figures below:



Figure(11) effect of (NaCl) of (a) for CV

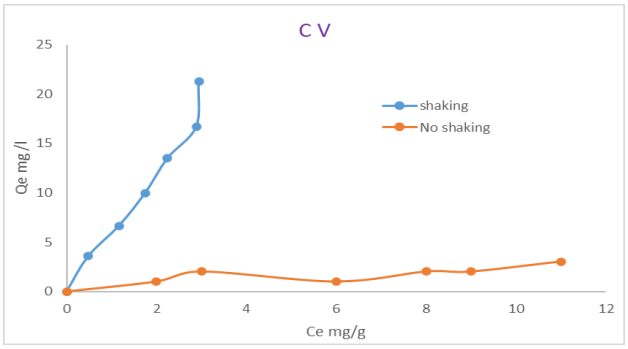


Figure(11) effect of (NaCl) of (b) for JG

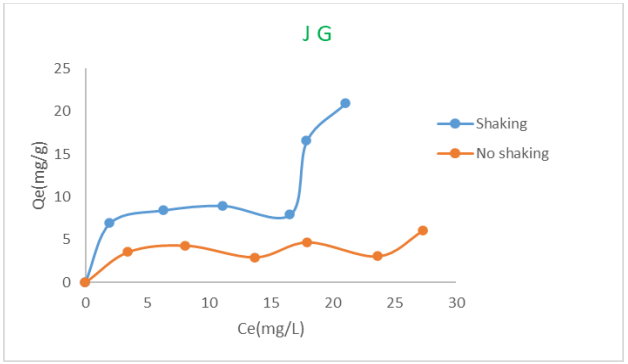
C. *Shaking effect*

At the same condition of adsorption a comparison between the adsorption process when it is shaking , in the other hand

the same concentration but without shaking .According to the results the adsorption when shaking is much more than without shaking as shown in figures below:-



Figure(12) effect of shaking of (a) for CV



(b) for JG

D. *Effect of wet Polyacrylic acid*

Adsorbent particles wear in water for a day. and a comparison between adsorption when using dry PAA and when using wet PAA at the same condition, by the results they are not note change of adsorption, the figure below shows:

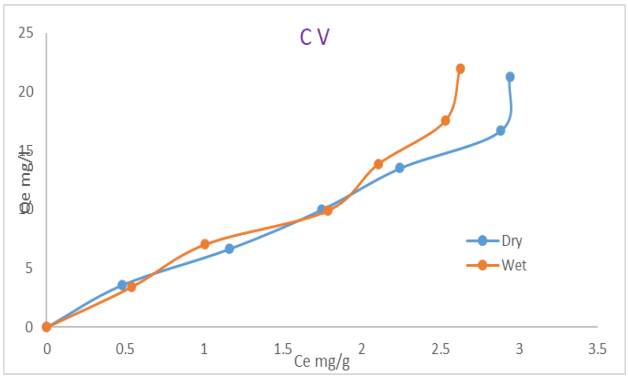
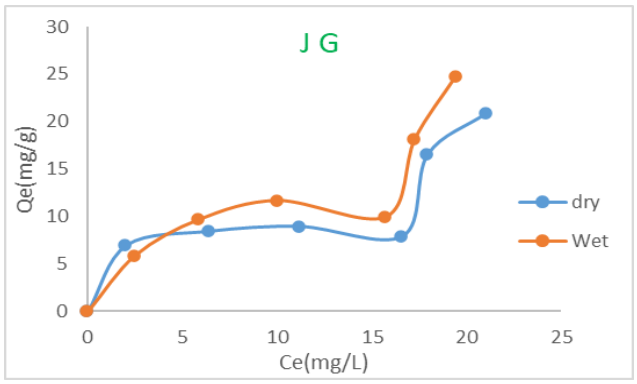


Figure (13) Effect of wet PAA (a) for CV



(b) for JG

E. *Adsorption Kinetic*

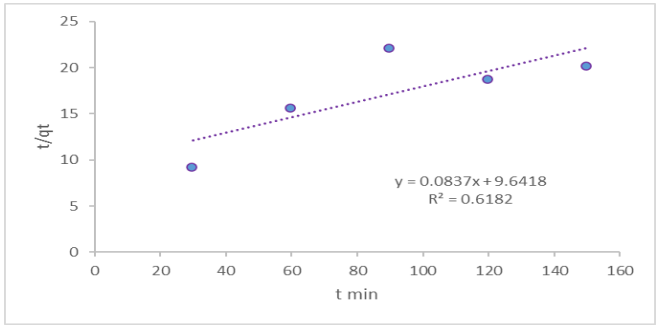
A kinetic of adsorption were studied by Lagergren and the second-order Lagergren equation :- it measured by:-

$Ln(qe-qt) = Ln\ qe - K_{ad}T$ ……..

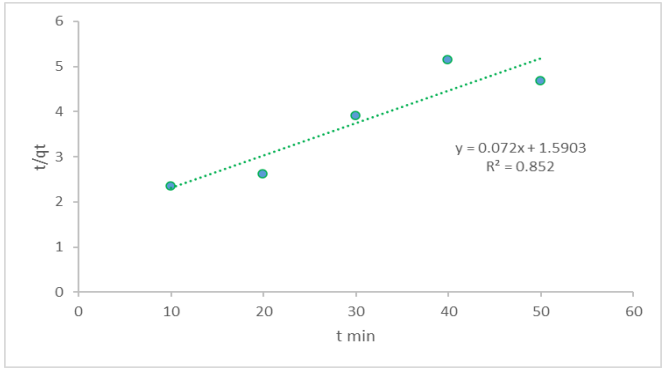
Where :-

(Qe,qt): equilibrium time (mg/L)

K_{ad}: Constant first order (min^{-1})



Figure(14) the application of Lagergren (a) for CV



(b) for JG

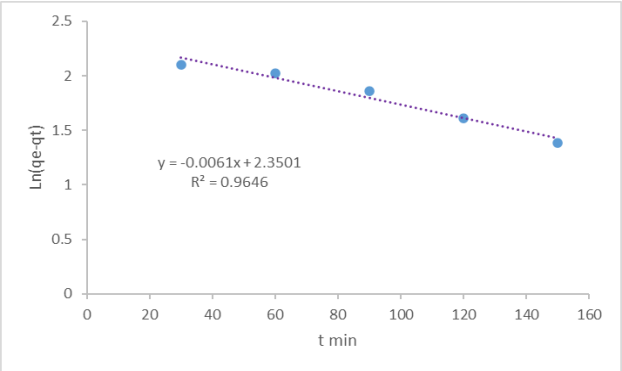
-

- **Second order**:- it is measured by the equation :-

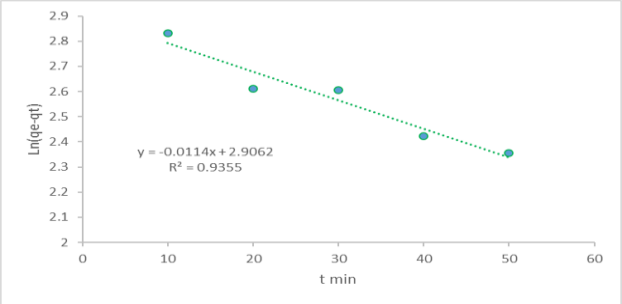
$$\frac{t}{qt} = \frac{1}{Kad} + \frac{t}{qe}$$ ……..

Where: -

K_{ad}: Constant of the second order (min^{-1})[27] .



Figure(15) application of second order (a) CV



(b) JG

According to the results the two dyes are obeys to second order .

F. Mixing dyes

The same concentrations of the two dyes were mixed with the polyacrylic acid , and by the results, it showed that Janus Green is favorite to adsorb by PAA more than the Crystal Violet as shown below :

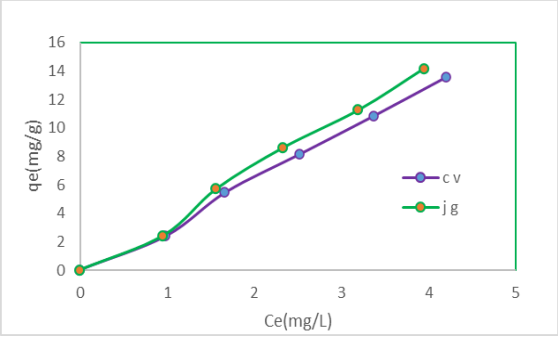


Figure (16) mixing dyes (CV, JG) on PAA .

G. Removal percentage :

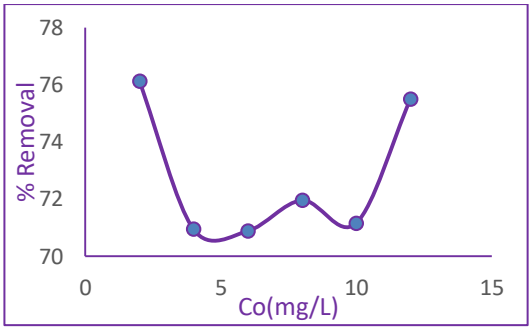
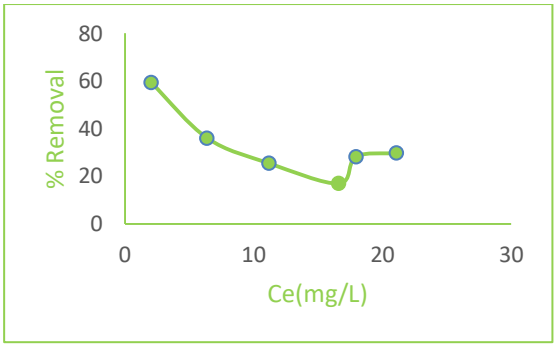


Figure (17) a: removal percentage of CV



B: removal percentage of JG

V. CONCLUSIONS

This search explains using polyacrylic acid beads (PAA) as a surface to adsorb or remove the Crystal Violet (CV) and the Janus Green (JG) dyes . calculated adsorption isotherm and the factors that impact it which are (Concentrations , Temperature , Ionic strength , Wet PAA, Shaking effect and mixing dyes) . According to the received results it showed that:- adsorption measured at a different temperatures (293K,303,313K,323K) the adsorption was progressive when the temperature is increased from the lowest to the heights of the two dyes . other the two dyes are obeyed friendlish equation more than Langmuir and Tempkin equations .Ionic strength was decreased the process of adsorption by using Sodium Chloride .The wet beads of polyacrylic acid are affecting that the adsorption is been height than the dry beads of the surface . Effect of no shaking bath was (the adsorption is lowest) compare with shaking . mix of the two dyes was calculated to know which one is favorite to PAA .Thermodynamic function was calculated and the kinetic of adsorption of the two dyes was measured on PAA . the process of adsorption are obeyed the second order of two dyes more than the first order (Lagergren) .

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