Advances in Physics Theories and Applications www.iiste.org
ISSN 2224-719X (Paper) ISSN 2225-0638 (Online)
Vol.39, 2015

Removal of Azure Dyes with Novel PMF Polymer from Aqueous Solution

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Abstract
This study includes the synthesis and characterized of new adsorbent of Porcelanite- Melamine- Formaldehyde Polymer (PMFP). The chemical structural formula of this adsorbent was confirmed by FTIR, XRD and SEM techniques. The adsorption ability of PMFP toward Azure dyes A, B and C has been studied using UV-Visible spectrophotometry. This technique has been utilized to construct the relation between the amount of adsorbate Azure dyes and the equilibrium concentration (isotherms). Factors affecting adsorption, such as contact time, pH, temperature and adsorbent dose, were evaluated. The equilibrium of adsorption was modeled by using the Langmuir and Freundlich isotherms models. The thermodynamic functions ΔH, ΔG and ΔS were calculated and were explain in the mean of the chemical structure of the adsorbate.
Keywords: PMF Polymer, Organic Azure A, B and C dyes, Langmuir and Freundlich isotherms

(I) Introduction

Organic dyes are integral part of many industrial effluents and demand for appropriate methods of dispose them in urgent. Most commercial dyes are chemically stable and are difficult to be removed from waste water[1]. At present, more than 10,000 dyes have been effectively commercialized[2]. The release of colored wastewater from these industries may present an eco-toxic hazard and introduce the potential dangerous of bioaccumulation, which may eventually effect man through the food chain. Physicochemical processes are generally used to treat dyes laden wastewater. These processes include flocculation, electro flotation, precipitation, electro kinetic coagulation, ion exchange, membrane filtration, electrochemical destruction, irradiation and ozonation. However ,all these processes are costly and cannot be used by small industries to treat wide range of dye wastewater[3-6]. Adsorption is one of the best conventional wastewater treatment methods compared to other treatment methods[7]. The removal of dyes from effluent using adsorption process provides an attractive alternation treatment, especially of the adsorbent is inexpensive and readily available[8]. Activated carbon is the most widely used adsorbent because it has excellent adsorption efficiency for organic compounds, but its use is usually limited due to its high cost[9]. Hence, production of low cost and effective adsorbents is still a field of interest and research is continuing in this area. In this study, low cost locally rocks (Porcelanite) was used to synthesis of the polymer PMF by the treatment of Porcelanite rocks with Melamine then by the polymerization of the complex PMC with Formaldehyde to obtained PMFP by the interaction of the polymer Melamine Formaldehyde with holes of the rocks. Then it studies the ability of PMFP as the adsorbent surface of Azure dyes from its aqueous solution and studies the effect of contact time, initial pH, adsorbent dose and temperature. The Langmuir and Freundlich isotherm equations were applied to the data and values of parameters of these isotherm equation were calculated. Results of this study will be useful for future scale up using this polymer a low cost adsorbent for the removal of dyes.

(II) Experimental Procedure

(1) Preparation of Porcelanite –Melamine Complex (PMC)

By mixing of 3.45g from melamine with 1.38g from Porcelanite in ceramic mortar and adding three drops of distilled water to the mixture and still about half an hour. Then transfer the mixture to the closed container and remained about (15) days in order to complete the distribution process of melamine molecules in porous of Porcelanite.

(2) Preparation of Porcelanite- Melamine- Formaldyhide Polymer (PMFP)

Sample of 17.25g of PMC was placed in 25 ml conical flask and 5.54ml formaldehyde was added to the mixture, about 5 minutes, the reaction take place in acidic media. The mixing process continued about half an hour then the mixture was put in water bath at 90 $^{\circ}$C for two hours to complete the cross linkage between the PMC and formaldehyde.

(3) Preperation of Azure Dyes Solution

Organic Azure A, B, and C dyes , were used. All the chemicals were of high purity, commercially available AR grade. The properties of the selected dyes are given in Table 1 and their structures are shown in Figure 1 .

Table 1. Physical Properties of Azure Dyes

Properties	***Azure A***	***Azure B***	***Azure C***
Empirical Formula	$C_{14}H_{14}CLN_3S$	$C_{16}H_{18}CLN_3S$	$C_{13}H_{12}CLN_3S$
Class	Thiazine	Thiazine	Thiazine
Source	Aldrich	Aldrich	Aldrich
Solubility in water	Soluble	Soluble	Soluble
Molecular Weight (g mol^{-1})	291.80	305.83	277.77
Dye Content	80%	89%	40%
λ_{max} (nm)	632	646.50	611.5
C.I. No.	52005	52010	52002

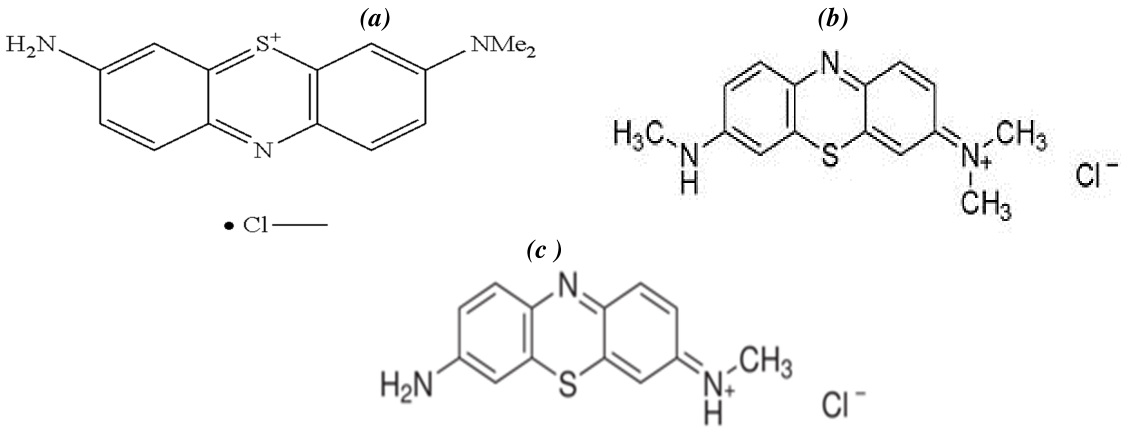


Figure 1. Molecular Structures of Organic Dyes(a)Azure A,(b)Azure B and (c) Azure C Dyes

The dyes stock solutions were prepared by dissolving dyes in distilled water to (50) mg/L, the experimental solutions were obtained by diluting the dye stock solutions in accurate proportions to different initial concentrations.

4. Adsorption Experiments

The adsorption experiments were carried out in thermo stated shaker water bath at (5000) rpm using 50 ml shaking flasks containing 25 ml of dye solutions at different concentration and initial pH values of dye solutions. The initial pH values of the solutions were previous adjusted with 0.1M HCl and 0.1M NaOH using a pH-mete. The adsorbent(0.03g) was added to each flasks, and then the flasks were sealed up to prevent any change of volume of solution during the experiments. After shaking the flasks for a predetermined time intervals(30 min.), the samples were withdrawn from the flasks and the dyes solutions were separated from the adsorbent by filtration after centrifugation. Dyes concentrations in the supernatant solutions were estimated by measuring absorbance at maximum wave lengths of dyes. The amount of dyes adsorbed by the PMFP were calculated using the following equation[10]:

$$\mathbf{Qe = \frac{Co-Ce}{m}\ V} \text{ ....(1)}$$

Where: Q_e (mg/g) is the amount of dye adsorbed at equilibrium (adsorbent capacity) ,C_o and C_e are (mg/L) the concentrations of dye at initial and equilibrium respectively . V and m is the volume of the solution (L) and M the adsorbent mass (g) respectively.

The percentage removal of the dye were calculated by the following relationship[10]:

% Removal = (C_o – C_e / C_o) x 100 ....(2)

The effect of each parameter (contact time, pH value, temperature and adsorbent dosage) were evaluated in an experiment by varying the parameter, while keeping the other parameters as constant.

(III) Results and Discussion:

(1) Characterization Studies FT-IR, XRD and SEM

The synthesis compound Pocelanite-Melamine-Formaldehyde polymer composite was characterized by FT-IR spectroscopy , X-ray diffraction and SEM technique, Figures 2, 3 and 4 respectively. The characteristic FT-IR absorption bands of PMFP are illustrated in Figure 2. The FT-IR spectra of the PMFP disappearing of the two sharp weak bands at the general range (3470-3132 cm^{-1}) attributed to asymmetric an symmetric stretching vibrations of ($-NH_2$) group and appearance of broad band at 3423 cm^{-1} due to the stretching vibration of hydroxyl group and other band at 3387 cm^{-1} belong to stretching vibration of (-N-H) band, [from this fact it can say that there is a reaction was been happened between two components melamine and formaldehyde [11] as a result of appearing two bands the first at 2979 cm^{-1} assigned to asymmetric vibration of methylene group (CH_2) and the second band at 2887 cm^{-1} assigned to symmetric stretching vibration of this group, the band at 1631 cm^{-1} attributed to binding vibration of (NH) group, while the two bands at 1550 and 1537 cm^{-1} assigned to stretching vibration of (C=N) inside melamine ring. The weak band at 1450 cm^{-1} attributed to asymmetric bending vibration of (CH_2) and the other weak band at 1371 cm^{-1} belong to symmetric bending of this group[12,13]

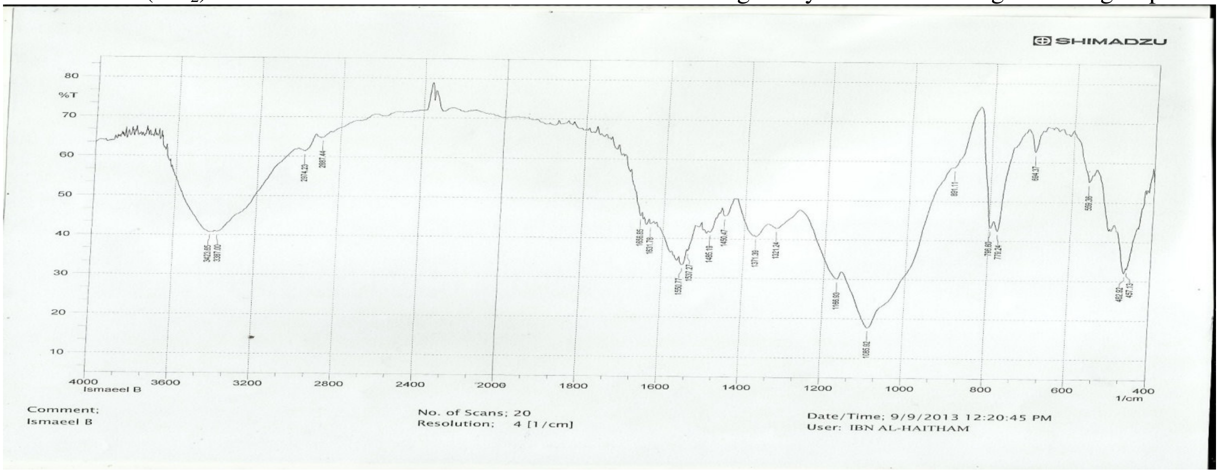
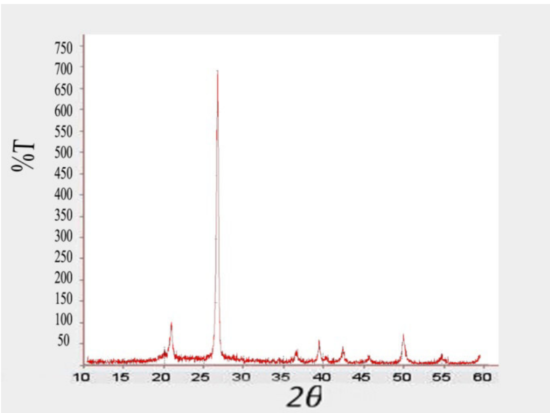


Figure 2. FT-IR spectrum of PMFP

The XRD spectrum of PMFP Figure 4 shows that the structure is maintained after modification because all peaks in modified form (PMFP) are broader and their intensities are lower when they are compared with that before modification, that may indicate change in crystal size of the modified sample (PMFP). More especially, Scherre equation showed that the crystal size was reduced to nano-scale in PMFP, it was 782nm in natural Pocelanite rocks and it decreased to 28nm after modification.

The surface morphology of PMFP was visualized via scanning electron microscopy (SEM) at 10000 magnification. Morphological description of PMFP in Figure 5 refers to the presence of very small nano-crystal which are attached together to form a big particles



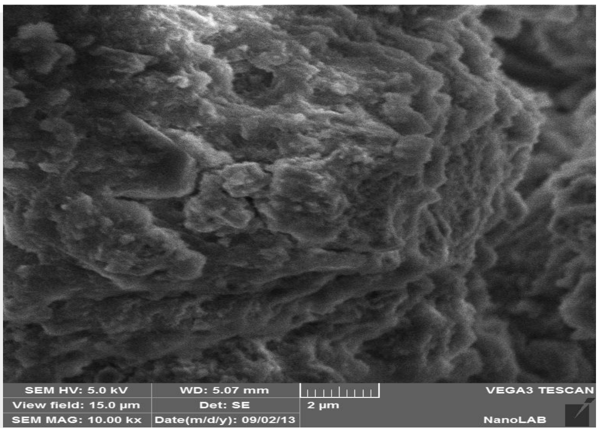


Figure 3. XRD Spectrum of PMFP ***Figure 4. SEM Photography of PMFP***

(2) Effect of Contact Time

The influence of the contact time on the adsorption capacity of three Azure A, B and C dyes by modified clay was conducted through batch experiments to achieve the equilibrium. The mechanism of colour removal can be described in migration of dye molecule from the solution to the adsorbent particle and diffusion through the surface. The result showed that the equilibrium time was reached within 30 min. of operation for Porcelanite modified rocks.

(3) Effect of Adsorbent Dose

The dependence of the adsorption of the Azure dyes on the amount of PMFP was studied by varying the adsorbent dose (0.005, 0.07, 0.09, 0.0125, 0.03 and 0.05)g at temperature 25°C and at their optimal pH, while keeping the volume and concentration of the solution constant. The results are given figure 5 . The figure indicates that sorption increased with increasing the sorbent dose up to 0.03g and then there was no further increase of sorption. The adsorption of the dyes increased rapidly with increase in the dose of the adsorbent due to greater availability of the exchangeable sites or surface area.

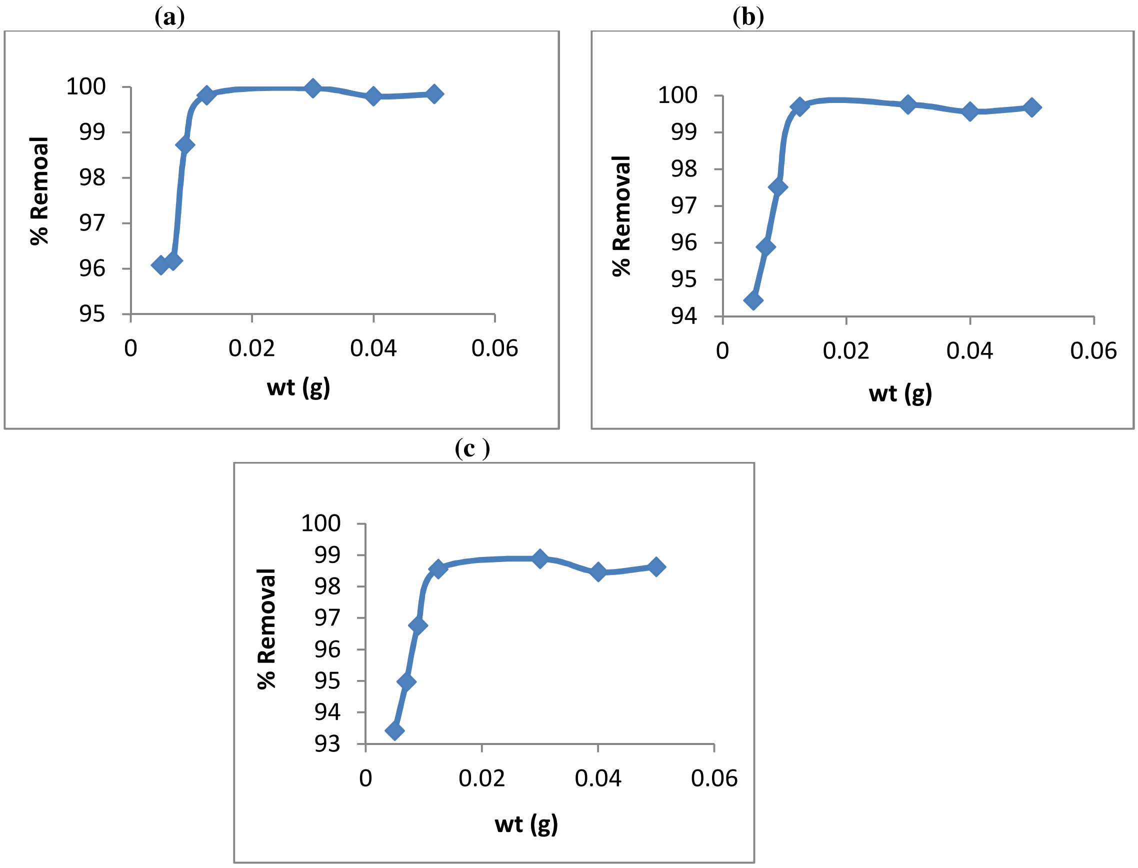


Figure 5. Effect of Adsorbent Dosage on the Percentage Removal of: (a)Azure A (b)Azure B (c)Azure C by Modified form of Iraqi Porcelanite rocks ,Temperature = 298 K, Initial Dye Concentration= 7mg/L, pH= 5.5, Contact Time (30 min) and Agitation Speed (5000 rpm).

(4) Effect of pH

The effect of initial PH of the dye solution on the removal of Azure dyes were determined at fixed concentration 50 mg/L of dyes over a PH range of 2.0 to 12.0 as shown in fig.6. The maximum adsorption of the dyes was observed above pH 5.5. There was no significant variation in adsorption capacity with change in pH above 4.0 Hence the rest of the parameters were optimized at the original pH of the respective dye solutions. Lower adsorption of dyes at low pH is probably due to the presence of H+ ions competing with the cationic group on the dye for adsorption sites. As surface charge density decrease with an increase in the solution PH, the electrostatic repulsion between the positively charge of Azure dyes is lowered ;this may result in an increase in the rate of adsorption[14].

(a) (b) (C)

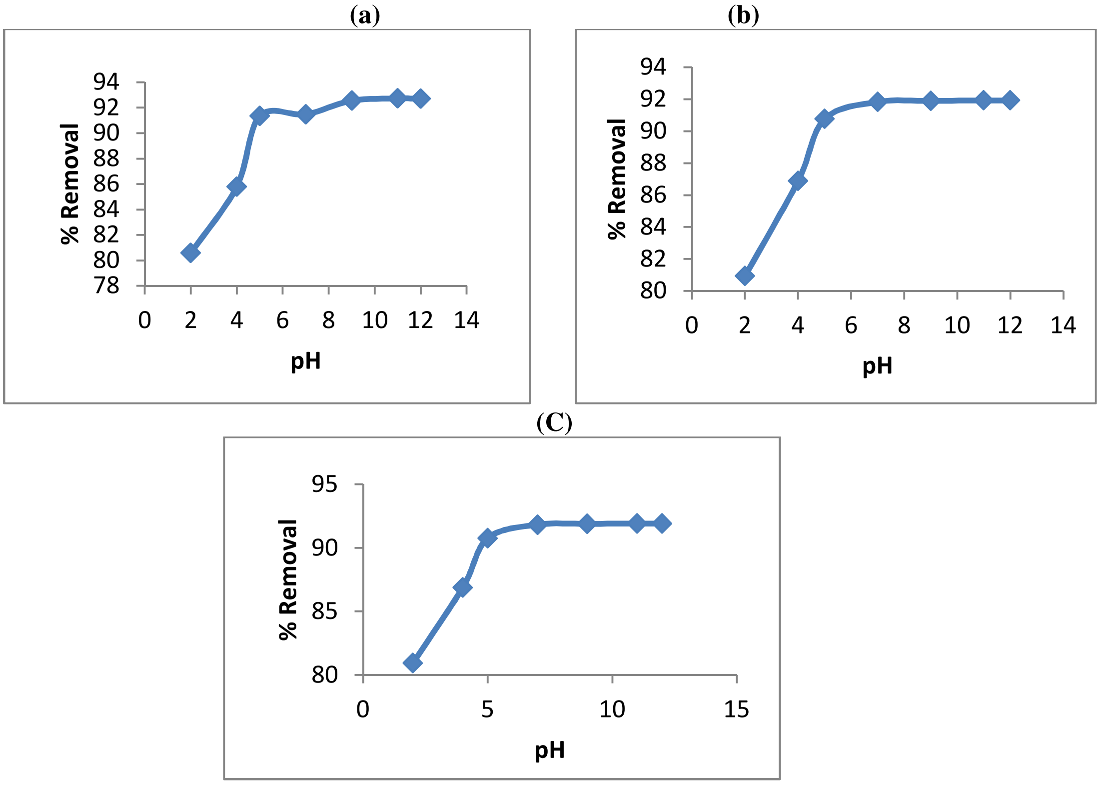


Figure 6. Effect of pH on the adsorption of: (a) Azure A (b)Azure B (c) Azure C by PMFP Temperature= 298, agitation speed (5000 rpm) and equilibrium time = 30 min.

(5) Temperature Effect and Thermodynamic Functions

The adsorption of PMFP at four different temperatures has been carried out. Variable temperature study will help in evaluating the basic thermodynamical functions. (ΔH, ΔS, ΔG) of adsorption processes increasing with increasing temperature, showing the exothermic nature of the process. The thermodynamic functions, Gibbs energy change (ΔG), enthalpy change(ΔH) and entropy change(ΔS) were calculated to evaluate the thermodynamic feasibility of the process and to confirm the nature of the adsorption process.The change in Gibbs free energy ΔG could be determined from the following equation[15] :

$$\Delta G = -RT\ln K_{eq.} \text{ ......(3)}$$

Where : ΔG is a Gibbs energy change(kJ/mol), R is the ideal gas constant (8.314 J/mol. K), K_{eq} :is the equilibrium constant for the adsorption process at each temperature. T :is the absolute temperature(K).

The thermodynamic equilibrium constant(K_{eq}) for the adsorption process at each temperature was calculated from the equation[16]:

$$K_{eq} = Q_e\, m / C_e\, V \text{ ....(4)}$$

Where: m is the weight of the adsorbent (0.03g of PMFP).

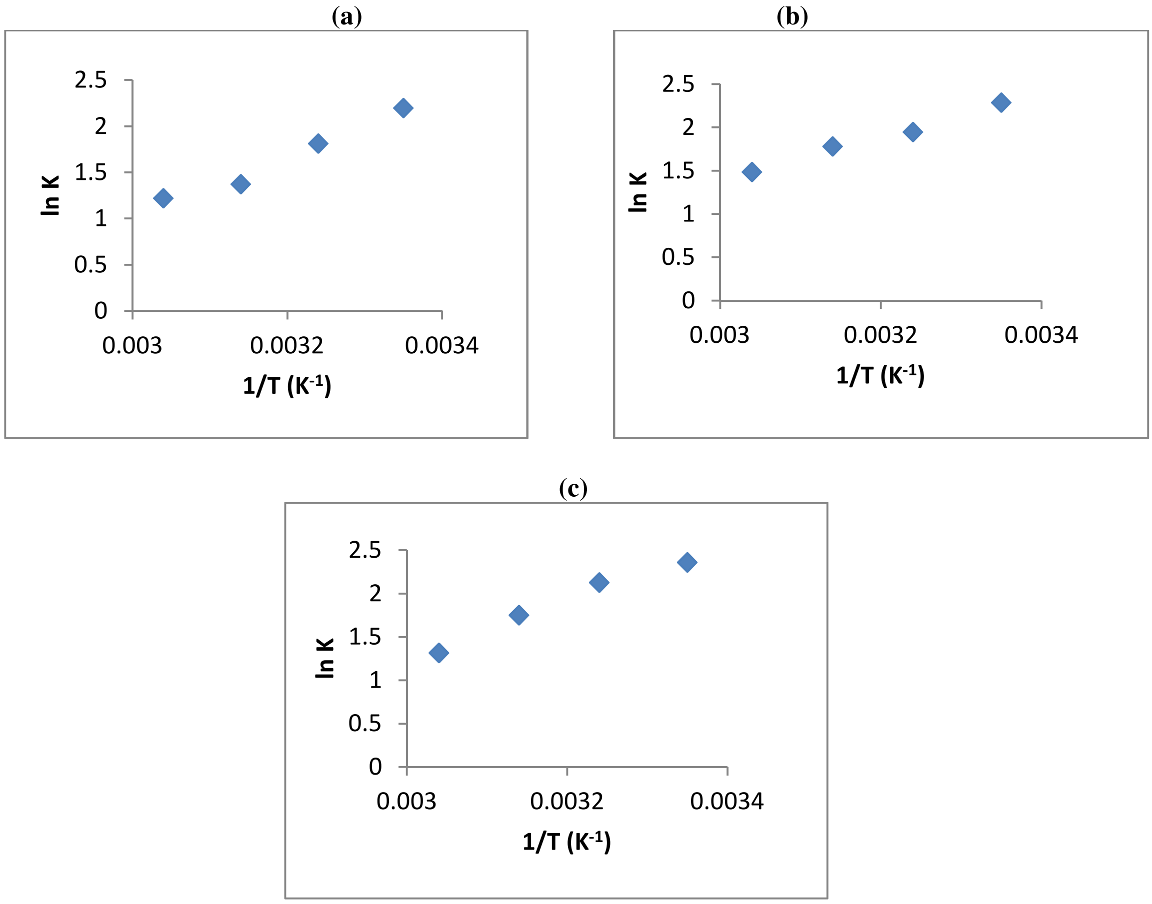
The heat of adsorption ΔH may be obtained from Vant Hoff s equation[15,10] and determined from the slope and intercept of Van' t Hoff 's plot of Ln K versus 1/T Figure 7 .

$$\text{Ln } K_{eq.} = \left(-\frac{\Delta H}{RT}\right) + con. \text{ ....(5)}$$

The entropy change ΔS was calculated from Gibbs- Helmholtz equation[10]:

$$\Delta S = \frac{\Delta H - \Delta G}{T} \text{ ....(6)}$$

Table 2 shows the thermodynamic functions ΔG, ΔH and ΔS for the removal of Azure dyes on PMFP at different temperatures.



Fiureg 7. Temperature Dependence of the Adsorption (a)Azure A (b)Azure B (c)Azure C on the Modified form of Iraqi Porcelanite rocks

Table 2. Thermodynamic Functions ΔG,ΔH and ΔS of Azure A, B and C Dyes on the Adsorbent Surface PMFP at Different Temperatures

298.15 K			
Adsorbate	G (kJ/Mol) Δ	H (kJ/Mol) Δ	S (kJ/Mol) Δ
Azure A	5.4449-	-27.5850	0.0742
Azure B	-5.6747	-20.8515	0.0502
Azure C	5.8512-	-28.2509	0.0744
308.15 K			
Adsorbate	G (kJ/Mol) Δ	H (kJ/Mol) Δ	S (kJ/Mol) Δ
Azure A	-4.6499	-27.5850	0.0744
Azure B	-4.9873	-20.8515	0.0520
Azure C	-5.4505	-28.2509	0.0745
318.15 K			
Adsorbate	G (kJ/Mol) Δ	H (kJ/Mol) Δ	S (kJ/Mol) Δ
Azure A	-3.6372	-27.5850	0.0752
Azure B	-4.7093	-20.8515	0.0507
Azure C	-4.6294	-28.2509	0.0742
328.15 K			
Adsorbate	G (kJ/Mol) Δ	H (kJ/Mol) Δ	S (kJ/Mol) Δ
Azure A	-3.3273	-27.5850	0.0739
Azure B	-4.0511	-20.8515	0.0511
Azure C	-3.5887	-28.2509	0.0751

From Table (2), it is evident that the higher negative values of apparent enthalpy change shows an exothermic physical adsorption favored by increased temperature. The negative values of ΔG confirm that the Azure dyes adsorption on PMFP is spontaneous process. It has been reported that ΔG up to -20 kJ/mol are due to electrostatic interaction between sorption sites and the Azure dyes (physical adsorption), while ΔG values more negative than -40 kJ/mol involve charge sharing or charge transfer from the PMFP surface to the Azure dyes [17]. The ΔG values obtained in this study for the three dyes are < -10 kJ/mol, which indicates that physical adsorption was the predominant mechanism in the sorption process. The apparent entropy change values are almost constant over the temperature range. The positive entropy characterized an increased disorder of the system due to the loss of water which surrounding the dye molecules at the sorption on the PMFP. It can be suggested that the driving force for adsorption process is an entropy effect[17,18].

(6) Adsorption Isotherm

Adsorption isotherm indicates the relationship between the adsorbate in the liquid phase and the adsorbate adsorbed on the surface of the adsorbent under equilibrium at constant temperature[19]. Adsorption isotherms are important to describe the interaction of adsorbate molecules with adsorbent surface.

The linearzed form of Langmuir equation[20]:

$$Ce/Qe = 1/ab + Ce/a \quad \ldots\ldots\ldots\ldots\ldots(7)$$

Where: (b) is the sorbent binding capacity, that is the maximum sorption upon complete saturation of adsorbent surface, and (a) is binding constant, i.e., elated to the adsorption/ desorption energy. It was well known that the Langmuir equation is intended for a homogeneous surface [21]. The (a) and (b) values are calculated from the slopes (1/a) and intercepts (1/ab) of linear plots of Ce/Qe versus Ce are shown in Figure 8 .

The separation factor R_L is calculated by the following equation to confirm the favorability of the adsorption process[22]:

$$RL = 1/(1 + b\,C_o) \quad \ldots\ldots\ldots\ldots\ldots(8)$$

The values of R_L are found to be between 0 and 1 and confirm that the adsorption process is favorable.

(a) **(b)**

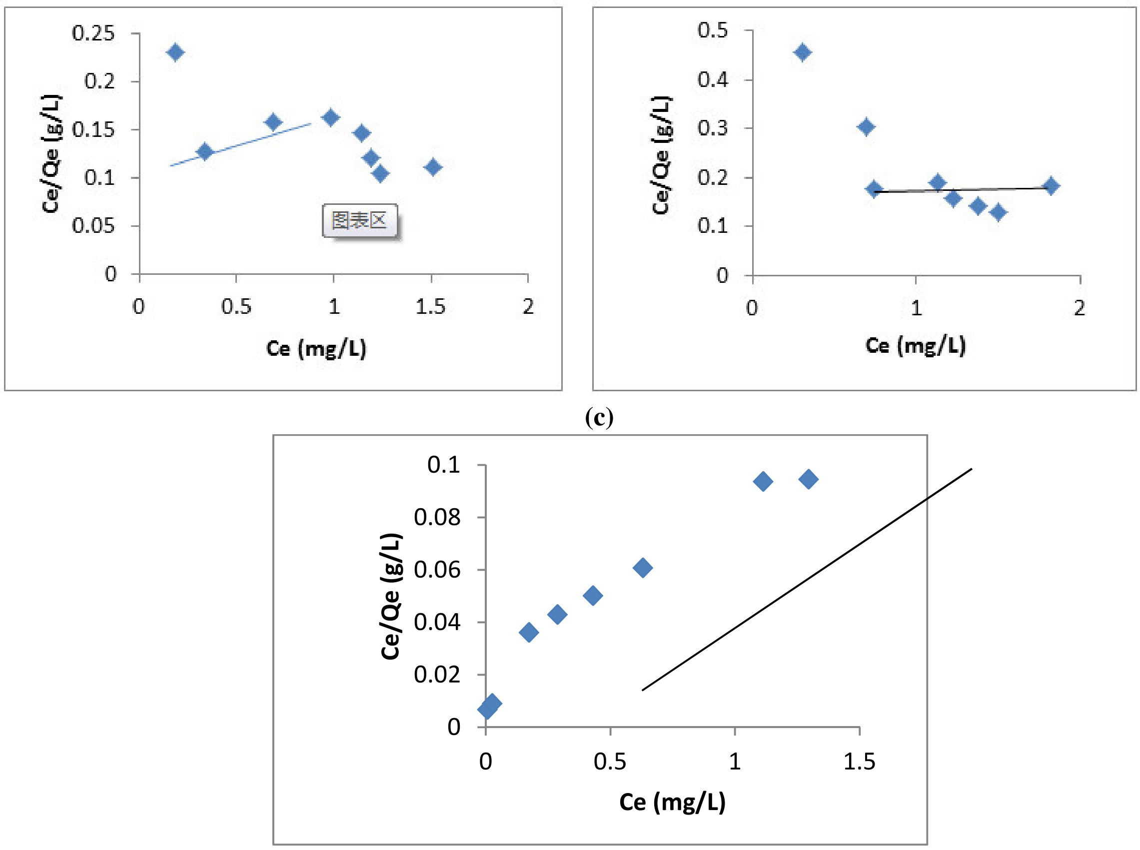


Figure 8. Langmuir Adsorption Isotherms for Adsorption of (a)Azure A (b) Azure B (c)Azure Con Adsorbent PMFP at 298.15 K

The linearized form of Freundlich equation[23] is as follows:

$$Log\ Qe = LogK_f + 1/n\ Log\ Ce \quad \ldots\ldots\ldots\ldots\ldots\ldots(9)$$

Here K_f and 1/n are empirical constants and indicate adsorption capacity and intensity, respectively. The values of K_f and n determine the steepness and cuvature of the isotherm [24]. The Freundlich equation frequently gives an adequate description of adsorption data over a restricted range of concentration between through it is not based on the theoretical background. A part from homogeneous surface, Feundlich equation is also suitable for a multi-layer adsorption [24]. A plot(Fig.9) of log Qe versus log Ce gives a linear line with a slope of 1/n and intercept of log K_f . Values 1/n>1 represent a favourable adsorption condition.

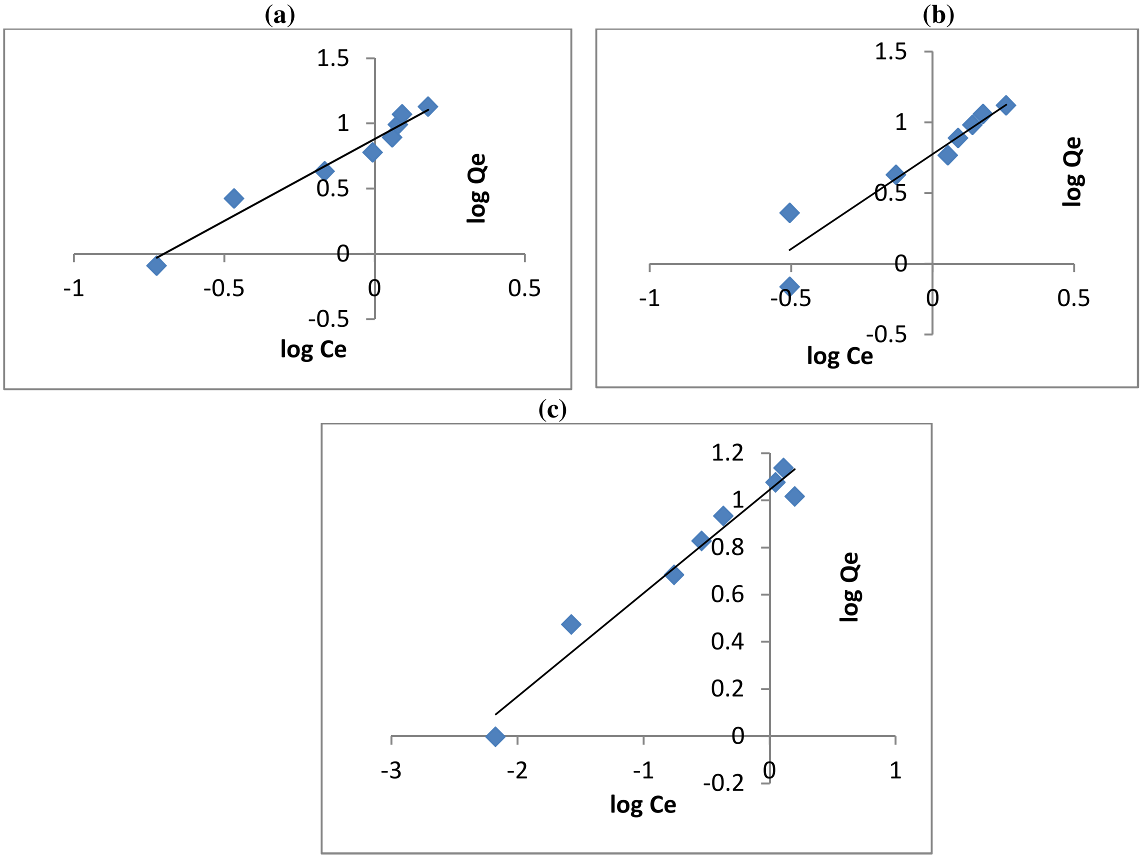


Figure.9 Freundilch Adsorption Isotherms for Adsorption of (a) Azure A(b) Azure B(c) Azure C on Adsorbent PMFP at 298.15 K

Table 3. Langmuir and Freundlich Functions of Adsorption Isotherms at Different Temperatures

298.15 K							
Adsorbate	Langmuir isotherm				Freundlich isotherm		
	a (mg/g)	**b (mg/L)**	**Correlation coefficient (r^2)**	**R_L**	**Intercept (K_f)**	**(1/n)**	**Correlation coefficient (r^2)**
Azure A	34.0136	0.2318	0.3636	0.3812	7.5683	0.7994	0.9614
Azure B	29.4985	0.3110	0.7166	0.3147	3.8672	0.4486	0.9496
Azure C	21.5053	2.1235	0.7542	0.0630	11.8113	0.1905	0.9736
308.15 K							
Adsorbate	Langmuir isotherm				Freundlich isotherm		
	a (mg/g)	**b (mg/L)**	**Correlation coefficient (r^2)**	**R_L**	**Intercept (K_f)**	**(1/n)**	**Correlation coefficient (r^2)**
Azure A	32.1118	0.0634	0.3792	0.6926	3.0012	0.7922	0.9804
Azure B	12.4533	0.9156	0.4595	0.1349	8.8328	0.7912	0.9477
Azure C	20.8768	1.1655	0.7246	0.1091	11.4340	0.4560	0.8646
318.15 K							
Adsorbate	Langmuir isotherm				Freundlich isotherm		
	a (mg/g)	**b (mg/L)**	**Correlation coefficient (r^2)**	**R_L**	**Intercept (K_f)**	**(1/n)**	**Correlation coefficient (r^2)**
Azure A	33.0033	0.1663	0.5715	0.4620	3.2824	0.7407	0.8187
Azure B	15.1057	0.8874	0.8301	0.1386	6.0214	0.9247	0.8311
Azure C	19.0476	0.0451	0.0281	0.7600	5.1499	0.0621	0.9601
328.15 K							
Adsorbate	Langmuir isotherm				Freundlich isotherm		
	a (mg/g)	**b (mg/L)**	**Correlation coefficient (r^2)**	**R_L**	**Intercept (K_f)**	**(1/n)**	**Correlation coefficient (r^2)**
Azure A	35.3356	0.1157	0.4539	0.5525	2.4188	0.3208	0.7966
Azure B	20.9219	0.0815	0.186	0.6364	5.2771	0.0439	0.9695
Azure C	26.2307	0.0058	0.0012	0.9607	4.4812	0.9451	0.9708

Conclusions

A modified form of Iraqi Pocelanite rocks (PMP) is a promising adsorbent for the removal of the cationic dyes Azure A, B and C aqueous solutions was investigated. The PMFP were characterized by FT-IR spectroscopy, XRD and SEM technique. Batch mode adsorption studies indicate that the adsorption was strongly dependent on contact time, pH of solution, adsorbent dose and reaction temperature. The equilibrium adsorption data obtained at different temperatures fitted well with the Freundlich isotherm model. Finally, it can be concluded that the PMFP can be used as a nano surface an economical adsorbent for the removal of Azure dyes from aqueous solutions. For Azure dyes adsorption on PMFP the thermodynamic functions of ΔG and ΔH are negative, indicating that the process is spontaneous and exothermic. Positive values of ΔS indicates that the degree of freedom increase at the solid-liquid interface during adsorption of these basic dyes on to PMFP.

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