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Removal of Azure Dyes Using Iraqi Porcelanite Rocks and Novel PMF Polymer

A Thesis

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بِسْمِ اللهِ الرَّحْمَنِ الرَّحِيمِ

وَعَلَّمَكَ مَالَمْ تَكُنْ تَعْلَمُ وَكَانَ فَضْلُ اللهِ عَلَيْكَ عَظِيماً

صدق الله العظيم

(النساء/113)

Dedication

To…….

My Dear Parents

My Husband "Ali "

My Kids "Ula and Ahmed "

My Brothers and Sisters

With Love and Respect.

Rusul

ACKNOWLEDGMEN

At the beginning , I Praise Allah Almighty for giving me health and determination to complete this thesis and shape its present form.

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Rusul

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In view of the available recommendation, I forward this thesis for debate by examining committee.

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We certify that we read this thesis "Removal of Azure Dyes Using Iraqi Porcelanite Rocks and Novel PMF Polymer" and as examining the thesis of the student (Rusul Azeez Jaafar) in its contents and that in our opinion it is adequate with (Excellent) standing as a thesis for the degree of master of science in chemistry.

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Summary

This Thesis is concerned with the study of adsorption of Azure A, B, and C dyes on Iraqi Porcelanite rocks and modified form of this rocks to introduce a new surface use as adsorbent for adsorption of Azure dyes. In this study Iraqi Porcelanite rocks was treated with melamine to prepare porcelanite - melamine complex. The complex was then polymerized with formaldehyde to obtain porcelanite – melamine – formaldehyde polymer (PMFP). Iraqi porcelanite rocks and novel PMF polymer were characterized by FT-IR, XRD, and SEM techniques. The purpose of this study is searching for surfaces that are highly applicable of adsorption Azure dyes in order to be useful in the water pollution treatment. Experiment were carried out to investigate the possible use of the Iraqi porcelanite rocks and prepared polymer (PMFP)for the removal of Azure A, B, and C dyes from aqueous solutions. UV – Visible spectrophotometry technique has been applied to study the adsorption isotherm and the factors influencing on it, such as contact time, adsorbent dose, pH and temperature. The results showed that the equilibrium time reached within 60 min and (0.05g) of adsorbent dose at pH (6.9)of operation for Iraqi porcelanite rocks while 30 min and (0.03g) of adsorbent dose at pH (5.5) for PMFP. The removal of Azure A, B, and C dyes using Iraqi porcelanite rocks and modified form has been studied at different temperatures (298.15, 308.15, 318.15, and 328.15)K to determine the adsorption isotherms and thermodynamic functions. The experimental isotherms data were analyzed using Freundlich and Langmuir isotherm models. The calculated dimensionless separation factor, $R_L < 1$ indicated that the adsorption of the three dyes onto both adsorbents were favorable. The data was found that Freundlich isotherm model fits the data very well for all three dyes on both adsorbents. The shapes of the isotherms obtained from the experimental data were found to be comparable in all cases to the (S- curve) type according to Giles classification.

Thermodynamic analysis was carried out for all three dyes – adsorbent systems. According to the results the thermodynamic functions (ΔG, ΔH, and ΔS) were calculated. It was found that the adsorption processes of all three dyes on Iraqi porcelanite rocks or PMFP were spontaneous and exothermic in nature from the negative values of ΔG and ΔH. The positive values of entropy over the temperature range characterize an increase disorder of the system and the driving force for adsorption is an entropy effect. The performance of both adsorbents to adsorb Azure A, B, and C dyes was also compared. It was found that the adsorption capacity of PMFP was higher than Iraqi porcelanite rocks. From the work, it was clearly shown that modified form of Iraqi porcelanite rocks has good adsorption capacity on Azure A, B, and C dyes.

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List of Abbreviations and Symbols

a	maximum adsorption capacity(mg/g).
b	constant Langmuir (L/g).
Ce	equilibrium solution concentration (mg/L).
C.I. No	Colour index number.
FT-IR	Fourier transform infrared.
ΔG	Gibbs energy change(kJ.mol^{-1}).
ΔH	Enthalpy change(kJ.mol^{-1}).
K_f	Freundich constant.
k	Scherrer’s constant.
L	Mean crystal size.
m	Weight of adsorbent (g).
n	Adsorption intensity.
PMFP	Porcelanite –Melamine –Formaldehyde Polymer.
Qe	The amount adsorbed in mg per one gram of adsorbent
r^2	Correlation Coefficient.
R	universal gas constant (8.314 J/mol K^{-1}).
rpm	Cycle per minute
% Removal	The percentage removal of the dye.

SEM	Scanning electron microscopy.
ΔS	Entropy change(kJ.mol^{-1}.K^{-1}).
T	absolute temperature (K).
t	Time (min).
v	Volume of the Azure dyes used solution that was used.
XRD	X-Ray diffraction.
ɵ	Diffraction angle.
2ɵ	Full width of half –maximum intensity.
ɵ	Fractional coverage of the surface.
λ	Wave length (nm).
λ_{max}	Maximum wave length (nm).

Chapter One

Introduction

CHAPTER ONE

INTRODUCTION

1.1General Introduction:

Water is one of the vital necessities for the survival of human beings. Earth is a planet with 71% of its surface covered by water, of the total available water on earth 97% is seawater and unavailable for human consumption, only 3% is available as fresh water. Out of this 3%, only a meager 0.06% can be easily accessed as the rest comprises of the frozen polar ice cap, groundwater and swamp[1]. The water demand doubles globally every 21 years due to the rapid increase in the population and the industrial activities. Compounded with this is the decrease in rainfall in the previous decade[2]. More than 80 countries accounting for 40% of the world’s population are facing major water crises. It has been estimated by UN that by 2025, 2.7 billion people will be affected by water deficiency[3].Many countries are facing the shortage of clean drinking water and it is estimated that 1.2 billion people are already drinking unclean water[1]. Furthermore, 5-10 million people die annually due to various diseases caused by the consumption of contaminated water. Thus, exploitation of safe water sources to overcome the scarcity of water has been a global challenge for many countries like Iraq.The selection of wastewater treatment technique is very critical and has to be made considering the contaminants present in wastewater. Industrial wastewaters largely possess organic and inorganic materials such as dyes, phenolic compounds, aromatic compounds and heavy metals[4]. Almost all the dyes, even the naturally occurring dyes, used today are now synthesized chemically. Annually, a total of more than 7 x 10^5tonnes of dyes are produced out of which azo dyes account for 60-70%[5]. Over the years the use of dyes has increased and is immensely used in industries like textile, cosmetics, pulp and paper, paint, pharmaceutical, food, carpet and printing.

The discharge from these industries is highly colored as enormous amount of dyes remains unfixed during coloring and washing[6]. Most of the currently available technologies are inadequate for the removal of colour-induced toxic pollutants such as dyes from textile wastewater[7].

Most of the conventional methods of wastewater treatment such as coagulation and flocculation, sedimentation and floatation, membrane filtration, disinfection are either expensive or not very effective. These technologies mostly transform pollutants from one phase to another and do not completely eliminate them[8]. Even though membrane filtration produces high quality water, it has a major limitation of clogging of micro- or ultra-filtration membranes adding to the operating cost[9]. In adisinfection process by chlorination, chlorine sometimes reacts with organic pollutants and produces disinfection by-products, such as trihalomethanes and haloacetic acid, which are mutagenic and carcinogenic and pose threats to human and aquatic life[10]. Adsorption has been recognized as a potential technology for the removal of dyes from wastewater. In comparison to other physical, chemical and biological methods available for the treatment of wastewater, adsorption is the most preferred technique due to simple and flexible design and easy operation. The adsorption process may generate little or no toxic pollutants and involve low initial capital and operating costs[11]. Moreover, it is does not have environment issues as it does not produce any sludge[12] and yields treated water with high quality[13]. Although adsorption is a proven technology for the removal of dye, it has a major limitation to its application due to sparse availability of low-cost adsorbents[14].The pollutant from dyeing industries is highly toxic. The removal of dyes from wastewater before its discharge is a necessary practice for water industry[15]. The significant increase in the use of dyes by various industries is causing severe damage to the environment due to non-biodegradability and high toxicity of these compounds.

1.2 Dyes and Water Pollution

Dye is an organic compound that imparts colour to substances such as textile fiber, leather, hair, plastic materials or wax either is solution or dispersion[16]. Dyes have long been known to man and in the prehistoric times they were derived from natural plants, mainly for colouring fabric. At present almost all the dyes are manufactured artificially even the natural dyes. The artificial dyes are thoughtfully delineated to have distinctive characteristics such as; ability to impart specific colour to the substance, resistance to fade when exposed to light, chemicals and washing[17] and resistance towards acids and bases. The groups that modify the ability of chromophores to absorb light are called auxochromes (NO_2, NO, N=N). The part of molecules which provides the colour by adsorbing wavelength is called chromophores (OH,NH_2, NHR, NR_2, Cl and COOH). Dyes can be broadly classified in two ways either based upon chemical composition or application. Table1.1 providethe classification of dyes based on chemical composition. Dyes have a wide range of application and are used as a colorin agent for many different substances. Dyes are widely used to impart colour to fabrics and plastics[16]. They are also used in food industry, printing and leather industry[18]. Recently, dyes have gained popularity in another field that is in hair coloring[19].

Table1.2 presents the classification of dyes based on their application.

[16,20-22]

Table 1.1 Classification of dyes based on chemical Composition

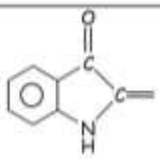
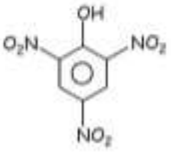
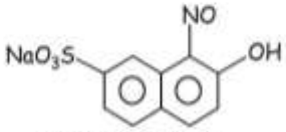
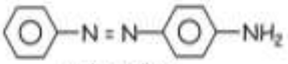
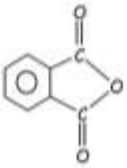
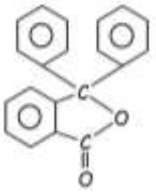
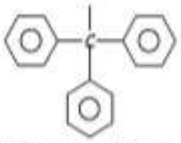
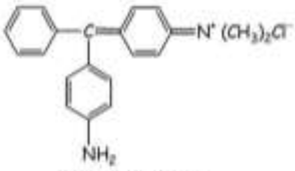
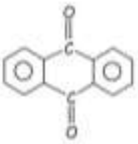
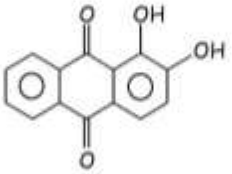
Type of dye	Structural unit	Example	
Indigoid dyes		Indigo Caramine	Oldest known dye, earlier isolated from plants of indigofera group but now prepared synthetically.
Nitro dyes	- NO_2 group	 Picric acid	Oldest known synthetic dyes but not commercially important
Nitroso dyes	-NO group	 Naphthahol green B	Generally possess hydroxyl group (OH) at ortho position to the nitroso (-NO) group
Azo dyes	– N = N –	 Aniline yellow (p-amino azobenzene)	Largest class of synthetic dye. Other examples include Congo red, Methyl orange, Methyl red.
Phthalein dye	 Phthalein group	 Phenolphthalein	Obtained by treating phenol with phthalic anhydride
Triarylmethane dyes	 Triphenylmethane	 Malachite Green	Prepared by introducing one or more – NH_2, NR_2 or OH groups into the triphenylmethane rings
Anthraquinoid dyes	 Anthraquionoid group	 Alizarin	

Table 1.2 Classification of dyes based on application [16,20-22]

Type of dye	Example	Application
Acid dyes	Methyl orange, Methyl red, Orange I, Orange II, and Congo red	Wool, Silk, Polyurethane fibers, nylon
Basic dyes	Aniline yellow, Butter yellow, Methylene blue and Malachite green and Azure	Reinforced nylon, polyesters Pharmaceutical
Direct dyes	Martius yellow and Congo red	Cotton, Rayon, Wool, Silk and Nylon
Disperse dyes	Celliton fast pink B, Celliton fast blue B	synthetic polyamide fibers, polyesters, nylon and polyacrylonitriles
Fiber Reactive dye	Procion dye (2, 4, 6-trichloro 1, 3, 5– triazine)	Cotton, Wool and Silk
Ingrain azo dyes	Para red	Cotton (Cellulose), Silk, Nylon, Polyester, Polyester and Leather, colouring agent in food
Vat dyes	Indigo, Tyrian purple, Benzanthrone	Wool, colouring agent in food
Mordant	Alizarin	Cotton and wools

1.3 Current Dye Removal Techniques

There are many techniques for dyes removal, Figure 1.1 shows these techniques:

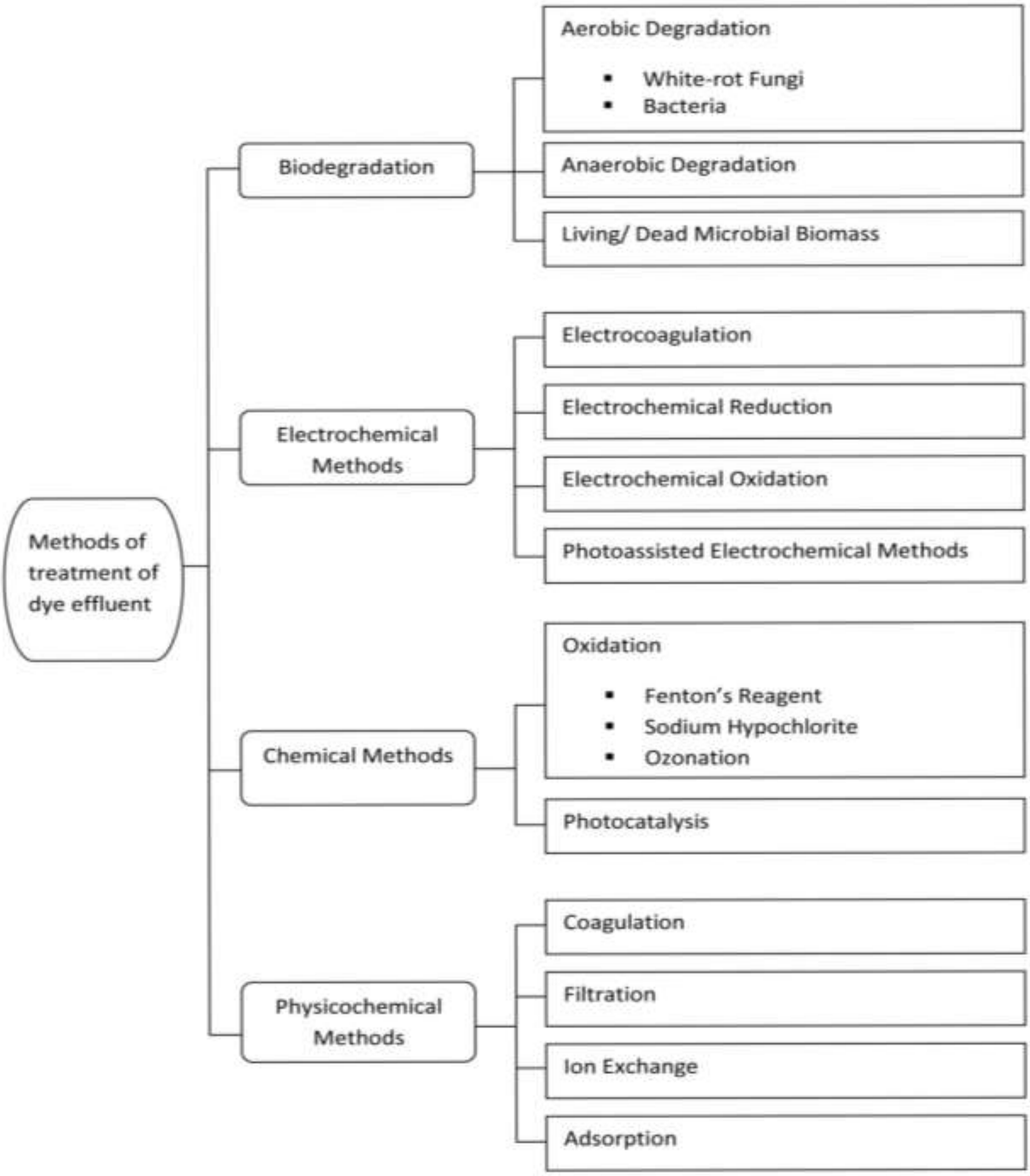


Figure 1.1 Current dye removal techniques

1.3.1 Physicochemical Methods

1.3.1.1 Coagulation

Coagulation is a popular conventional physico-chemical method employed for the treatment of wastewater. Coagulants such as alum and iron salts are added to wastewater to increase the tendency of the smaller particles to aggregate[22]. The coagulation alone cannot be applied for the removal of pollutants from wastewater. It requires subsequent processes such as sedimentation, filtration and disinfection[23].

1.3.1.2 Filtration

Filtration is usually employed to remove any particulate matter present in the wastewater. Membrane filtration has a high affinity towards the effluent. Most importantly membrane filtration can be used for the continuous removal of dyes from the dye effluent[24]. Unlike other physico-chemical methods filtration is resistant to temperature, chemical and microbial attack. The treated dye effluent can be recycled within the textile industry; however reuse of water treated by filtration is not very feasible. On the flip side, the disposal of sludge formed during treatment is a major problem. In addition, filtration involves high capital cost and tendency of membranes to clog which affects the performance of the filtration process[25].

1.3.1.3 Ion exchange

Ion exchange is the process of removing cations and anions present in the wastewater. Synthetic resins are normally used for ion exchange. Ion exchange finds extensive application for the softening of hard water. However the use in dye effluent is limited[26]. The advantages of ion exchange include the availability of a wide range of resins for specific application and there is no loss of sorbent. Ion exchange can be used for the removal of soluble dyes, however, it is ineffective for insoluble dyes. Drawbacks of ion exchange are high capital cost and expensive organic solvents[27].

1.3.1.4 Adsorption

The phenomenon of attracting and retaining the molecules on the surface of a solid is called adsorption. The substance that adsorbs on the surface is called adsorbate, and the substance on which it adsorbs is called adsorbent. The removal of adsorbed substance from the surface is called desorption[28]. Adsorption occurs due to the difference in the properties of the surface of the adsorbent than the bulk. The unbalanced inward forces of attraction or free valances at the surface have the property to attract and retain the molecules onto their surface with which they come in contact[29]. When the molecules of an adsorbate are held on the surface of adsorbent by Van der Waal forces without resulting into the formation of any chemical bond between them is called physical adsorption or physisorption[28].When the molecules of an adsorbate are held on the surface of an adsorbent result in the formation of a chemical bond between them is called chemical adsorption or chemisorption[29]. Adsorption is widely used for the removal of colour from dye effluent, edible oils, and sugar industry. Adsorption process can operate independently for the removal of colour. It has the capability of degrading organic compounds that are chemically and biologically stable[30,31].

1.4 Advantages of Adsorption

Adsorption is one of the preferred processes for dye removal over conventional methods due to its high efficiency, fast and easy operation and simple and flexible design. Moreover the adsorbent can be easily recovered and reused[17]. Adsorption is widely used for the removal of textile pollutants from wastewater due to its low capital costs and the wide availability of low cost adsorbents. The adsorption process may generate little or no toxic pollutants and has low initial capital and operating costs[11]. Adsorption is safe from the environmental point of view as no sludge is produced[12].The effluent produced after adsorption is generally of high-quality[32] .In adsorption the pollutants present in the wastewater attach to the surface of the adsorbent. The interactions between the adsorbate and the adsorbent can be expressed by adsorptive characteristics and physical properties[33]. Physico-chemical methods are very simple and feasible compared to all other dye treatment methods. Major drawback associated with most physico-chemical methods is the handling and disposal of sludge produced during the removal of dyes[32]. Adsorption is the preferred physico-chemical method due to its wide range of applicability. A wide variety of low-cost adsorbents are available[11]. The adsorption capacity of these low-cost adsorbents can be easily enhanced with simple and economically feasible methods.

1.5 Types of Adsorption

Adsorption can be classified as either physical or chemical. Physical adsorption(physisorption) involves weak forces, and is therefore reversible. Physical adsorption occur at low temperatures. It is very similar to acondensation process, and thus it is exothermic with a heat of adsorption similar to that of the latent heat of condensation[34].

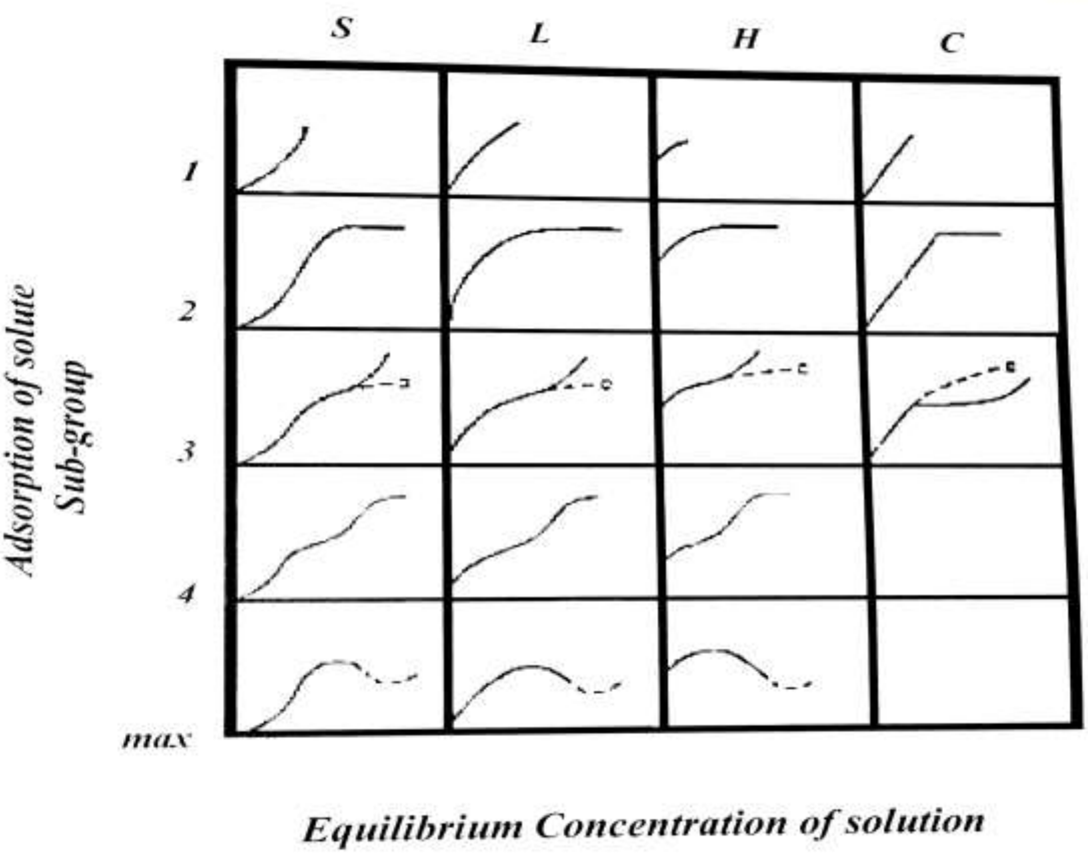
Chemical adsorption(chemisorptions) it is important in gas phase catalysis, but is not generally relevant to liquid- solid adsorption at ordinary temperatures. Chemisorption occur at high temperatures with a significant activation energy, which involves strong bonds and is not reversible. The heat of adsorptionis typically high in chemisorption and is similar to heat generated during a chemical reaction[34]. The differences between the physical and chemical adsorption are summarized in Table 1.3.

Table 1.3 Characteristics of Physisorption and Chemisorption

	Physisorption	***Chemisorption***
1	Nature of the forces is vanderWaales forces.	Nature of forces is chemical bonds.
2	Heat of adsorption less than 20kJmol^{-1}	Heat of adsorption less than 80kJmol^{-1}
3	No electron transferred or shared between the adsorbed species and the adsorbent surface.	Electron transferred or shared between the adsorbed species and the adsorbent surface.
4	Takes place without needing of activation energy.	Activation energy may be needed.
5	The process is non specific.	The process known by its specify.
6	Multi layer adsorption may occur because the forces act as great distances.	Activation lead to a monolayer, may befollowed by incorporation.
7	Adsorption is appreciable only at temperatures below the boiling point of the adsorbate.	Adsorption can occur at high temperatures.
8	The process is reversible; the adsorbed layer canbremoved by evacuating or warming to moderate temperature.	The process can be irreversible which may lead to a chemical reaction.
9	Temperature of occurrence depend on boiling point of the adsobate and is usually low.	Temperature of occurrence depend onactivation energy and is usually high

1.6 Adsorption Isotherm

The bases for adsorption is the equilibrium distribution of molecules between two phases, which could be liquid, solid, or gas[35].The variation of the extent of adsorption as a function of equilibrium concentration of the adsorbate at a fixed temperature is known as adsorption isotherm[36]. The graphic representation of the adsorption isotherm is obtained by plotting the amount of solute adsorbed on the surface of solid (Qe) against the equilibrium concentration of the solute in the solution (Ce) [37]. The equilibrium concentration is the concentration of solute in the liquid phase after it attains equilibrium in contact with the solid surface[38]. A great variety of adsorption isotherm shapes are found [36,37]. Chemisorption is usually accompanied an initial steeply rising curve that gradually flattens. The initial rise is taken as corresponding to the strong tendency of the surface to bind the adsorbed molecules, and the leveling off can be attributed to the saturation of these forces. Different isotherms ofadsorption from solution on solid active surface which were classified by Giles was presented in Figure 1.2.[39].



Figure(1.2):Adsorption Isotherms as in Giles Classification(10,11)

Giles has divided the isotherms into four major classes(S, L, H, and C) depending on their initial section plotted when the solution is very dilute. These classes include subclasses (1, 2, 3, 4 and max) depending on the increase in the solute concentration[40].

Giles tried to interpret the adsorption mechanism and the orientation of the adsorbed molecules and the other factors affecting the adsorption. He illustrated the shapes as follows:

(I) S- Curve, indicative of vertical or flat orientation of adsorbate, there is a strong inter-molecular attraction within the adsorbed layer, and the adsorbate is monofunctional in the initial part of an S- curve, the more solute is already adsorbed, the easier it is for additional amounts to become fixed [38,39].

(II) L- Curve, where the sites are few and widely separated and a monolayer adsorption is formed, so as this type refers tonormal isotherms indicative of molecules adsorbed flat on the surface like carbon series or cyclic hydrocarbons. The more solute is adsorbed; the harder it is for the additional amounts to become fixed.

(III) H- Curve, is attained when there is a high adsorption affinity as in the case of high molecular weight compounds like proteins and polymers, this isotherm can be observed even if the solution is very dilute.

(IV) C- Curve, constant – partition linear curve is given by substances, which penetrate into the adsorbent more readily than the solvent does[40-42].

1.7 Theories of Adsorption

There are many theories that would describe the adsorption process:

1.7.1 Freundlich Adsorption Isotherm

In, 1909, Freundlich gave an empirical expression representing the isothermal variation of adsorption of a quantity ofgasadsorbed by unit mass of solid adsorbent with pressure. This equation is called Freundlich adsorption isotherm or Freundlich adsorption equation[43].

$$\mathbf{Log\ Qe = Log\ X/m = Log\ K_f + 1/n\ LogP} \quad \ldots\ldots\ldots.(1.1)$$

Where: X is the gas adsorbed by ($mg.g^{-1}$) of the adsorbent at a pressure p, thus ($Qe=X/m$) is the amount of gas adsorbed by the adsorbent. k_f and n are constants at a particular temperature and for a particular adsorbent and adsorbate (gas), n is always greater than one, indicating that the amount of the gas adsorbed does not

increase as rapidly as the pressure. The constants k_f and n incorporating all factors affecting the adsorption capacity and the adsorption intensity, respectively.

Disadvantage or limitation of Freundlich's adsorption isotherm are:

1) Freundlich equation is purely empirical and has no theoretical basis.

2)The equation is valid only upto a certain pressure and invalid at high pressure.

3) The constants k and n are not temperature independent, they vary with temperature.

4) Freundlich's adsorption isotherm fails when the concentration of the adsorbate is very high[44].

1.7.2 Langmuir Adsorption Isotherm

In, 1916. Irving Langmuir presented his model for the adsorption of species onto simple surfaces. Langmuir was awarded the Nobel prize in 1932 for his work concerning surface chemistry. He derived a simple adsorption isotherm, on theoretical considerations based on kinetic theory of gases. This is named as Langmuir adsorption isotherm[45].

In the case of adsorption from solution, however, it seems more plausible to consider an alternative phrasing of the model. Adsorption is still limited to monolayer, but this layer is now regarded as an ideal two-dimensional solution of solute and solvent molecules[45] .

In this case, the adsorption is considered as a competition between solute and solvent toward the active sites of the surface.The algebraic formulation of the two-dimensional solution picture express the surface concentration of the solute and solvent in terms of mole fraction(N). The adsorption process can now be written as: [46]

$$A_{(\text{solute in solution})} + B_{(\text{adsorbed solvent})} = A_{(\text{adsorbed solute})} + B_{(\text{solvent in solution})}$$

N_2 N^s_1 N^s_2 N_1

Where:

Number 1 refers to a solvent

Number 2 refers to a solute

Letter s refers to adsorbed species.

The equilibrium constant for this process in a dilute solution is:

$$K = N^s_2 C_1 / N^s_1 C_2 \Rightarrow K/C_1 = N^s_2 / N^s_1 C_2 \quad \text{..............(1.2)}$$

(It is more convenient to write equilibrium concentration as C_e rather than C_2). In a dilute solution, the concentration of a solvent (C_1) is constant, so we can write $k/C_1 = b$ (constant); also the summation of mole fractions of the two-dimensional solution = $N^s_1 + N^s_2 = 1$ so that, equation (1.2) becomes:

$$N^s_2 = bC_e/1 + bC_e \quad \text{.........(1.3)}$$

Since, $N^s_2 = n^s_2/n^s$ is the number of moles of adsorption sites per gram. The ratio n^s_2/n^srepresents the fraction of surface (Θ) which is occupied by the adsorbed molecules. The equation (1. 3) will be:

$$\theta = bC_e/1 + bC_e \quad \text{...........(1.4)}$$

The quantity adsorbed (x) as (mg) per (gram) of adsorbent (m) is expressed as (x/m) which is proportional to the fraction of the surface occupied:

$x/m \; \alpha \; \theta \Rightarrow x/m = a\theta$ where a is a proportional constant; substitute in equation[46] (1.5).

$$Qe = (x/m) = abCe/1 + bCe \quad \text{........(1.5)}$$

Equation(1.5) represents Langmuir for adsorption in solution[45]

Where: Qe : Is the quantity of the adsorption at the equilibrium adsorbed concentration(mg/g).

Ce: Is the equilibrium concentration of the adsorbate (mg of adsorbate per liter of solution).

b: Is the constant Langmuir related to energy of adsorption or equilibrium constant(L/mg).

a: Is the maximum adsorption capacity upon a complete saturation of an adsorbent surface.

Also, we can write the linear form of this equation as :

$Ce/Qe = 1/ab + Ce/a$ ………….(1.6) [46]

1.7.3 Redlich- Peterson Adsorption Isotherm

A general isotherm incorporating features of both Langmuir and the Freundlich isotherms, represents the equilibrium adsorption at the surface of the particle. A combination of both isotherms approaches Freundlich's equation as a limit at low concentrations, and that of Langmuir's for high concentrations.
The following was suggested for the modified version[47]:

$q_e = bC_{eq}/1+a_m C_{eq}^2$……….(1.7)

where: q_{eq} and c_{eq} have the same meaning mentioned earlier, am and bm are constants. The linearized form of the above equation is as follows:

$Log(\frac{bCeq}{qeq} - 1) = \log a_m + B_m \log C_{eq}$……(1.8)

Hence a plot of log $(\frac{b\,Ceq}{a} - 1)$ versus log C_{eq}yields a straight line with a slope of B_m and an intercept of log a_m. The value of the exponent B_m lies between 0 and 1. i.e $0 \leq B_m \leq 1$. The value of K_L used in the ordinate term is that obtained from the Langmuir isotherm.

1.8Factors Influencing in the Adsorption Process

Some factors affecting the adsorption process are summarized in the following points:

1.8.1 Concentration of Adsorbate

The amount of material adsorbed by a given weight of the adsorbent at a constant temperature increase with the increase in concentration of the solute, but in some cases, adsorption may be confined to only one layer of the adsorbed solute. Further increase of concentration of solute can produce no further adsorption because the surface of the adsorbent is covered[48]. For the gas adsorption, the increase in the gas pressure leads to an increase in the amount adsorbed by a given amount of the adsorbent[49].

1.8.2 Ionic Strength

Ionic strength enhanced the extent of adsorption if the electrolyte that used to increase the ionic strength is more soluble in the solvent than the adsorbate[50]. The reverse effect happen if there is an ion exchange adsorbent used, in this case the ionized species adsorbed preferentially on the surface[51].

1.8.3 Effect of pH

The extent of adsorption may increase, decrease or remain unchanged as a result of changing the pH. Many variables can take part in this process such as the nature of chemical state of the adsorbent, the adsorbate, and the solvent.A competition is expected to take place as a consequence of H^+ or OH^- ions interaction with the solute, surface or the solvent. Such an interaction can change the chemical state, which may lead to stronger or weaker extent of adsorption[28,29].

1.8.4 Effect of Temperature

The effect of temperature on the adsorption extent depends on the type of adsorption and the nature of both the adsorbent and the adsorbate[52].Usually the process of adsorption is an exothermic process and thus, according to Le-Chatelier's principle, a decrease in temperature of a system would result in an increase in adsorption[53]like, the physical adsorption where a decrease in temperature enhanced the extent of adsorption. In chemisorptions, the quantity adsorbed may increase or decrease with the rising temperature depending on the type of interaction and bonding between the surface and the adsorbed molecules. on the other hand, the increasing adsorption with a rise in temperature means that the process is endothermic[49].

1.8.5 Surface Area of Adsorbent

The surface area for a given weight of the adsorbent is inversely proportional to the particle size of a solid. It follows from this that the more finely divided or the more porous the solid is, the greater is the surface area and hence, the greater is the adsorption capacity. Subsequently, the increase in the active sites of the surface will lead to an increase in the adsorptive capacity[54,55].

1.8.6 Nature of the Adsorbent and Adsorbate

The amount of material adsorbed depends on three properties of the adsorbent; the chemical nature of its surface, the specific surface area, and the extent of its porosity. The properties of the adsorbate also play an important role in the extent of the adsorption such as polarity, size of molecule, orientation and the presence of different functional groups in the molecule govern the ability of the molecule to be adsorbed on a certain surface[56].

1.8.7 The Solubility of Adsorbate and Traube's Rule

There is generally an inverse relationship between the extent of adsorption of a species and its solubility in the solvent used, that is, the less soluble the material the more strongly will tend to be adsorbed.

The rule that a polar (non-polar) adsorbent will preferentially adsorb the more polar (non-polar) component of a non-polar (polar) solvent. Polarity is used here in the general sense of ability to engage in hydrogen bonding or dipole-dipole type interactions as opposed to nonspecific dispersion interactions[56].

Traube's rule, which was given by Freundlich states that “The adsorption of an organic substance from aqueous solution increases strongly and regularly as the homologous series is ascende”[57] .

1.9 Adsorbate (Azure Dyes)

Azure is the name of color between blue and cyan like sky color on a clear day. Azure, a methylated thiazine dye, is a metachromatic basic dye ranging from green and blue, to red color. There are many methylated homologues used as components of many polychrome stains in combination with eosin and methylene blue in pH adjusted solutions[58].

1.10 Adsorbents

The applicability of adsorption process depends on the adsorbents and their physical and chemical properties. An adsorbent is expected to have high selectivity, high adsorption capacity and long life. Furthermore, an adsorbent should be available in abundance at economical costs[29]. A wide variety of adsorbent are commercially available and successfully used for the removal of organic and inorganic pollutants.

1.10.1 Iraqi Porcelanite Rocks

Porcelanite is a term used by Iraqi geologist to identify siliceous rock resemble to diatomite. These rocks are found in Iraq in different places. Porcelanites these rocks, composed of Opal-CT (cristobalite-tridymite crystal stratification) derived from biogenic amorphous opal silica (mainly from diatoms). They are part of the phosphorite-bearing sequences of the mastrichtianin the Western Desert (Digma and Akaashat formations respectively several Porcelanite horizons were identified as 0.5-1.5 m thick layers associated with shale phosphorite and chert[59,60,61].Porcelanite rocks are largely composed of sponge spicules (pore)and some other siliceous microfossils(diatoms and radiolarian), as well as silicified foraminifera and non plankton[62]. Diatomite deposits have been found in many different countries and varies in their quality, purity, and uses from one area to another.

Figure 1.3 Natural Porcelanite Rocks

1.10.2 Modification of Rocks

Modification can alter the rock structure to enlarge its surface area, therefore increasing the adsorption capacities[36]. Modification of Porcelanite rocks is vital to increase the range of applicability of Porcelanite for the adsorption of cationicdyes[37]. The chemical composition of Porcelanite rocks varies depending upon the origin influencing the layer charge, cation exchange capacity, adsorption capacity and morphology. These factors play a significant role in the modification of the natural rock[60]. The physical, chemical and biological properties of modified adsorbents are different from the original adsorbent[28].

1.11 Aim of The Present Work

The essential aim of the present work is to investigate the removal of Azure dyes A, B, and C from water by using Iraqi porcelanite rocks and then modified it to increase the adsorption capacity.

This study was set to achieve the following:

1- Modification the Iraqi porcelanite rocks.
2- Determination the optimum removal conditions to adsorbe higher quantity of Azure dyes such as (contact time, pH, adsorbent dose and temperature).
3- Evaluation a suitable adsorption isotherms and know the adsorbent capacity of the Iraqi Porcelanite rocks and modified form.
4- Determination a thermodynamic functions such as Gibbs energy (ΔG), enthalpy (ΔH) and entropy (ΔS).

Chapter Two

Experimental

Chapter Two

Experimental

2.1 Instruments.

The instruments used in this study with their models and companies are shown in Table 2.1

Table 2.1 Instruments Used in this Work and their Models and Company

No	*Instrument*	*Model*	*Company, Source*
1	UV-Visible Spectrophotometer	UV-1650	Shimadzu -Japan
2	Thermo stated shaker	GFL(D-3006)	Germany
3	pH – meter	211-Instrument	Hanna- Romania
4	Centerifuge	Hettich	Universal II-Germany
5	Oven	Memort LDO- 080+N	Labtech- Korea
6	Electronic Balance	BL 210S	Sartorius-Germany
7	Water Bath	WB 710M	Optima- Japan
8	X-Ray Diffraction Spectroscopy	Lab X XRD – 6000	Shimadzu- Japan
9	Fourier Transform Infrared (FT-IR)	8400s	Shimadzu- Japan
10	Scanning Electron Microscopy (SEM)	Tescan, Vega 3	Czech

2.2 Chemicals.

Chemical used in the present work are given in Table 2.2 together with their purity and suppliers. All were used without further purification.

Table 2.2 Chemicals Used in this Work and their Suppliers and Purity

No	Chemicals	Company Supplied	Purity %
1	Porcelanite rock	B.D.H	90%
2	Azure dyes	Aldrich	99%
3	Sodium hydroxide	B.D.H	98%
4	Hydrochloric acid(36.5%)	B.D.H	37%
5	Formaldehyde	B.D.H	98%
6	Melamine	B.D.H	88%

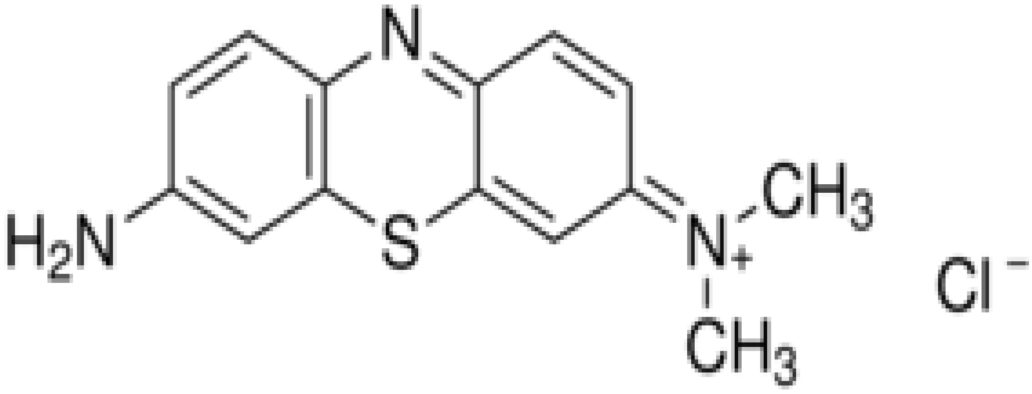
2.3 Dyes Used in this Study:

Azure (A, B and C) dyes were used in this study some physical properties of the selected dyes are given in Table 2.3

Table 2.3 Physical Properties of Azures Dyes

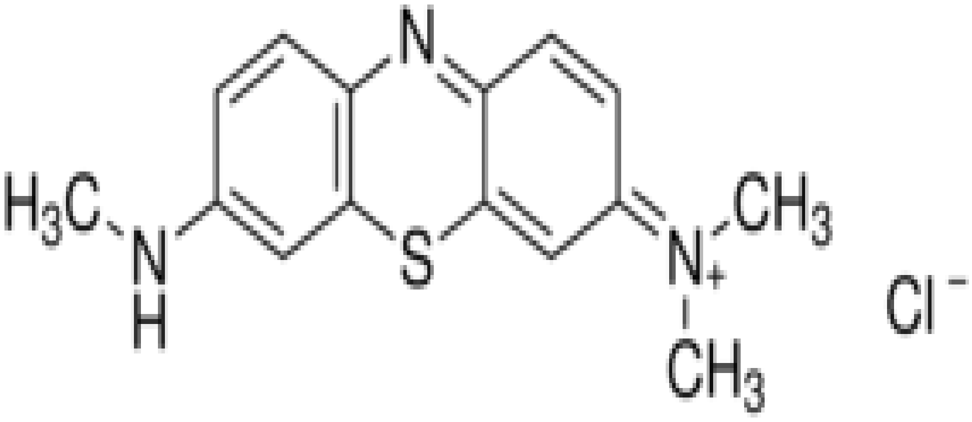
Properties	Azure A	Azure B	Azure C
Empirical Formula	$C_{14}H_{14}ClN_3S$	$C_{16}H_{18}ClN_3S$	$C_{13}H_{12}ClN_3S$
Class	Thiazine	Thiazine	Thiazine
Solubility in water	Soluble	Soluble	Soluble
Mol.Weight (g/mol)	291.80	305.83	277.77
Dye Content	80%	89%	40%
λ_{max} (nm)	632	646.50	611.5
C.I. No.	52005	52010	52002

Clarified shapes indicate the following structural formulas for each dye.



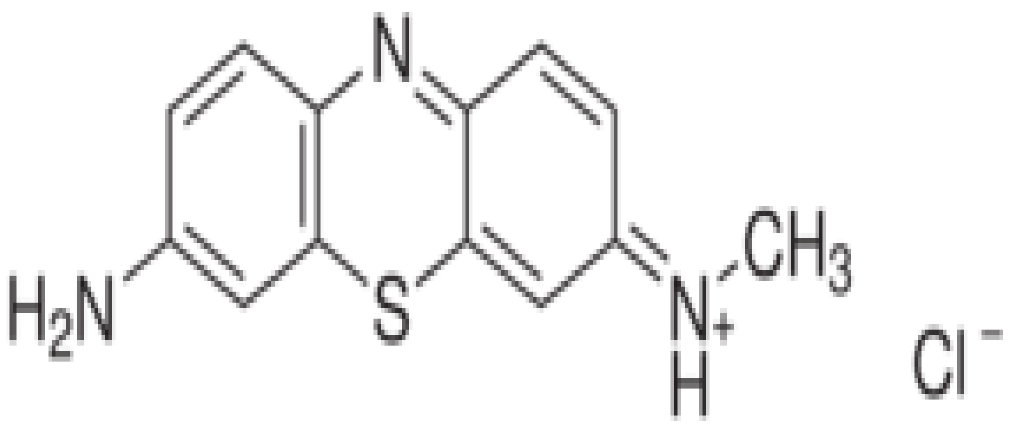
3-Amino-7-(dimethylamino)phynothiazinium chloride

Figure 2.1 Structural Formula of Azure A Dye



N-Methyl-N-(7-methylamino)-3-phenothiazine-3-

Figure 2.2 Structural Formula of Azure B Dye



N-(7-aminopheno thiazine-3-ylidene)methanaminiumchloride

Figure 2.3 Structural Formula of Azure C Dye

2.4 Determination of λ_{max} and Calibration Curves for Azure (A,B and C) dyes.

The maximum wavelength of Azure (A,B and C) dyes was specified by using spectrophotometer in the range of (200-800nm) ,and recording the spectra of absorption as shown in the Figures 2.4 to 2.6 . It is found that the highest absorbance of the azure A dye at wavelength(λ_{max} =632nm) , and prepared solution of Azure B dye at wavelength (λ_{max}=646.5nm). While the solution of azure C dye at wavelength(λ_{max} =611.5nm).

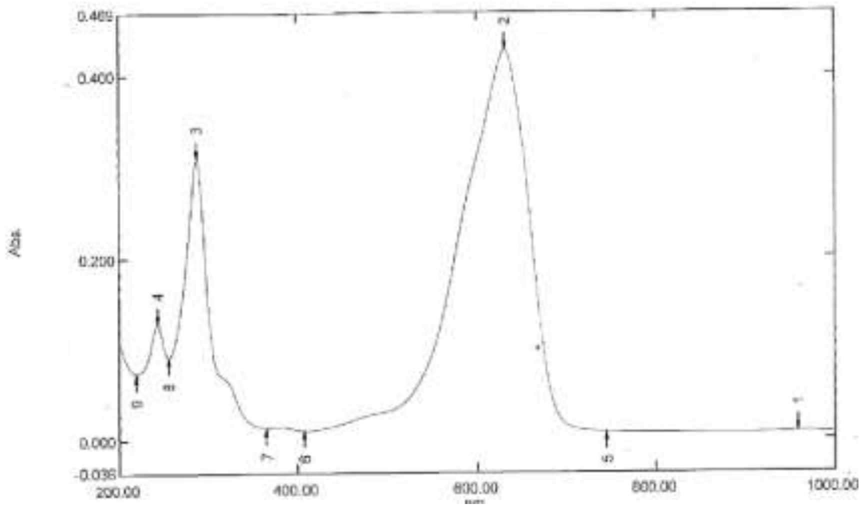


Figure 2.4 UV-Visible Spectrum of Aqueous Solution of Azure A Dye

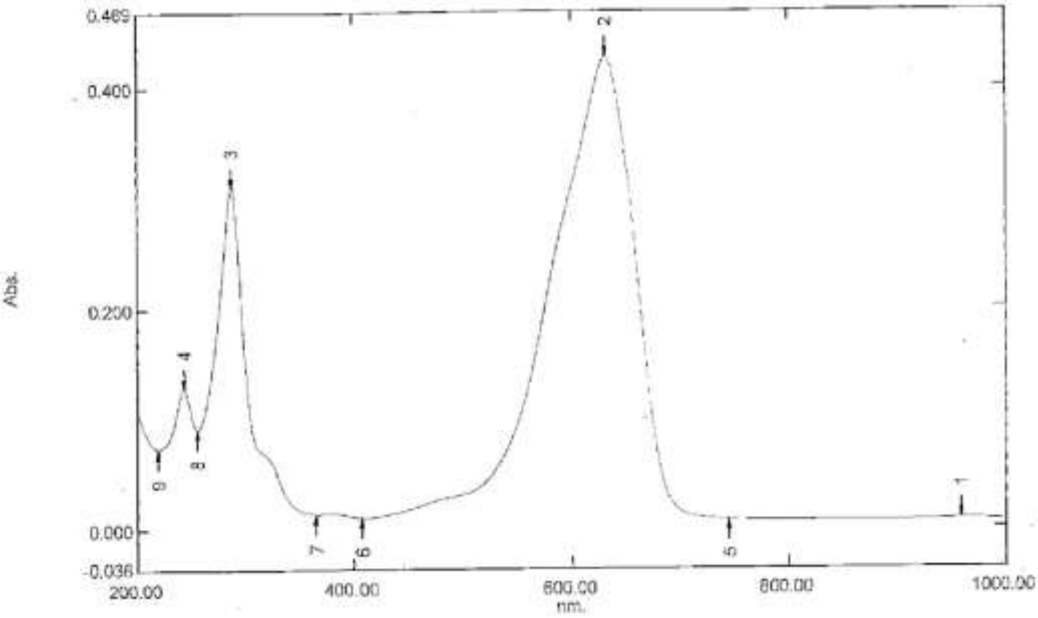


Figure 2.5 UV-Visible Spectrum of Aqueous Solution of Azure B Dye

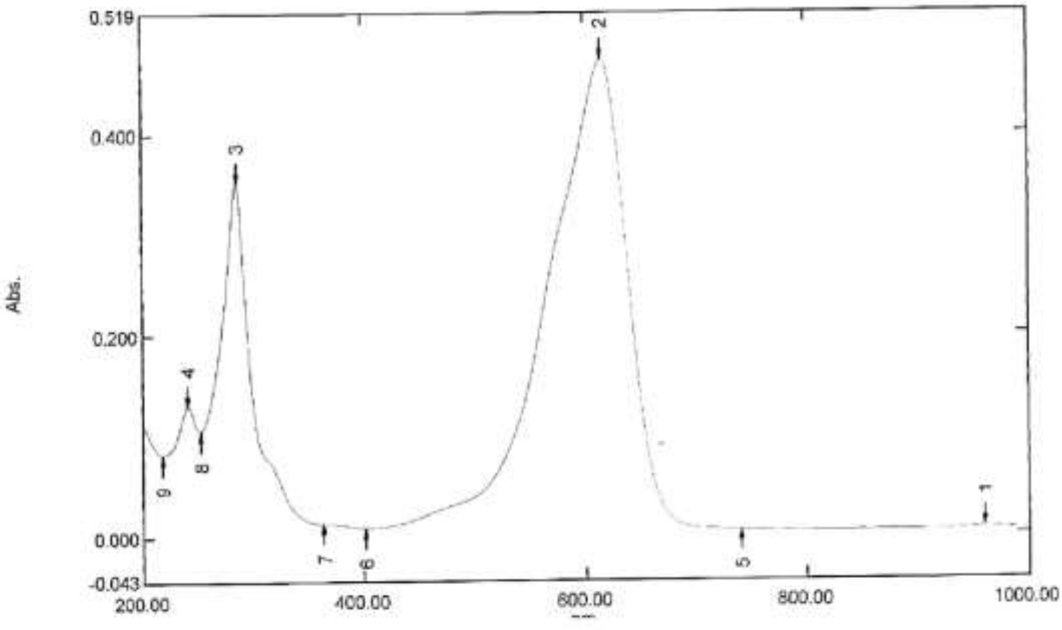


Figure 2.6 UV-Visible Spectrum of Aqueous Solution of Azure C Dye

The determination of calibration curve of the Azure dyes which explains the relation between absorbance and concentrations solutions were prepared by using eight successive concentration from the azure dyes for range between 1-15 mg/L. Then, the absorbance of these solutions were measured in the specified wavelength as Figures 2.7 to 2.9 clarify.

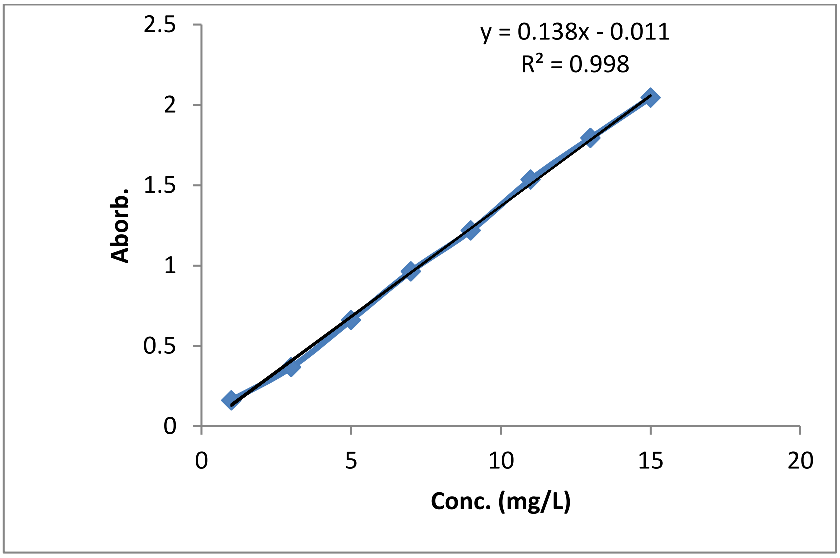


Figure 2.7Calibration Curve for Azure A Dye

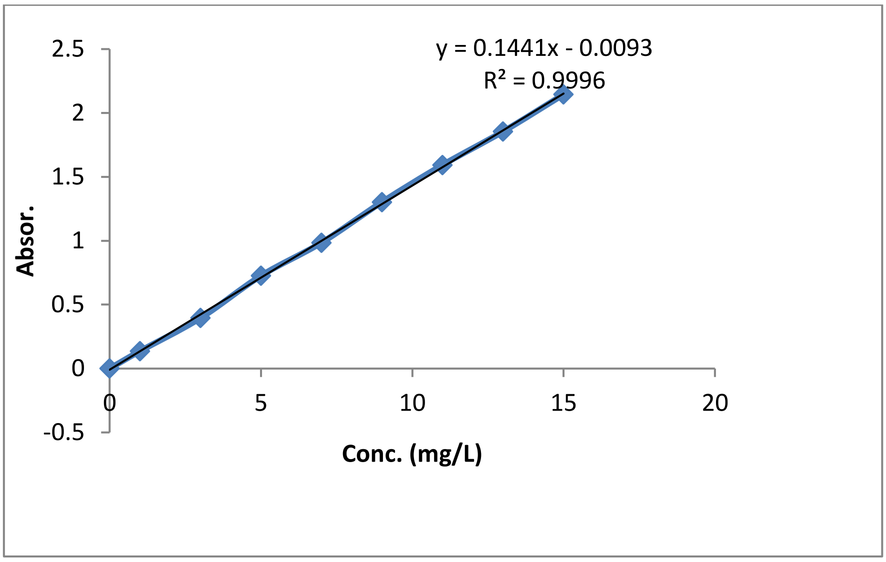


Figure 2.8CalibrationCurve for Azure B Dye

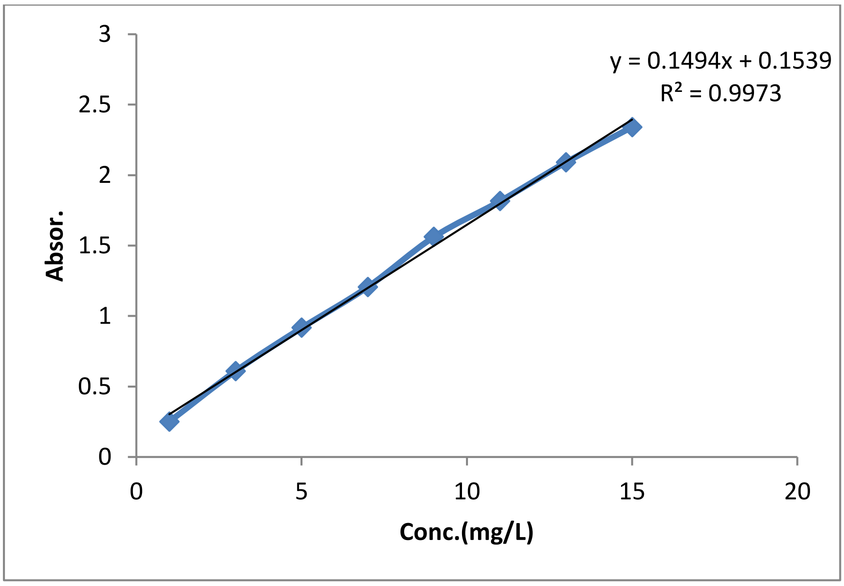


Figure 2.9Calibration Curve for Azure C Dye

2.5 Adsorbent Surfaces

2.5.1 Iraqi Porcelanite rocks

Porcelanite rocks in Iraq are from an industrial bed of (0.5 to 1.5m) thickness in the sefra, and Trafawi site of the Jeed formation in Al-Rutba region, western of Iraq. The sample of Porcelanite was obtained from The Iraqi State Company for Geological Survey and Material Investigation. Porcelanite are supplied as rocks. Some of the chemical analysis for the porcelanite is shown in Table 2.4.

Table 2.4 Chemical Analysis of Iraqi Porcelanite Rocks *[61]*

No.	Chemical Composition	X-Ray Analyzer%
1	SiO_2	74.0313
2	CaO	5.6296
3	MgO	3.6556
4	Al_2O_3	3.6539
5	P_2O_5	1.1600
6	Fe_2O_3	0.9794
7	TiO_2	0.1773
8	K_2O	0.1707
9	Na_2O	0.0662
10	Cr_2O_3	0.0245
11	SO_3	0.0090
12	MnO	0.0043
13	L.O.I	11.2000
	Sum	100.7617

The crushed and milled samples of porcelanite was washed several times with deionised water then dried at (110˚C) by using drying oven. Each sample was sieved and the fraction of 75 µm and below was collected for adsorption experiments

2.5.2 Modification of the Rock

I. Preparation of Porcelanite- Melamine Complex(PMC)

By mixing 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[17].

II. Preparation of Porcelanite- Melamine- Formaldehyde 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 °C for two hours to complete the cross linkage between the PMC and formaldehyde[17].

2.6 Equilibrium Time of Adsorption System

The adsorption experiments were carried out by agitating(0.05 g of Iraqi Porcelanite rocks and 0.03 g of PMFP) adsorbent with (25 ml) of dye solutions (7)mg/L at (150) rpm on an thermo stated shaker water bath. Centrifuge at 5000 rpm for 60 and 30 min for Iraqi Porcelanite rocks and PMFP, respectively. And unabsorbed supernatant liquid was analysed for the residual dye concentration using Shimadzu UV-Vis 1650 at a wavelength corresponding to the λmax of each dye. All experiments were carried out in duplicate and the mean values are reported.

The time that is sufficient for the adsorption process to reach the equilibrium state at a certain temperatures was determined according to the following procedure:

A volume (25ml) of an initially fixed concentration (7mg/L) of Azure dyes solution was shaken with (0.05g) of Iraqi Porcelanite rocks and (0.03g) of PMFP at a specified temperature (25°C). The concentration of unadsorbed Azure dyes solution was determined after (10, 20, 30, 40,50,60and70)minutes[31].

2.7 Adsorption Isotherm

The adsorption isotherm for the Azure dyes solutions was determined by using the following procedure:

Aliquots(25ml) of Azure dyes solutions of aknown concentration (1-15)mg/L were added indiridually to stoppered flasks containing (0.05g of Porcelanite rocks and 0.03 g of PMFP)of adsorbent. At a certain temperature (25°C), the flasks were shaken in thermo-stated shaker for a required equilibrium time. The mixture were then separated by centrifugation at (5000 rpm) for (10 minutes) and were filtered by using filter paper.

The concentrations of Azure dyes at equilibrium were measured by using UV-Visib. Spectroscopy.

The amount of Azure dyes adsorbed was calculated from the following equation:

$$Qe = X/m = V(C_o - Ce)/m \quad \ldots\ldots\ldots(2.1)$$

Where:X= The quantity of adorbed (mg).

V= Volume of Azure dyes solution (L) that was used.

C_O= Initial concentration(mg/L).

C_e= Equilibrium concentration (mg/L).

m= Weight of adsorbent (g).

The amount of adsorption is expressed by the ratio (X/m) or (Qe) which is defined

as the quantity of adsorbate in (mg) held by weight of adsorbent in (g)[46].

$$\%\ Removal=(C_o - C_e/C_o) \times 100 \quad \ldots\ldots\ldots\ldots(2.2)$$

2.8 Factors Influencing Adsorption Process

2.8.1Effect of Adsorbent Weight

The effect of adsorbent weight change on adsorption was studied in this work by using a fixed concentration (7mg/L) of Azure A, b and C dyes with different weights of adsorbent (0.0125, 0.02, 0.03, 0.05, 0.06 and 0.07)g for Porcelanite rocks and (0.005, 0.007, 0.009, 0.0125, 0.03 and 0.05)g for PMFP.

2.8.2 Effect of pH

Adsorption experiments were carried out as mentioned in paragraph (2.6) as a function of pH by using a fixed concentration (7mg/L) of Azure dyes in different pH media. NaOH (0.1N) and HCl (0.1N)were used to adjust the pH in the range (2-12), the pH of the two system at the concentration of the adsorption was measured by using pH-meter.

2.8.3Effect of Temperature

Adsorption experiments were performed in the same manner as mentioned in paragraph (2.6) at temperatures (25, 35, 45 and 55°C) to estimate the basic thermodynamic functions.

2.9 Characterization Methods of the Adsorbents

2.9.1 X-Ray Diffraction Spectroscopy(XRD)

X-ray diffraction (XRD) data were analyzed by Lab X, XRD 6000 instrument equipped. This instrument was employing CuKα 1as a target source (wave length1.54060 A°, at 40 mA and 40 KV) 2Ɵ range from 10 to 80° .

XRD data was employed to calculate the mean crystallite size (L) by Scherrer's formula in the following equation[63]:

$$L = \frac{k\,\lambda}{\beta \cos \Theta} \quad \ldots\ldots\ldots\ldots(2.3)$$

Where : L is the mean crystallite size, k is the Scherrer's constant (0.94) which depends on the shape of the crystal,λ is the wave length of the X- ray radiation (o.15406 nm for CuKα), β is the measured in degrees then multiply by (π/180) to convert to radians and ϴ is diffraction (Bragg) angle. The analysis was performed at the, Chemistry Dept., College of Education/Ibn Al-Haitham, University of Baghdad.

2.9.2 Fourier Transform Infrared Spectroscopy (FT-IR)

Fourier Transform Infrared spectra for Iraqi Porcelanite rocks and PMFP were recorded as (KBr) discs by using Shimadzu (FT-IR) spectrophotometer in the range (4000-400) cm^{-1}. The spectra were recorded at the, Chemistry Dept., College of Education/Ibn Al-Haitham, University of Baghdad.

2.9.3 Surface Morfology /SEM Analysis

The surface morphology of the Porcelanite rocks and PMP were studies by using scanning electron microscopy (SEM) type Vega 3, Tescan(Czeck). The analysis was made at the Ministry of Sciences and Technology, Baghdad.

Chapter Three

Results and Discussion

Chapter Three

Results and Discussion

3.1 Characterization Studied of Iraqi Pocelanite Rocks and PMFP

3.1.1 XRD Analysis for Iraqi Porcelanite Rocks

The XRD spectrum Figure 3.1 indicates existence of certain amount of Quartz (silicon dioxide) and Opal: which are known as irregular interferents between two phases, kretoplyte and traidamayte-alpha; and also some other (kaolin and samktite) which can be found together with fine size silica[64].

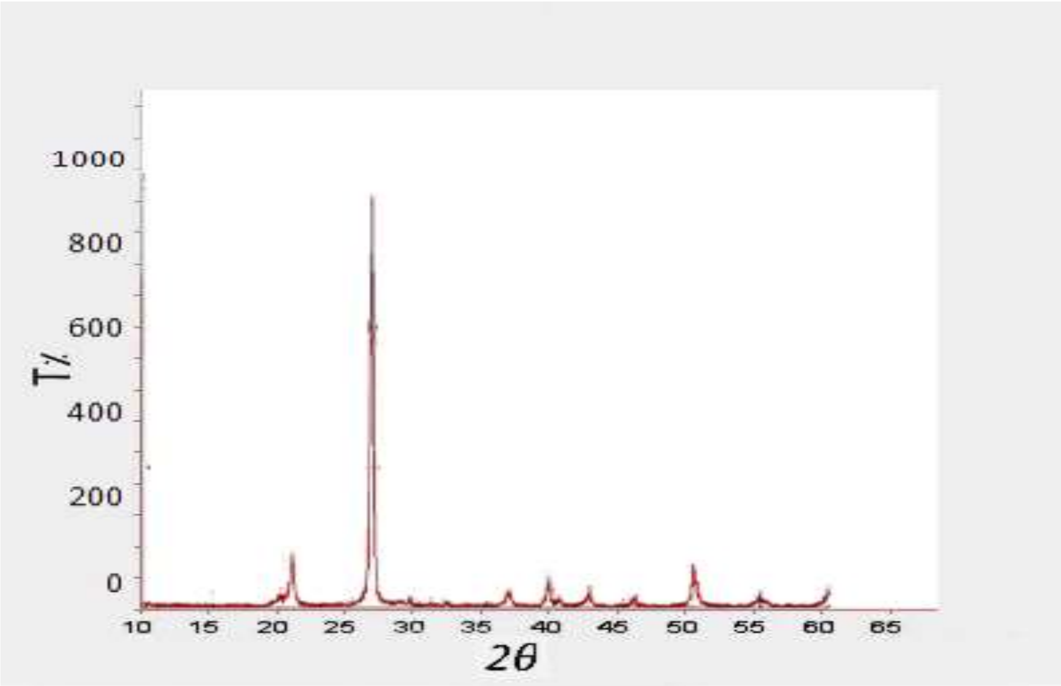


Figure 3.1 XRD Spectrum of Iraqi Porcelanite Rocks

3.1.2 XRD Analysis for PMFP

The XRD spectrum of PMFP Figure 3.2 it seems that the structure is maintained after modification because all peaks in the modified sample are broader and their intensities are lower when they compared with that befor modification, that may indicates to change in crystal size of modified sample.

More specifically, Scherre’s equation showed that the crystal size was reduced to nano-scale in modified sample, it was 782nm in natural Porcelanite and it decreased to 28nm after modification.

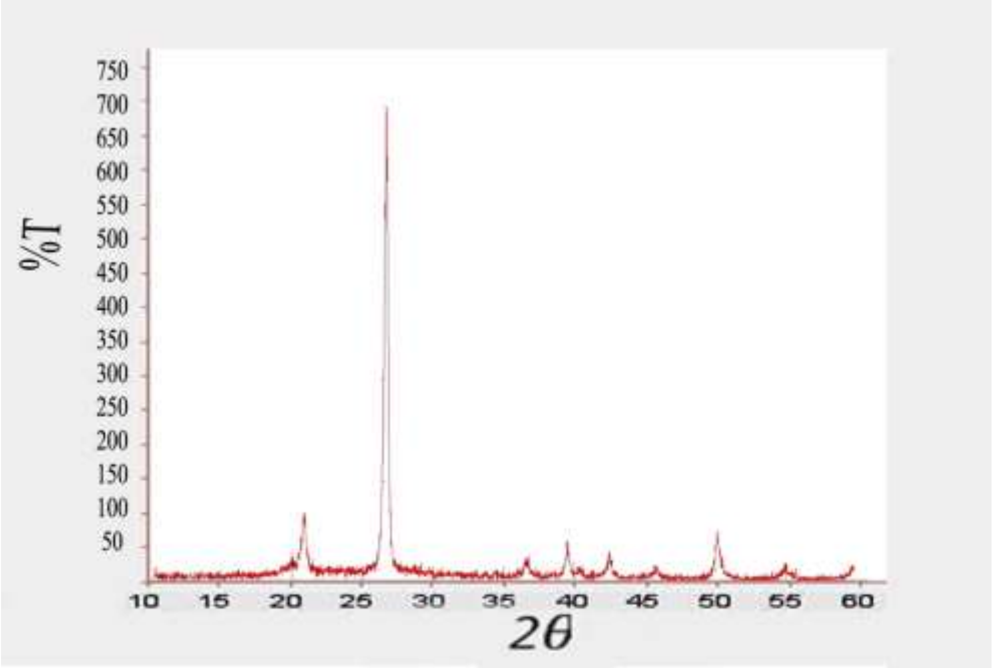


Figure 3.2 XRD Spectrum of PMFP

3.1.3 FT-IR Analysis for Iraqi Porcelanite Rocks

The FT-IR spectra Figure 3.3 shows existence of the terminal silanol-OH and to the brighe Si-OH-Si .The band at (1600 cm^{-1}) could be attributed to the deformation of water molecules $\beta(H_2O)$. The band at (1100 cm^{-1}) that appear as strong band can be assigned to($^{\gamma}{}_{Si\text{-}O\text{-}Si}$) stretching viberations . The bands at (796 cm^{-1}) are characteristic of Quartz and those at (455 cm^{-1}) can be attributed to β(Si-O-Si) bending vibrations [65].

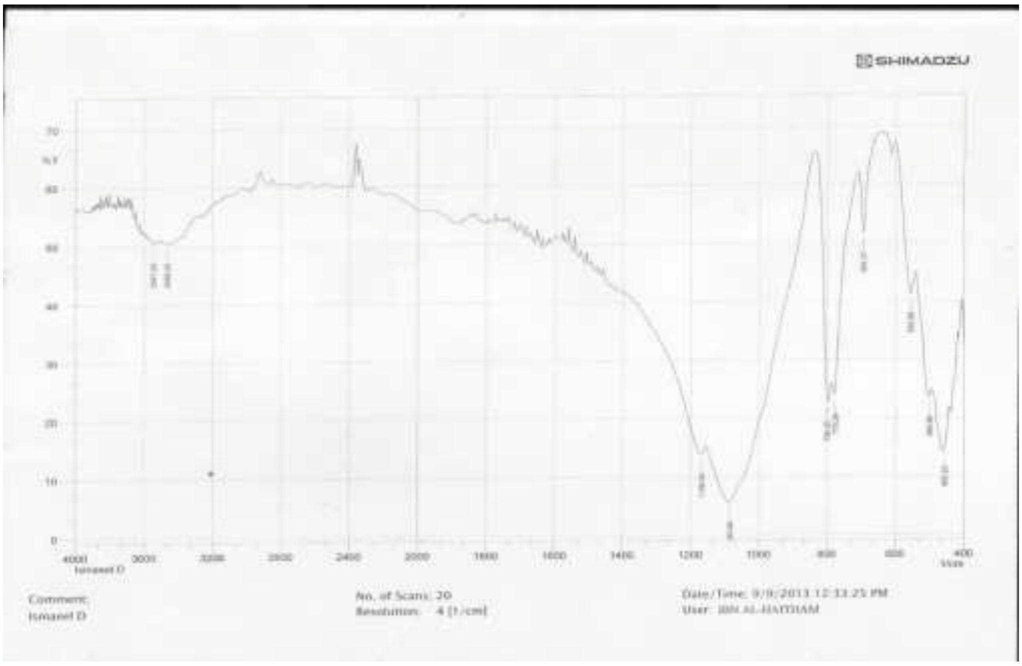


Figure 3.3 FT-IR Spectrum of Iraqi Porcelanite Rocks

3.1.4 FT-IR Analysis for PMFP

Figure 3.4 shows the IR spectra of the PMFP appearing of two sharp weaks band at the general range (3470-3132 cm^{-1}) attributed to asymmetric and 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 component melamine and formaldehyde[66], 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 bending 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[67].

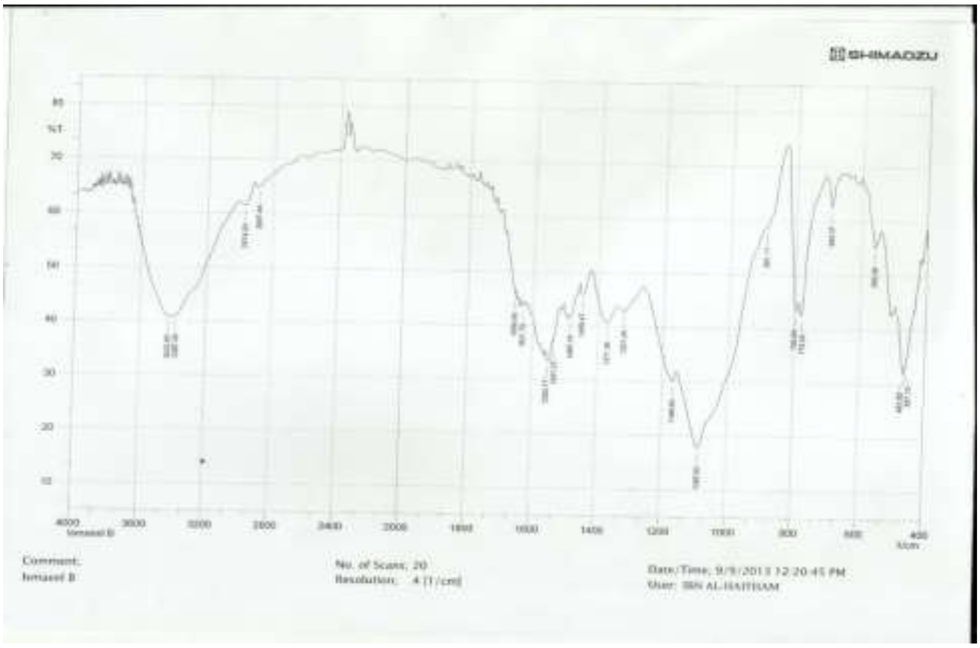


Figure 3.4 FT-IR Spectrum of PMFP

3.1.5 Surface Morphology / SEM Analysis for Iraqi PorcelaniteRocks

The surface morphology of porcelanite rocks was visualized via scanning electron microscope (SEM) at 10000 magnification. Examination of SEM micrographs of the porcelanite rocks particles showing clearly the porous nature of the sample surface Figure 3.5.

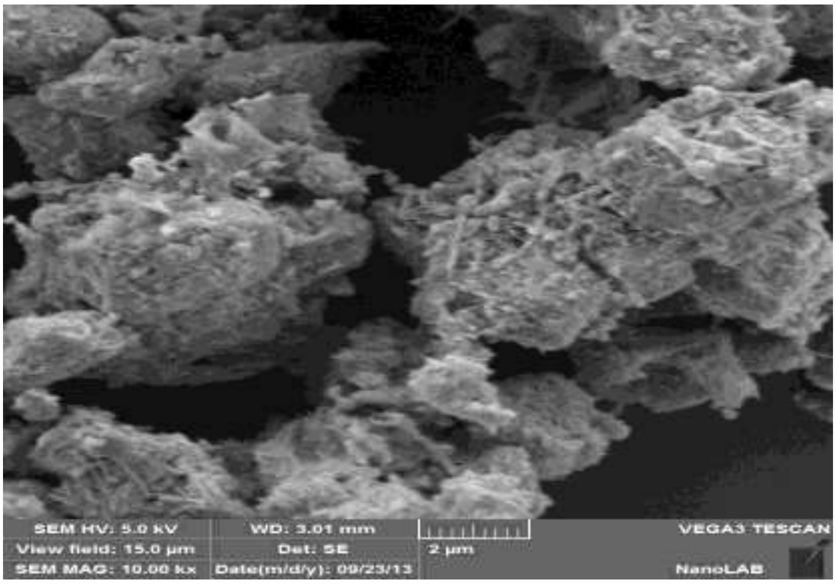


Figure 3.5 SEM Photography of Iraqi Porcelanite Rocks

3.1.6 Surface Morphology / SEM Analysis for PMFP

The surface morphology of PMFP was visualized via scanning electron microscope (SEM) at 10000 magnification. Morphological description of modified Porcelanite in Figure 3.6 refers to the presence of very small nano-crystals which are attached together to form big particles.

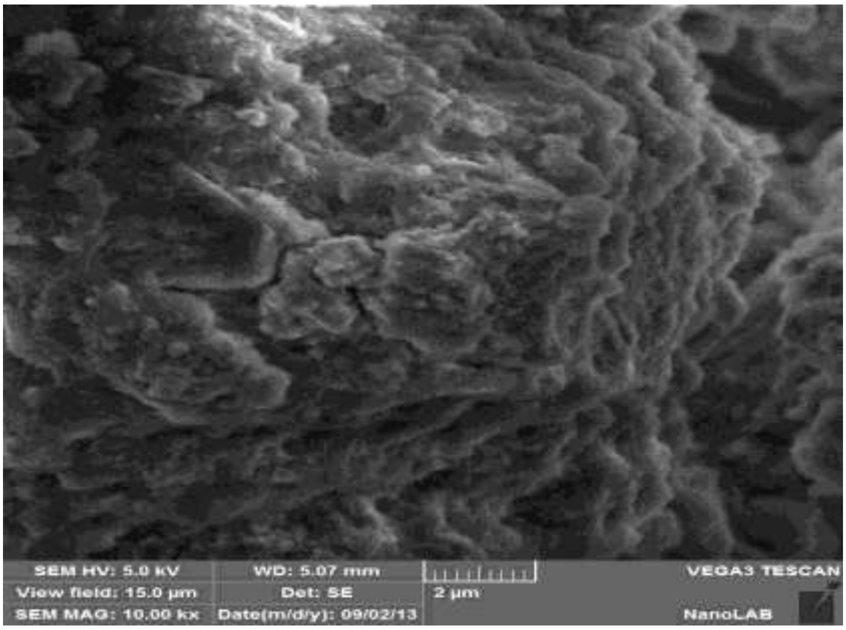


Figure 3.6 SEM Photography of PMFP

3.2 Removal of Azure Dyes from Water by the Porcelanite Rocks and PMFP

This part includes the various investigations that could elucidate all the factors affecting the utilizing of the Porcelanite rocks and PMFP in the removal of Azure dyes pollutant from water. Furthermore the work includes the adsorption isotherms, the theoretical models that describe the isotherms and the thermodynamics of the adsorption process.

3.2.1 Equilibrium Time of Adsorption Systems

The contact times between the adsorbents (Porcelanite rocks and PMFP) and fixed concentration of Azure dyes (7 mg/L) as adsorbate, that is sufficient for the adsorption process to reach the equilibrium at 25°C were studied at different periods (10, 20, 30, 40, 50, 60and 70) minutes until reaching equilibrium. Equilibrium times of adsorption systems studied here were 60 minutes for Azure dyes – Porcelanite and 30 minutes for Azure dyes - PMFP.

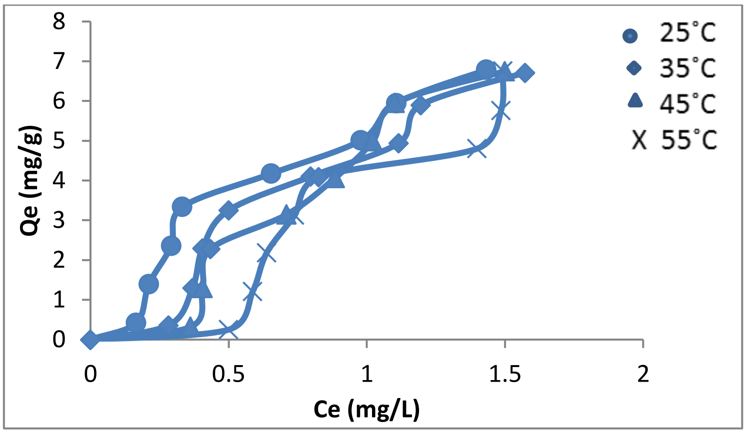
3.2.2 Adsorption Isotherm

The general shape of the Azure dyes adsorption isotherm on the Porcelanite rocks and PMFP are shown in Figures3.7 and 3.8 and Tables 3.1 and 3.2,where the quantities of adsorbed on Porcelanite rocks (Qe) are plotted a function of equilibrium concentration (Ce) at (25, 35, 45 and 55)°C. The shape of the adsorption isotherms of Azure dyes on the two surfaces Porcelanite rocks and PMFP is in consistent with (S-type) on the Giles classification [39,40]. In the adsorption of dyes such as Azure dyes on Porcelanite rocks or PMFP surfaces, there is an electrostatic attraction between the surface or crystal structure of the rocks or polymer which are negatively charge, and the positively charge dye ion. Therefore, an isotherm of (S-type) is expected and in this case has a high probability, to behave like an ion exchange. According to Giles interpretation for the adsorption isotherm shape, the Azure dyes could be oriented in a direction which is parallel to the surface of the Porcelanite rocks or PMFP[40].

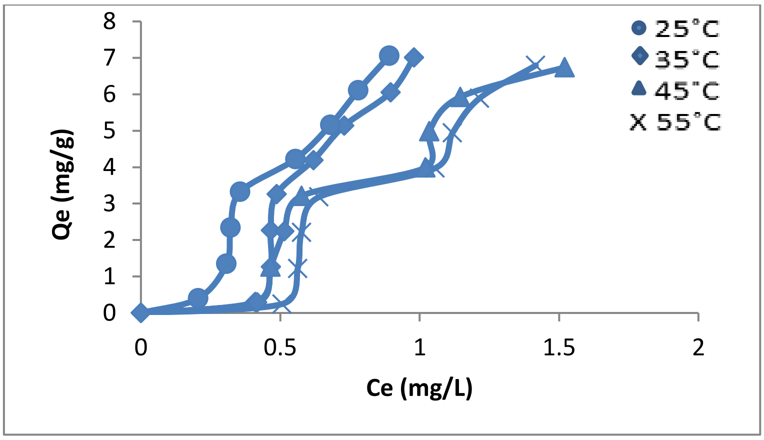
Table 3.1 Adsorption Values of Azure Dyes on Iraqi Porelanite Rocks at Different Temperatures

Temp.	**25˚C**			**35°C**		**45°C**		**55°C**	
Adsorbate	**Co (mg/L)**	**Ce (mg/L)**	**Qe (mg/g)**	**Ce (mg/L)**	**Qe (mg/g)**	**Ce (mg/L)**	**Qe (mg/g)**	**Ce (mg/L)**	**Qe (mg/g)**
Azure A	1	0.1657	0.4171	0.2826	0.3587	0.3623	0.3188	0.5000	0.2500
	3	0.2114	1.3943	0.3695	1.2971	0.4057	1.2971	0.5869	1.2065
	5	0.2921	2.3539	0.4057	2.2971	0.4347	2.2826	0.6376	2.1812
	7	0.3324	3.3338	0.5000	3.25	0.7101	3.1449	0.7391	3.1304
	9	0.6541	4.1729	0.7971	4.1014	0.8840	4.058	0.8260	4.087
	11	0.9786	5.0107	1.1159	4.9420	1.0217	4.9891	1.3985	4.8007
	13	1.1072	5.9464	1.1956	5.9022	1.1014	5.9493	1.4855	5.7572
	15	1.4329	6.7835	1.5726	6.7137	1.5000	6.7500	1.4927	6.7536
Azure B	1	0.2051	0.3974	0.4097	0.2951	0.4166	0.2917	0.5069	0.2465
	3	0.3072	1.3464	0.4652	1.2674	0.4652	1.2674	0.5625	1.2187
	5	0.3217	2.3391	0.4652	2.2674	0.5138	2.2431	0.5763	2.2118
	7	0.3566	3.3217	0.4861	3.2569	0.5763	3.2118	0.6388	3.1806
	9	0.5542	4.2229	0.6180	4.191	1.0208	3.9896	1.0555	3.9722
	11	0.6801	5.1599	0.7291	5.1354	1.0347	4.9826	1.1180	4.941
	13	0.7804	6.1098	0.8958	6.0521	1.1458	5.9271	1.2152	5.8924
	15	0.8915	7.0542	0.9791	7.0104	1.5208	6.7396	1.4166	6.7917
Azure C	1	0.1191	0.4404	0.5302	0.2349	0.5369	0.2315	0.2818	0.3591
	3	0.1988	1.4006	0.5637	1.2181	0.5906	1.2047	0.3825	1.3087
	5	0.2925	2.3537	0.6241	2.1879	0.5973	2.2013	0.4228	2.2886
	7	0.3254	3.3373	0.6778	3.1611	0.7583	3.1208	0.4362	3.2819
	9	0.5009	4.2495	0.7852	4.1074	0.9597	4.0201	0.4496	4.2752
	11	0.6527	5.1736	0.9798	5.0101	1.1275	4.9362	0.4630	5.2685
	13	0.7339	6.1330	1.2885	5.8557	1.1744	5.9128	0.5771	6.2114
	15	0.8216	7.0892	1.2214	6.8893	1.2617	6.8691	0.7516	7.1242

(a)



(b)



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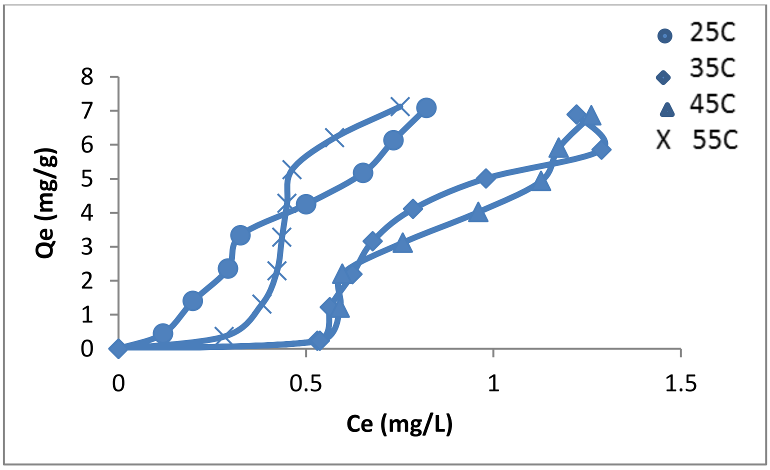


Figure 3.7 Adsorption Isotherm of Azure Dyes (a) Azure A, (b) Azure B and (c) Azure C Dyes on Iraqi Porcelanite Rocks at pH 6.9 at Different Temperatures

Table 3.2 Adsorption Values of Azure Dyes on PMFP at Different Temperatures

Temp.		**25°C**		**35°C**		**45°C**		**55°C**	
Adsorbat	**Co (mg/L)**	**Ce (mg/L)**	**Qe (mg/g)**	**Ce (mg/L)**	**Qe(mg/g)**	**Ce (mg/L)**	**Qe (mg/g)**	**Ce (mg/L)**	**Qe(mg/g)**
Azure A	1	0.1884	0.8116	0.3478	0.6522	0.4782	0.5218	0.9130	0.087
	3	0.3405	2.6595	0.7173	2.2827	0.6319	2.368	1.3254	1.6746
	5	0.6811	4.3189	1.0579	3.9421	0.7925	4.2075	1.5019	3.4981
	7	0.9855	6.0145	1.5144	5.4856	1.1351	5.8649	1.9270	5.073
	9	1.1449	7.8551	2.1014	6.8986	1.8936	7.1064	2.0595	6.9405
	11	1.1956	9.8044	2.1003	8.8997	2.0745	8.9255	2.8142	8.1858
	13	1.2391	11.7609	2.4057	10.5943	2.6137	10.3863	3.1537	9.8463
	15	1.5072	13.4928	2.8112	12.1888	3.0275	11.9725	3.4201	11.5799
Azure B	1	0.3125	0.6875	0.1805	0.8195	0.2777	0.7223	0.1805	0.8195
	3	0.7013	2.2987	0.2916	2.7084	0.3819	2.6181	0.3680	2.632
	5	0.7430	4.257	0.7361	4.2639	0.4166	4.5834	0.8402	4.1598
	7	1.1319	5.8681	0.8055	6.1945	0.9652	6.0348	1.0763	5.9237
	9	1.2291	7.7709	0.9513	8.0487	1.1944	7.8056	1.25	7.75
	11	1.3819	9.6181	1.0277	9.9723	1.6180	9.382	1.8125	9.1875
	13	1.5069	11.4931	1.1944	11.8056	1.9236	11.0764	2.1875	10.8125
	15	1.8194	13.1806	1.8750	13.125	2.1666	12.8334	2.7708	12.2292
Azure C	1	0.0067	0.9933	0.0671	0.9329	0.1543	0.8457	0.2147	0.7853
	3	0.0268	2.9732	0.0738	2.9262	0.3892	2.6108	0.5637	2.4363
	5	0.1744	4.8256	0.2013	4.7987	0.9194	4.0806	0.9463	4.0537
	7	0.2885	6.7115	0.3154	6.6846	1.4093	5.5907	1.1476	5.8524
	9	0.4301	8.5699	0.7114	8.2886	1.7181	7.2819	1.4563	7.5437
	11	0.6308	10.3692	0.9664	10.0336	1.8053	9.1947	1.6033	9.3967
	13	1.1140	11.886	1.1677	11.8323	1.8120	11.188	2.4161	10.5839
	15	1.2953	13.7047	1.5953	13.4027	2.2214	12.7786	3.1744	11.8256

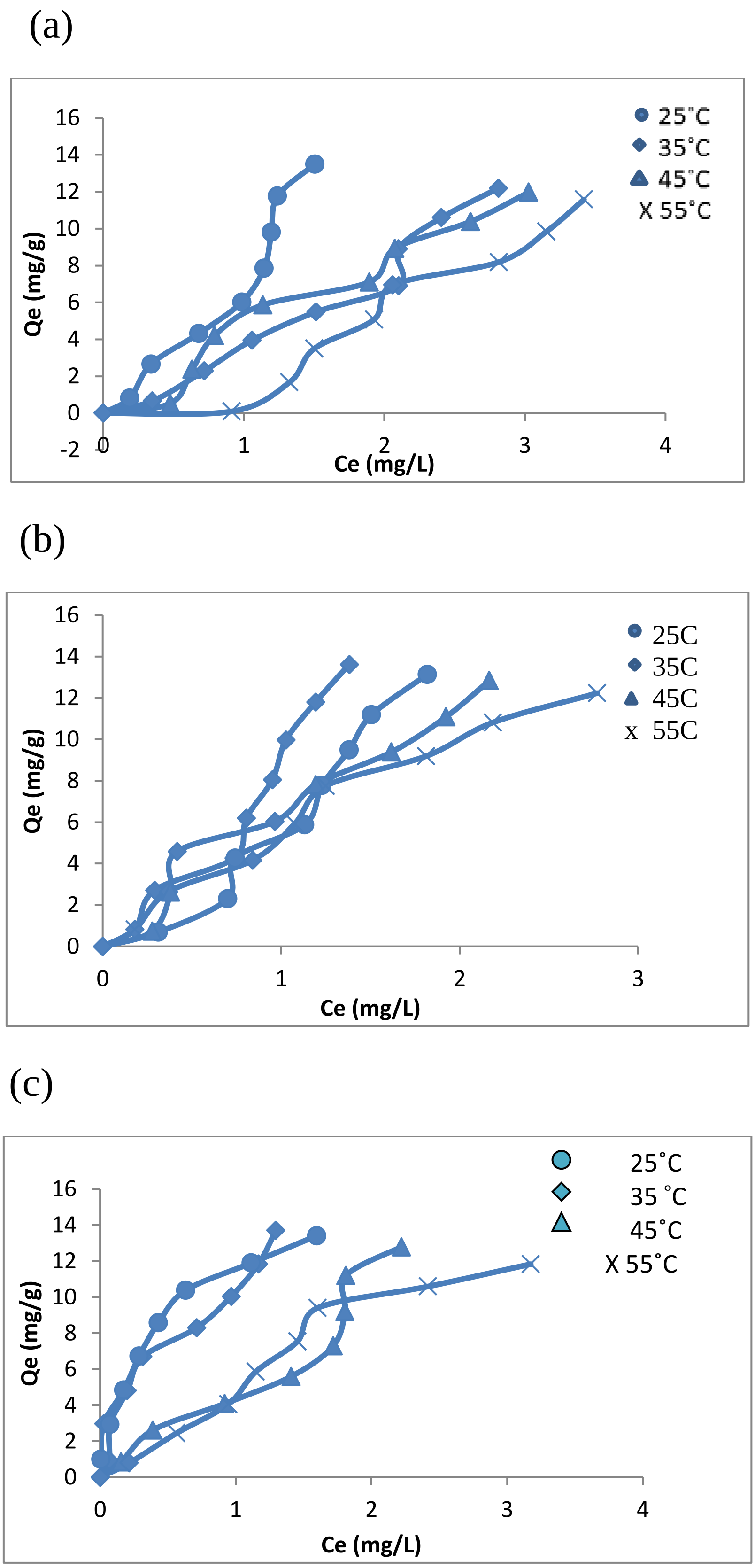


Figure 3.8 Adsorption Isotherm of Azure Dyes (a) Azure A, (b) Azure B and (c) Azure C Dyes on PMFP at pH 5.5 at Different Temperatures

3.2.3 Effect of Adsorbent Dose

Effect of adsorbent dose change on adsorption process of Azure dyes on(adsorbent) Porcelanite rocks without any purification from the quartz and PMFP was studied by using a fixed concentration of Azure dyes(7mg/L) and different weights of adsorbents (0.0125, 0.02, 0.03, 0.04, 0.05, 0.06 and 0.07)g of Iraqi Porcelanite rocks and (0.005, 0.007, 0.009, 0.0125, 0.03, 0.05 and 0.07)g of PMFP at 25˚C. Figure 3.9 and Table3.3demonstrate the influence of the adsorbent weight change on the adsorption quantity for Azure dyes. The percent of the adsorption increased with increasing adsorbent doses. The increase in the percent removal of dyes with the increase in adsorbents dosage is due to the availability of larger surface area with more active functional groups[68]. Initially the rate of increase in the percent dye removal has been found to be rapid which slowed down as the dose increased. This phenomenon can be explained , based on the fact that at lower adsorbent dose the adsorbate (dye) is more easily accessible and because of this , removal per unit weight of adsorbent is higher. With rise in adsorbent dose, there is less commonsurate increase in adsorption , resulting from many sites remaining unsaturated during the adsorption[68]. The result obtained indicate that the PMFP has a large potential as an Porcelanite for dye removal.

Table 3.3 Effect of Adsorbent Dose on Adsorption of Azure Dyes on(a) Iraqi Porelanite Rocks and (b)PMFP at 25°C

(a)

Adsorbate	**Wt. (g)**	**%Removal ($\frac{Co-Ce}{Co}\times 100$)**
Azure A	0.0125	92.75
	0.02	93.68
	0.03	94.47
	0.05	95.28
	0.06	95.37
	0.07	95.58
	0.09	95.61
Azure B	0.0125	91.82
	0.02	93.17
	0.03	94.69
	0.05	94.94
	0.06	95.01
	0.07	95.1
	0.09	95.15
Azure C	0.0125	92.13
	0.02	93.97
	0.03	95.01
	0.05	95.31
	0.06	95.37
	0.07	95.61
	0.09	95.67

(b)

Adsorbate	**Wt. (g)**	**%Removal ($\frac{Co-Ce}{Co}\times 100$)**
Azure A	0.005	94.07
	0.007	96.17
	0.009	98.72
	0.0125	99.81
	0.03	99.97
	0.04	99.79
	0.05	99.84
Azure B	0.005	94.43
	0.007	95.88
	0.009	97.51
	0.0125	99.69
	0.03	99.75
	0.04	99.56
	0.05	99.67
Azure C	0.005	93.42
	0.007	94.98
	0.009	96.77
	0.0125	98.56
	0.03	98.88
	0.04	98.46
	0.05	98.63

(a) ***(b)***

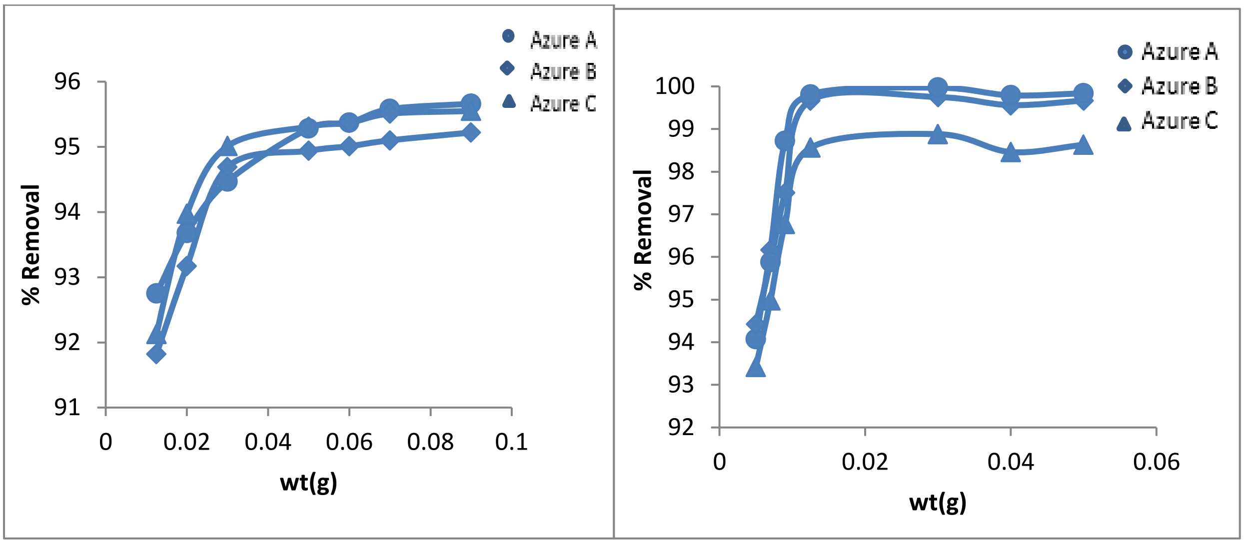


Figure 3.9 Effect of Adsorbent Dose on Adsorption of Azure Dyes on (a)Iraqi Porcelanite Rocks and (b) PMFP Surfaces at25 ̊C

3.2.4 Effect of pH

The adsorption of Azure dyes on Iraqi Porcelanite rocks and PMFP surfaces in a different media (pH= 2, 4, 5, 7, 9, 11 and 12) was studied by using affixed concentration of Azure dyes (7mg/L) at 25 ̊C. Figure 3.10 and Table3.4demonstrate the influence of pH on adsorption. The pH is the important factor which controls the adsorption process especially for Azure dyes[69].As elucidated in Figure 3.10, the dyes removal were minimum at pH 2 and the dyes adsorbed increased as the pH was increased from 2 to 6.9 for Porcelanite rocks and 2 to 5.5 for PMFP. Then, beyond pH 6.9 for Porcelanite rocks and 5.5 for PMFP there was no notable change.

For this reason, pH 6.9 for Porcelanite rocks and 5.5 for PMFP was selected for further experiments. After adsorption experiments, it was found that at low pH and at high pH , the dye become protonated, the electrostatic repulsion between the protonated dyes and positively charged adsorbent sites result in decreased adsorption. Higher adsorption at pH 6.9 for Porcelanite rocks and 5.5 for PMFP may be due to increased protonation by the neutralization of the negative charges at the surface of the adsorbent, that indicates the reactions of acid with the different oxides in the rocks, causing the decrease in the adsorption in the acidic media more than the basic media , which facilitates the diffusion process and provides more active sites for the adsorbent. Figure 3.10 shows that the adsorption of these positively charged dye groups on adsorbent surface is primarily influenced by the surface charge on the adsorbent which in turn is influenced by the solution pH. The result showed that availability of negative charge groups at the adsorbent surface is necessary for the adsorption of basic dyes to proceed which we see at pH=2 is almost unlikely as there is a net positive charge in the adsorption system due to the presence of H_3O^+. Therefore as the pH increased, more negatively charged on the surface was available thus facilitating greater dye removal. We see that the trend is increasing with increasing pH[69].

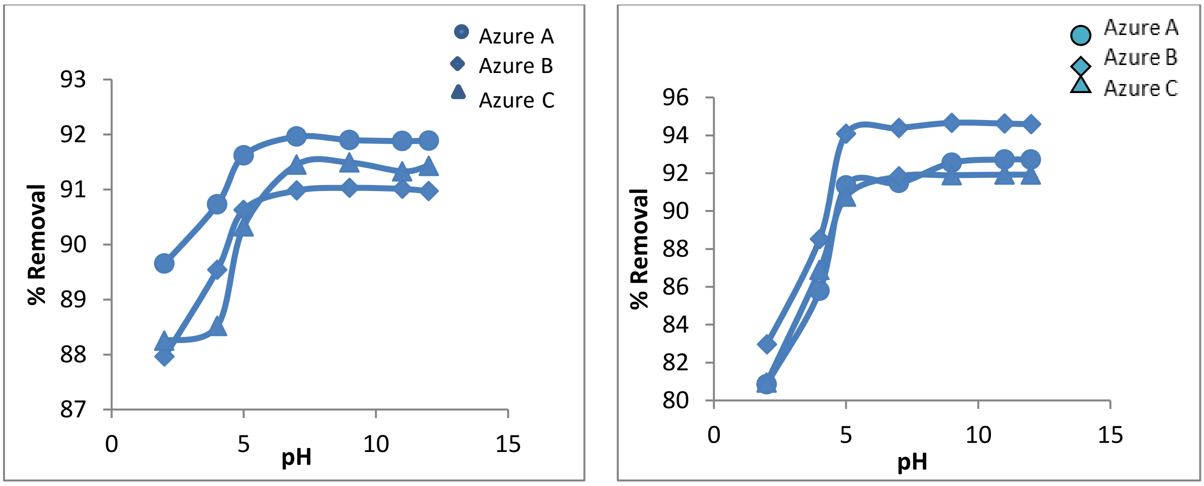
Table 3.4 Effect of pH on Adsorption of Azure Dyes on (a)Iraqi Porcelanite Rocks and (b)PMFP

(a)

Adsorbate	**pH**	**%Removal ($\frac{Co-Ce}{Co} \times {}^{100}$)**
Azure A	2	89.65
	4	90.73
	5	91.62
	7	91.96
	9	91.90
	11	91.88
	12	91.89
Azure B	2	87.96
	4	89.54
	5	90.63
	7	90.98
	9	91.03
	11	91.01
	12	90.97
Azure C	2	88.25
	4	88.52
	5	90.33
	7	91.45
	9	91.49
	11	91.33
	12	91.43

(b)

Adsorbate	pH	**%Removal** ($\frac{Co-Ce}{Co} \times 100$)
Azure A	2	80.58
	4	85.79
	5	91.35
	7	91.48
	9	92.55
	11	92.72
	12	92.71
Azure B	2	82.95
	4	88.52
	5	94.07
	7	94.38
	9	94.66
	11	94.62
	12	94.58
Azure C	2	80.94
	4	86.89
	5	90.76
	7	91.83
	9	91.89
	11	91.92
	12	91.92



(a) (b)

Figure 3.10 Effect of pH on adsorption of Azure dyes on(a)Iraqi Porcelanite rocks and (b) PMFP at 25°C .

3.2.5 Effect of Temperature

The effect of temperature on the adsorption extent of Azure dyes on Porcelanite rocks and PMFP was studied at different temperatures (25, 35, 45 and 55) °C. The results of this study are depicted in Figure 3.11 and Table 3.5.The results indicated an decrease in the amount of Azure dyes which is adsorbed on Porcelanite rocks or PMFP with increase of temperature; hence the adsorption process is appeared to be an exothermic in nature [52].

The study of temperature effect on adsorption of Azure dyes on Porcelanite rocks and PMFP surfaces would help in evaluating the basic thermodynamic functions, the Gibbs energy(ΔG), the enthalpy (ΔH) and the entropy (ΔS) of the adsorption process.

The change in Gibbs energy (ΔG) could be determined from the following equation [70,71].

$$\Delta G = -RT \ln K_{eq} \quad \ldots\ldots\ldots\ldots\ldots(3.1)$$

Where;

ΔG :is the Gibbs energy change (kJ.mol^{-1})

R : is the gas constant (8.314 J. mol^{-1}. K^{-1})

K_{eq}: is the thermodynamic equilibrium constant.

The thermodynamic equilibrium constant (K) for the adsorption process at each temperature was calculated from the equation [72]

$$K_{eq} = \frac{Qe\ m}{Ce\ V} \ldots\ldots\ldots\ldots\ldots(3.2)$$

Where:

m: is the weight of asorbents(0.05g of Porcelanite rocks and 0.03g of PMFP).

Table(3.5) gives K_{eq} values at different temperatures

The heat of adsorption (ΔH) may be obtained from Van't Hoff's equation [70,73] :

$Ln\ K_{eq} = -\Delta H/RT + constant$ ……………..(3.3)

Plotting (lnK_{eq}) versus (1/T) should produce a straight line with a slope =

(- ΔH/R) as shown in Figure 3.11

Table 3.5 Equilibrium Constant Values(a) Iraqi Porcelanite Rocks and (b) PMFP at Different Temperatures

(a)

Adsorbate	**Ln K_{eq}**	**T (K)**	**1/T (K^{-1})**
Azure A	2.2485	298.15	0.00335
	2.2031	308.15	0.00324
	2.1972	318.15	0.00314
	2.1449	328.15	0.00304
Azure B	2.7655	298.15	0.00335
	2.6648	308.15	0.00324
	2.2610	318.15	0.00314
	2.1824	328.15	0.00304
Azure C	2.9469	298.15	0.00335
	2.8500	308.15	0.00324
	2.4242	318.15	0.00314
	2.3890	328.15	0.00304

(b)

Adsorbate	**Ln K_{eq}**	**T (K)**	**1/T (K^{-1})**
Azure A	2.1966	298.15	0.00335
	1.8150	308.15	0.00324
	1.3751	318.15	0.00314
	1.2196	328.15	0.00304
Azure B	2.2893	298.15	0.00335
	1.9467	308.15	0.00324
	1.7804	318.15	0.00314
	1.4849	328.15	0.00304
Azure C	2.3605	298.15	0.00335
	2.1275	308.15	0.00324
	1.7502	318.15	0.00314
	1.3154	328.15	0.00304

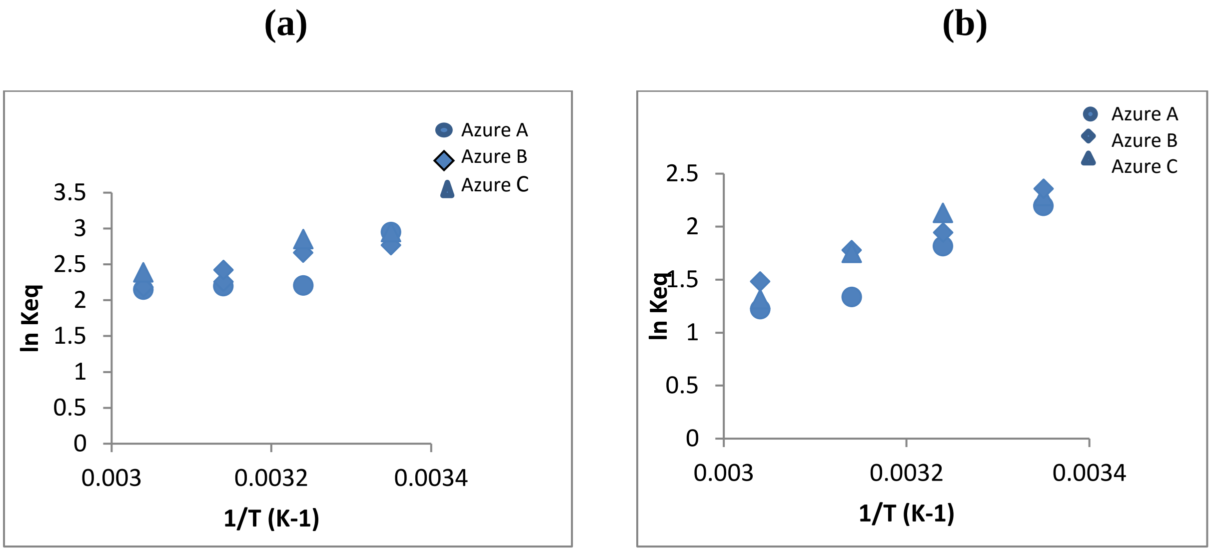


Figure 3.11 Plot of $\ln K_{eq}$ Versus 1/T of Azure Dyes on the Adsorbent Surfaces for (a) Porcelanite Rocks and (b) PMFP

The entropy change (ΔS) was calculated from Gibbs- Helmholtz equation[46]:

$\Delta G = \Delta H - T\Delta S$ ***………(3.3)***

Table 3.6 and 3.7 shows the thermodynamic functions ΔG,ΔH and ΔS and for the removal of Azure A,B and C by Iraqi porcelanite rocks and PMFP respectively at different temperatures.

Table 3.6 Thermodynamic Functions ∆G, ∆H and ∆S of Azure A, B and C Dyes on the Adsorbent Surface Iraqi Porcelanite Rocks at Different Temperatures

298.15 K			
Adsorbate	∆G (kJ/mol)	∆H (kJ/mol)	∆S (kJ/mol)
Azure A	-5.5736	-19.8288	0.0448
Azure B	-6.8552	-17.3288	0.0351
Azure C	-7.3048	-16.9048	0.0321
308.15 K			
Adsorbate	∆G (kJ/mol)	∆H (kJ/mol)	∆S (kJ/mol)
Azure A	-5.6443	-19.8288	0.0463
Azure B	-6.8271	-17.3288	0.0340
Azure C	-7.3016	-16.9048	0.0311
318.15 K			
Adsorbate	∆G (kJ/mol)	∆H (kJ/mol)	∆S (kJ/mol)
Azure A	-5.8118	-19.8288	0.0454
Azure B	-5.9806	-17.3288	0.0356
Azure C	-6.4123	-16.9048	0.0326
328.15 K			
Adsorbate	∆G (kJ/mol)	∆H (kJ/mol)	∆S (kJ/mol)
Azure A	-5.8518	-19.8288	0.0463
Azure B	-5.9541	-17.3288	0.0346
Azure C	-6.5178	-16.9048	0.0319

Table 3.7 Thermodynamic Function ΔG,ΔH and ΔS of Azure A, B and C Dyes on the Adsorbent Surface PMFP at Different Temperatures

298.15 K			
Adsorbate	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (kJ/mol)
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	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (kJ/mol)
Azure A	-4.6499	-27.5850	0.0744
Azure B	-4.9873	-20.8515	0.0520
Azure C	-5.4505	-28.2515	0.0745
318.15 K			
Adsorbate	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (kJ/mol)
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	ΔG (kJ/Mol)	ΔH (kJ/Mol)	ΔS (kJ/Mol)
Azure A	-3.3273	-27.5850	0.0739
Azure B	-4.0511	-20.8515	0.0511
Azure C	-3.5887	-28.2509	0.0751

The ΔG values are found to be negative at all tested temperatures (25- 55˚C), indicating that the adsorption of Azure A, B and C dyes on the adsorbent surfaces(Iraqi Porcelanite rocks and PMFP) are spontaneous and thermodynamically favorable. The negative values of apparent enthalpy change shows an exothermic physical adsorption favored by increased temperature[74],i.e., physisorption conducted with van der waals forces .The apparent entropy change values are almost constant over the temperature range.

The positive entropy characterize an increased disorder of the system due to the loss of water which surrounding the dye molecules at the sorption on the Iraqi Porcelanite rocks and PMFP. It can be suggested that the driving force for adsorption process is an entropy effect and the interaction of molecules caused random of the total system[75].

3.3 Adsorption isotherms

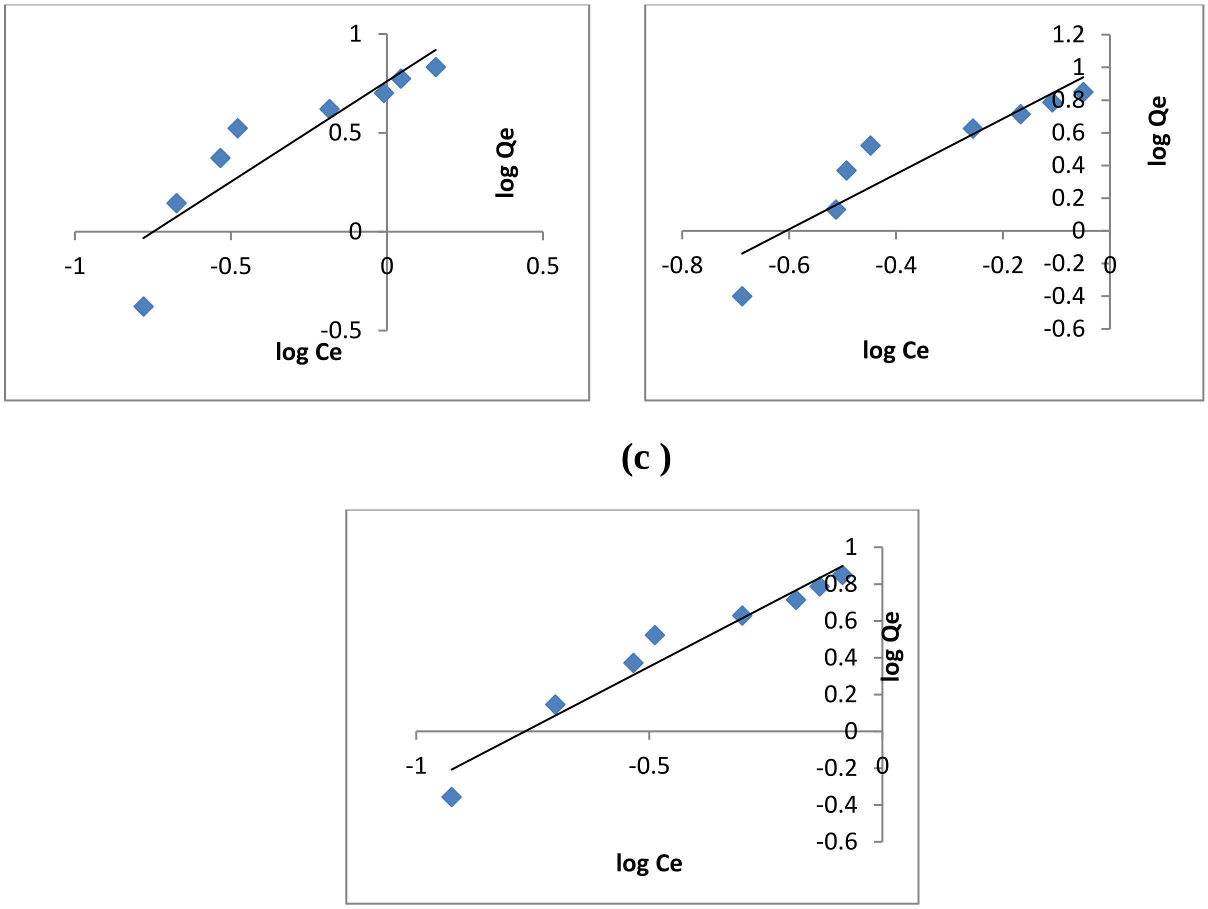
The experiment equilibrium adsorption data were analyzed using Freundlich and Langmuir adsorption isotherm models[43,45]:

3.3.1 Freundlich Adsorption Isotherm

Freundlich adsorption isotherm model used to explain the adsorption phenomenon is represented by equation(1.1).Linear plot of $\log Q_e$ versus $\log C_e$ shows that the adsorption of Azure A, B, and C dyes follows the Freundlich isotherm Figures3.12 , 3.13 and Tables 3.8, 3.9. The values of K_f and n were calculated from the intercept and slope of the plot. The magnitude of the exponent (n) gives an indication of the favourability and K_f the capacity of the adsorbent/adsorbate. The values of 1/n , less than unity represent favourable adsorption and values of $1/n>1$ indicate unfavourable adsorption. The results for Azure dyes adsorption systems of this study are favourable[76].

Table 3.8Freundlich Data of Adsorption of Azure Dyes on Iraqi Porcelanite Rocks at Different Temperatures

Temp.	**25˚C**		**35˚C**		**45˚C**		**55˚C**	
Adsorbate	**Log Ce**	**Log Qe**	**LogCe**	**Log Qe**	**Log Ce**	**Log Qe**	**Log Ce**	**Log Qe**
Azure A	-0.7806	-0.3797	-0.5488	-0.4452	-0.4409	-0.4964	-0.3010	-0.6020
	-0.6748	0.1443	-0.4323	0.1129	-0.3917	0.1129	-0.2314	0.0815
	-0.5344	0.3717	-0.3917	0.3611	-0.3618	0.3584	-0.1954	0.3386
	-0.4783	0.5229	-0.3010	0.5118	-0.1486	0.4976	-0.1312	0.4956
	-0.1843	0.6204	-0.0984	0.6129	-0.0535	0.6083	0.0830	0.6114
	-0.0093	0.6998	0.0476	0.6939	0.0093	0.6980	0.1456	0.6813
	0.0442	0.7742	0.0775	0.7710	0.0419	0.7744	0.1718	0.7602
	0.1562	0.8314	0.1966	0.8269	0.1760	0.8293	0.1739	0.8295
Azure B	-0.6880	-0.4007	-0.3875	-0.5300	-0.3802	-0.5350	-0.2950	-0.6080
	-0.5125	0.1291	-0.3323	0.1029	-0.3323	0.1029	-0.2498	0.0859
	-0.4925	0.3690	-0.3323	0.3555	-0.2892	0.3508	-0.2393	0.3447
	-0.4478	0.5213	-0.3132	0.5128	-0.2393	0.5067	-0.1946	0.5025
	-0.2563	0.6256	-0.2090	0.6223	0.0089	0.6009	0.0234	0.5990
	-0.1674	0.7126	-0.1372	0.7105	0.0148	0.6974	0.0484	0.6938
	-0.1076	0.7860	-0.0477	0.7819	0.0591	0.7728	0.0846	0.7702
	-0.0498	0.8484	-0.0091	0.8457	0.1820	0.8286	0.1512	0.831
Azure C	-0.9240	-0.3561	-0.2755	-0.6291	-0.2701	-0.6353	-0.5500	-0.4447
	-0.7015	0.1463	-0.2489	0.0857	-0.2287	0.0808	-0.4173	0.1168
	-0.5338	0.3717	-0.2047	0.3400	-0.2238	0.3426	-0.3738	0.3595
	-0.4875	0.5233	-0.1688	0.4998	-0.1201	0.4942	-0.3603	0.5161
	-0.3002	0.6283	-0.1050	0.6135	-0.0178	0.6042	-0.3471	0.6309
	-0.1852	0.7137	-0.0088	0.6998	0.0521	0.6933	-0.3344	0.7216
	-0.1343	0.7876	-0.1100	0.7675	0.0698	0.7717	-0.2387	0.7931
	-0.0853	0.8505	0.0868	0.8381	0.1009	0.8369	-0.1240	0.8527



(a)

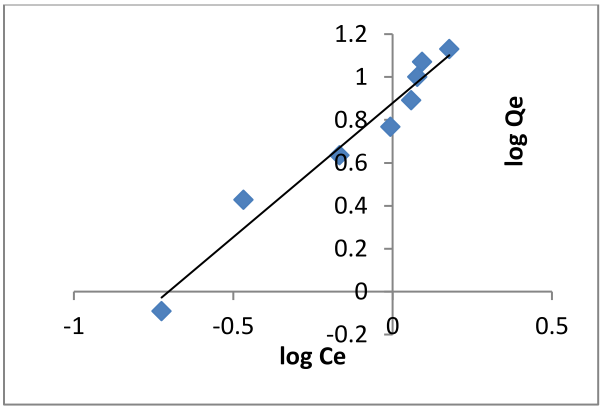
(b)

(c)

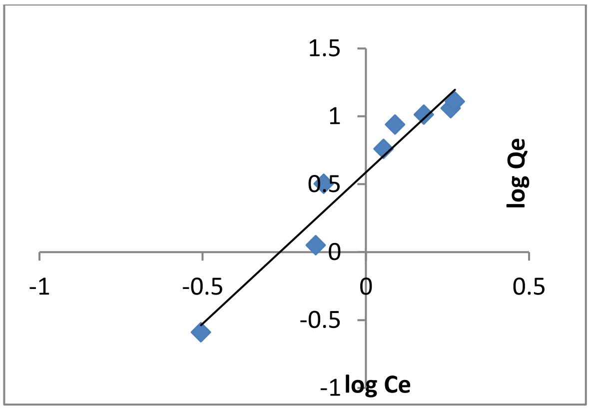
Figure 3.12Freundlich Isotherm of Adsorption of Azure Dyes on Iraqi Porcelanite Rocks at 25°C

Table 3.9Freundlich Data of Adsorption of Azure Dyes on PMFP at Different Temperatures

Temp.	**25˚C**		**35˚C**		**45˚C**		**55˚C**	
Adsorbate	**Log Ce**	**Log Qe**	**Log Ce**	**Log Qe**	**Log Ce**	**Log Qe**	**Log Ce**	**Log Qe**
Azure A	-0.7249	-0.0906	-0.4586	-0.1856	-0.3203	-0.2824	-0.0395	-1.0604
	-0.4678	0.4247	-0.1442	0.3584	-01993	0.3743	0.1223	0.2239
	-0.1667	0.6353	0.0244	0.5957	-0.1010	0.6240	0.1766	0.5438
	-0.0063	0.7791	0.1802	0.7392	0.0550	0.7682	0.2848	0.7052
	0.0587	0.8951	0.3225	0.8387	0.2772	0.8516	0.3137	0.8413
	0.0775	0.9914	0.3222	0.9493	0.3169	0.9506	0.4493	0.9130
	0.0931	1.0704	0.3812	1.0250	0.4172	1.0164	0.4988	0.9932
	0.1781	1.1301	0.4488	1.0859	0.4810	1.0781	0.5340	1.0637
Azure B	-0.5051	-0.1627	-0.7435	-0.0864	-0.5564	-0.1412	-0.7435	-0.0864
	-0.1540	0.3614	-0.5352	0.4327	-0.4180	0.4179	-0.4341	0.4202
	-0.1290	0.6291	-0.1330	0.6298	-0.3802	0.6611	-0.0756	0.6190
	0.0538	0.7684	-0.0939	0.7920	-0.0153	0.7806	0.0319	0.7725
	0.0895	0.8904	-0.0216	0.9057	0.0771	0.8924	0.0969	0.8893
	0.1404	0.9830	0.0118	0.9987	0.2089	0.9722	0.2582	0.9631
	0.1780	1.0604	0.0771	1.0720	0.2841	1.0443	0.3399	1.0339
	0.2599	1.1199	0.2730	1.1180	0.3357	1.1083	0.4426	1.0873
Azure C	-2.1739	-0.0029	-1.1732	-0.0301	-0.8116	-0.0727	-0.6681	-0.1049
	-1.5718	0.4732	-1.1319	0.4663	-0.4098	0.4167	-0.2489	0.3867
	-0.7584	0.6835	-0.6961	0.6811	-0.0364	0.6107	-0.0239	0.6078
	-0.5398	0.8268	-0.5011	0.8250	0.1490	0.7474	0.0597	0.7673
	-0.3664	0.9329	-0.1478	0.9184	0.2350	0.8622	0.1632	0.8775
	0.2001	1.0157	-0.0148	1.0014	0.2565	0.9635	0.2050	0.9729
	0.0468	1.0750	0.0673	1.0730	0.2581	1.0487	0.3831	1.0246
	0.1123	1.1368	0.2033	1.1271	0.3466	1.1064	0.5016	1.0728



(a)



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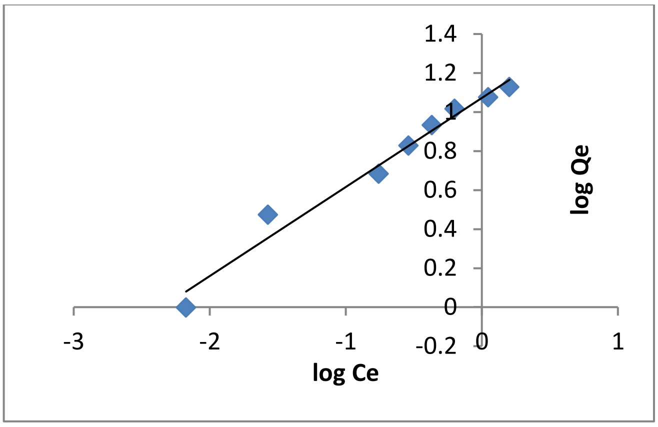

Figure 3.13 Freundlich Isotherm of Adsorption of Azure Dyes on PMFP at 25°C

3.3.2 Langmuir Adsorption Isotherm

The Langmuir isotherm is represented by the equation(1.6). The linear plots of C_e/Q_e versus C_e suggest the applicability of the Langmuir isotherms. The values of a and b were determined from slope and intercept of the plot shows in Figures 3.14, 3.15 and Tables3.10, 3.11. This isotherm is less fitting than Freundlich isotherm that means the results indicates multi-layers adsorption.

Table 3.10 Langmuir Data of Adsorption of Azure Dyes on Iraqi Porcelanite Rocks at Different Temperatures

Temp.	**25˚C**		**35˚C**		**45˚C**		**55˚C**	
Adsorbate	**Ce(mg/L)**	**Ce/Qe(g/L)**	**Ce(mg/L)**	**Ce/Qe(g/L)**	**Ce(mg/L)**	**Ce/Qe(g/L)**	**Ce(mg/L)**	**Ce/Qe(g/L)**
Azure A	0.1657	0.3972	0.2826	0.7878	0.3623	1.1364	0.5	2.000
	0.2114	0.1516	0.3695	0.2848	0.4057	0.3127	0.5869	0.4864
	0.2921	0.1240	0.4057	0.1766	0.4347	0.1904	0.6376	0.2923
	0.3324	0.0997	0.5	0.1538	0.7101	0.2257	0.7391	0.2361
	0.6541	0.1567	0.7971	0.1943	0.8840	0.2178	0.8260	0.2021
	0.9786	0.1953	1.1159	0.2257	1.0217	0.2047	1.3985	0.2913
	1.1072	0.1861	1.1956	0.2025	1.1014	0.1851	1.4855	0.2580
	1.4329	0.2112	1.5726	0.2342	1.5000	0.2222	1.4927	0.2210
Azure B	0.2051	0.5161	0.4097	1.3883	0.4166	1.4281	0.5069	2.0563
	0.3072	0.2281	0.4652	0.3670	0.4652	0.3670	0.5625	0.4615
	0.3217	0.1375	0.4652	0.2051	0.5138	0.2290	0.5763	0.2605
	0.3566	0.1073	0.4861	0.1492	0.5763	0.1794	0.6388	0.2008
	0.5542	0.1312	06180	0.1474	1.0208	0.2558	1.0555	0.2657
	0.6801	0.1318	0.7291	0.1419	1.0347	0.2076	1.1180	0.2262
	0.7804	0.1277	0.8958	0.1480	1.1458	0.1933	1.2152	0.2062
	0.8915	0.1263	0.9791	0.1396	1.5208	0.2256	1.4166	0.2085
Azure C	0.1191	0.2704	0.5302	2.2571	0.5369	2.3192	0.2818	0.7847
	0.1988	0.1419	0.5637	0.4627	0.5906	0.4902	0.3825	0.2922
	0.2925	0.1242	0.6241	0.2852	0.5973	0.2713	0.4228	0.1847
	0.3254	0.0975	0.6778	0.2144	0.7583	0.2429	0.4362	0.1329
	0.5009	0.1178	0.7852	0.1911	0.9597	0.2387	0.4496	0.1051
	0.6527	0.1261	0.9798	0.1955	1.1275	0.2384	0.4630	0.0878
	0.7339	0.1196	1.2885	0.2200	1.1744	0.1986	0.5771	0.0929
	0.8216	0.1158	1.2214	0.1772	1.2617	0.1836	0.7516	0.1054

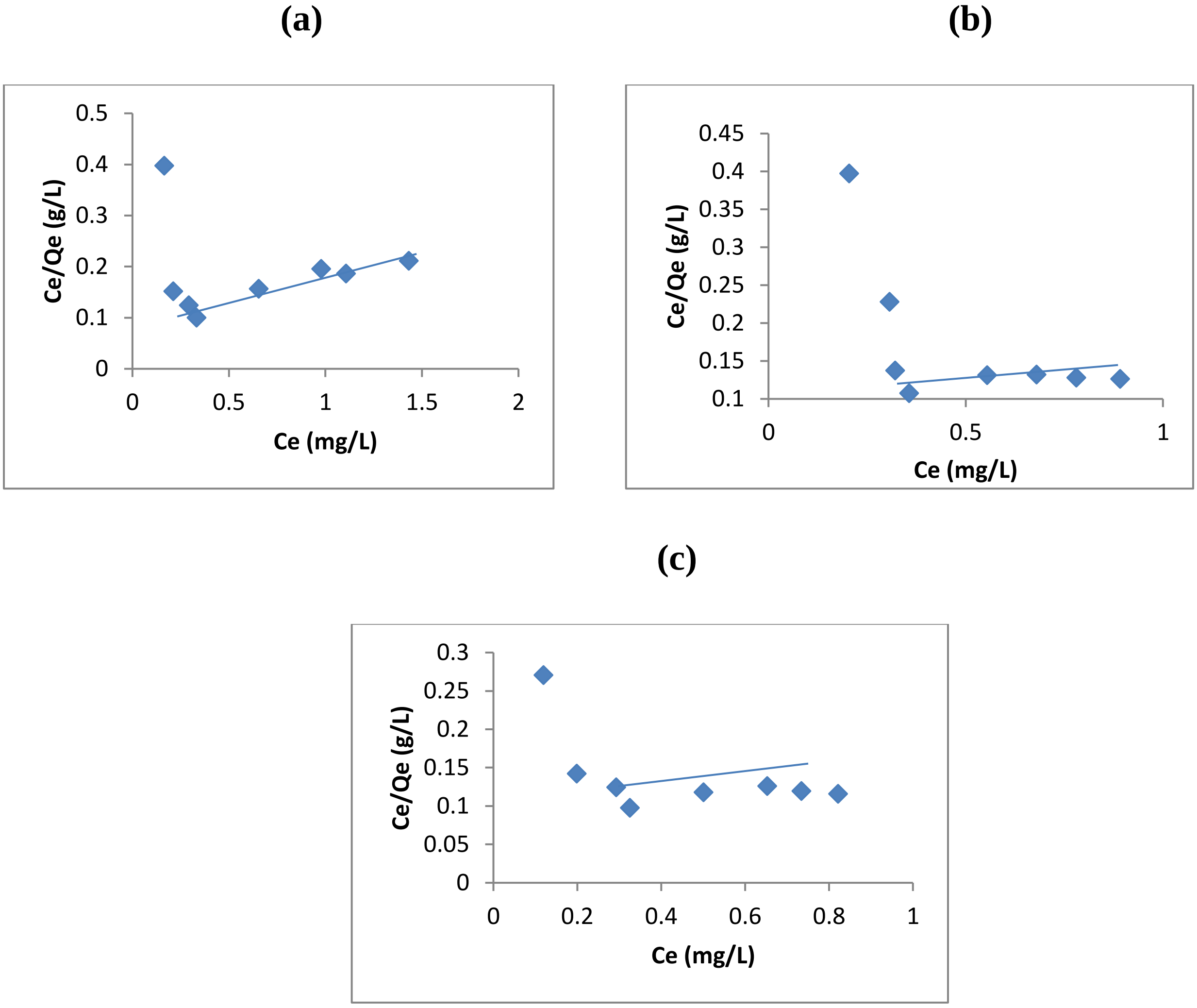

Figure 3.14 Langmuir Isotherm of Adsorption of Azure Dyes on Iraqi Porcelanite Rocks at 25°C

Table 3.11 Langmuir Data of Adsorption of Azure Dyes on PMFP at Different Temperatures

Temp.	**25°C**		**35°C**		**45°C**		**55°C**	
Adsorbate	**Ce(mg/L)**	**Ce/Qe(g/L)**	**Ce(mg/L)**	**Ce/Qe(g/L**	**Ce(mg/L)**	**Ce/Qe(g/L)**	**Ce(mg/L)**	**Ce/Qe(g/L)**
Azure A	0.1884	0.2321	0.3478	0.5332	0.4782	0.9164	0.9130	10.4942
	0.3405	0.1280	0.7173	0.3142	0.6319	0.2668	1.3254	0.7914
	0.6811	0.1577	1.0579	0.2683	0.7925	0.1883	1.5019	0.4293
	0.9855	0.1638	1.5144	0.2760	1.1351	0.2303	1.9270	0.3798
	1.1449	0.1457	2.1014	0.3046	1.8936	0.2664	2.0595	0.2967
	1.1956	0.1219	2.1003	0.2359	2.0745	0.2324	2.8142	0.3437
	1.2391	0.1053	2.4057	0.2270	2.6137	0.2516	3.1537	0.3202
	1.5072	0.1117	2.8112	0.2306	3.0275	0.2518	3.4201	0.2953
Azure B	0.3125	0.4545	0.1805	0.2202	0.2777	0.3844	0.1805	0.2202
	0.7013	0.3050	0.2916	0.1076	0.3819	0.1458	0.3680	0.1398
	0.7430	0.1745	0.7361	0.1726	0.4166	0.0908	0.8402	0.2019
	1.1319	0.1928	0.8055	0.1300	0.9652	0.1599	1.0763	0.1816
	1.2291	0.1581	0.9513	0.1181	1.1944	0.1530	1.25	0.1612
	1.3819	0.1436	1.0277	0.1030	1.6180	0.1724	1.8125	0.1972
	1.5069	0.1311	1.1944	0.1011	1.9236	0.1736	2.1875	0.2023
	1.8194	0.1380	1.8750	0.1428	2.1666	0.1688	2.7708	0.2256
Azure C	0.0067	0.0067	0.0671	0.0719	0.1543	0.1824	0.2147	0.2733
	0.0268	0.0090	0.0738	0.0252	0.3892	0.1490	0.5637	0.2313
	0.1744	0.0361	0.2013	0.0419	0.9194	0.2253	0.9463	0.2334
	0.2885	0.0429	0.3154	0.0471	1.4093	0.2520	1.1476	0.1960
	0.4301	0.0501	0.7114	0.0858	1.7181	0.2359	1.4563	0.1930
	0.6308	0.0608	0.9664	0.0963	1.8053	0.1963	1.6033	0.1706
	1.1140	0.0937	1.1677	0.0968	1.8120	0.1619	2.4161	0.2282
	1.2953	0.0945	1.5953	0.0746	2.2214	0.1738	3.1744	0.2684

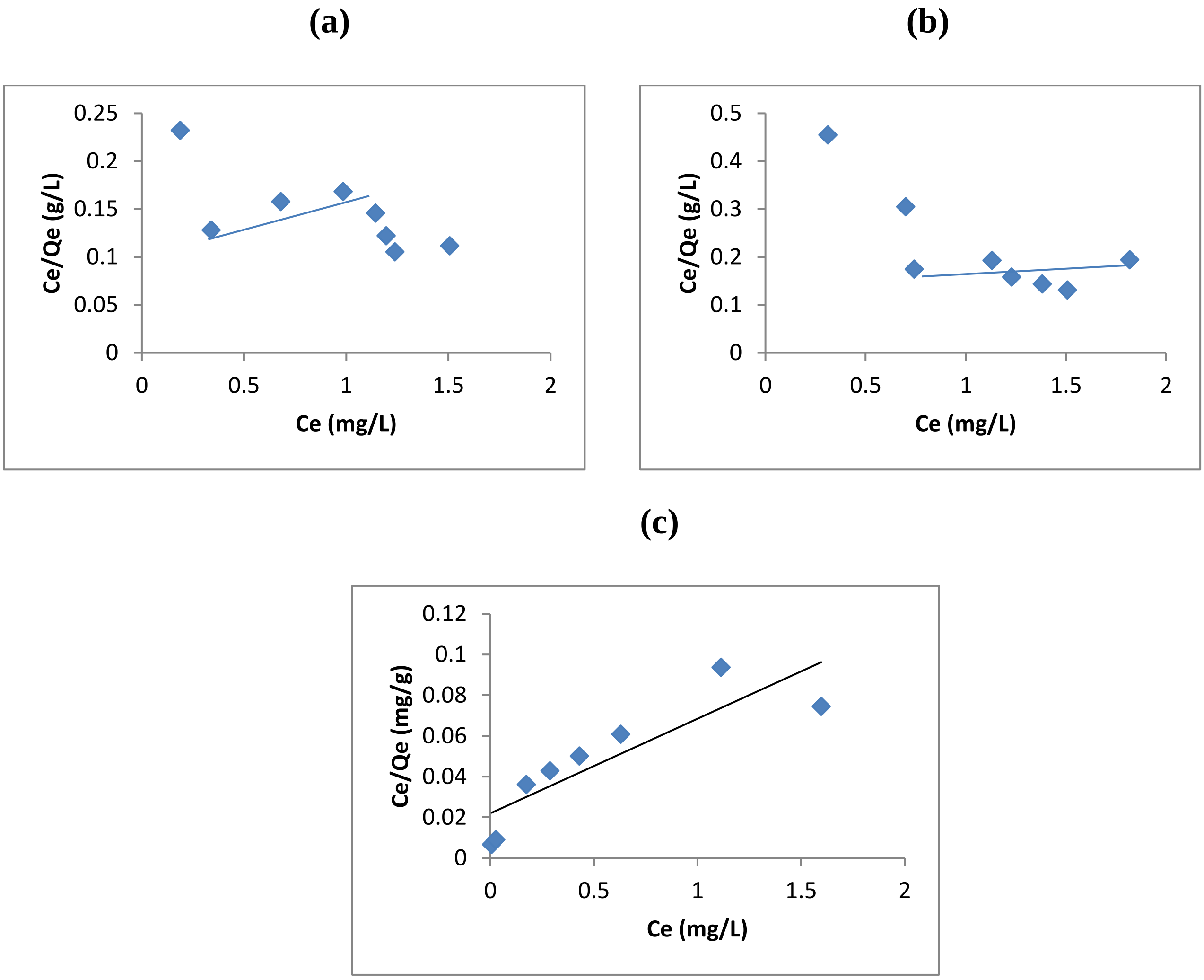

Figure 3.15 Langmuir Isotherm of Adsorption of Azure Dyes on PMFP at 25°C

The essential features of Langmuir isotherm can be expressed in terms of dimensionless constant separation factor (R_L)defined by Webber and Chakkravorti[77]can be represented as:

$$\mathbf{R_L = 1 / (1 + bCo)......(3.4)}$$

Lower value of R_L reflects that adsorption is more favourable. In a deeper explanation , R_L value indicates the adsorption nature to be either favourable ($0 < R_L < 1$), unfavourable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$)[78].

Table 3.12Langmuir and Freundlich Parameters of Adsorption Isotherms on Porcelanite Rocks 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	10.9409	1.0258	0.9053	0.1222	5.7655	0.9840	0.9024
Azure B	14.7928	0.5523	0.0278	0.2955	10.7374	0.5916	0.852
Azure C	26.4550	0.3791	0.2323	0.2736	10.0716	0.7584	0.9456
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	5.7636	0.4152	0.154	0.5244	4.7741	0.7304	0.7853
Azure B	1.0063	1.0319	0.2462	0.1729	9.9884	0.3848	0.6647
Azure C	0.8580	0.7917	0.2325	0.2201	4.6892	0.3783	0.6665
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	2.5451	0.6024	0.2343	0.3108	4.6676	0.5921	0.7734
Azure B	2.0242	0.6182	0.2166	0.1204	4.3171	0.5557	0.7123
Azure C	0.7249	0.7975	0.3019	0.2182	4.1619	0.3610	0.7334
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	15.7932	0.0543	0.2348	0.7245	3.2696	0.4901	0.7007
Azure B	1.1196	0.1196	0.244	0.1067	3.8627	0.4548	0.6777
Azure C	0.9140	1.4825	0.4194	0.1729	32.3072	0.3219	0.7994

Table 3.13 Langmuir and Freundlich Parameters of Adsorption Isotherms on PMFP 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	16.2866	0.1463	0.4342	0.8163	3.0012	0.7922	0.9804
Azure B	14.5137	0.3659	0.4442	0.6404	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	9.3109	0.2167	0.184	0.9334	3.2824	0.7407	0.8187
Azure B	36.3636	0.1297	0.0546	0.8577	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	0.4436	0.3472	0.3274	0.6989	2.4188	0.3208	0.7966
Azure B	70.9219	0.0815	0.186	0.3320	5.2771	0.0439	0.9695
Azure C	76.2307	0.0058	0.0012	0.9607	4.4812	0.9451	0.9708

The data obtained from the isotherm studies were tested for applicability to the above two isotherm models Table (3.12) and (3.13) show the values of the parameters of the two in isotherms and the related correlation coefficients the higher regression values showed that the equilibrium data for all three dyes studied here fitted well to the Freundlich isotherm in the studied concentration range. The Freundlich equation frequently gives adequate description of adsorption data over a restricted range of concentration. Apart from homogeneous surface, the Freundlich equation is also suitable for a multi – layer adsorption [79] . It was well known that the Langmuir equation is intended for a homogeneous surface and monolayer adsorption [80] . From Tables (3.12)and (3.13) it could be concluded that the Langmuir model give a poor fit to the sorption process when compared to the Freundlich model. That adsorption capacity of Azure B is match higher than other Azure dyes A and C. This difference most be related to higher affinity and modified form (PMFP) than Azure A and C also this may b due to tendency for the dye molecule to escape from the solute phase to the liquid phase of dye with decrease in temperature of solution.

Conclusions

The main object of the present work was to explore the possibility of using Iraqi porcelanite rocks Porcelanite – Melamine –Formaldehyde Polymer (PMFP) as adsorbents for the cationic dyes water pollutants.

The results demonstrated the possibility of using Porcelanite and PMFP for the removal Azure dyes A, B and C from water.

The Porcelaniterocks and PMFP were characterized by FT-IR, XRD spectroscopy and SEM technique.

The adsorption capacity of Azure dyes on the PMFP is high when compared with Porcelanite rocks.

The experimental data at four temperatures (25, 35, 45and 55 ˚C) for Porcelanite and PMFP for the removal of Azure dyes were fitted to the Langmuir and Freundlich isotherms models, and the shape of isotherms was (S-type) on Giles classification.

For Azure dyes adsorption the thermodynamic values of ΔG and ΔH are negative in two adsorbents; indicating that the process is spontaneous and exothermic. Positive values of ΔS in each of two adsorbents indicates an increase of disorder (decrease of order).

The effect of various operating parameters, such as contact time, pH, adsorbent dosage and temperature was estimated.

The thermodynamic functions are very useful if the present results are to be utilized on large scale industrial processes.

Publishing Papers

1. E.T. K. Al-Rubaeey and R.A. J. Al-Myali, (Thermodynamic Study of Adsorption of Azure Dyes on Iraqi Porcelanite Rocks), J. Natural and Sciences Research, Vol.3, No.15, PP: 68-79, 2013.
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الخلاصة :

تتضمن الرسالة دراسة امتزاز صبغات الأزور على سطوح صخور البورسلينات العراقية و شكلها المحور.تمت معاملة صخور البورسلينات العراقية مع الميلامين لتحضير معقد بورسلينات – ميلامين ثم تمت عملية البلمرة للمعقد مع الفورمالديهايد لتحضير بوليمر بورسلينات – ميلامين – فورمالديهايد. تم تشخيص صخور البورسلينات العراقية و شكلها المحور بأستخدام تقنيات الأشعة ما تحت الحمراء(FTIR) ,حيود الأشعة السينية (XRD) و تم تعيين المظهر الخارجي بأستخدام المجهر الألكتروني الماسح (SEM). الهدف في هذه الدراسة هو البحث عن سطوح لها قابلية امتزاز عالية لأمتزاز صبغات الأزور وبذلك تكون مهمة للاستعمال في تنقية المياه الملوثة. أجريت التجارب للتحقق من إمكانية استخدام صخور البورسلينات العراقية و شكلها المحور لإزالة صبغات الأزور من محاليلها المائية. تم استخدام تقنية مطيافية الأشعة فوق البنفسجية لدراسة ايزوثيرمات الأمتزاز و العوامل المؤثرة عليها : زمن التماس, وزن السطح الماز, الدالة الحامضية ودرجة الحرارة. النتائج بينت ان الاتزان يحصل عند 60 دقيقة و0,05 غم من وزن السطح الماز ودالة حامضية 6,9 بالنسبة لصخور البورسلينات العراقية بينما 30 دقيقة و 0,03 غم من وزن السطح الماز ودالة حامضية 5,5 بالنسبة للشكل المحور للبورسلينات. تمت دراسة ازالة صبغات الازوربأستخدام صخور البورسلينات العراقية و شكلها المحور كسطوح مازة بدرجات حرارية مختلفة (318.15,308.15,298.15 و328.15) كلفن لتعيين ايزوثيرمات الأمتزاز و الدوال الثرموديناميكية.

تم تحليل نتائج ايزوثيرمات الأمتزاز بأستخدام ايزوثيرمات فريندلش و لانكماير. عامل الفصل المحسوب كانت قيمته اقل من واحد مما يدل على ان امتزاز صبغات الازور على كلا السطحين مفضل ديناميكيا. وتبين ان النتائج تنطبق مع ايزوثيرم فريندلش للامتزاز. وأشكال الايزوثيرمات للصبغات الثلاثة تأخذ شكل حرف Sطبقا لتصنيف جيلز. أيضا تم التحليل الثرموديناميكي لنظام الصبغات الثلاثة – السطح الماز و تم حساب قيم الثوابت الثرموديناميكية وهي التغير في طاقة جبس والتغير في الانثالبي والتغير في الانتروبي ومنه تبين إن عملية امتزاز صبغات الازور على سطوح البورسلينات العراقية و شكلها المحور هي عملية تلقائية ,باعثة للحرارة من قيم التغير في طاقة جبس الانثالبي السالبة . قيم التغير في الانتروبي مع درجة الحرارة يدل على زيادة اللانظام تحت تأثير الانتروبي. تمت المقارنة بين أفضلية استخدام كلا السطحين لأمتزاز صبغات الازور وقد وجد إن قابلية امتزاز صبغات الازور على الشكل المحور لصخور البورسلينات كانت أعلى من صخور البورسلينات العراقية.

جمهورية العراق

وزارة التعليم العالي و البحث العلمي

جامعة كربلاء

كليه العلوم

قسم الكيمياء

أزالة صبغات الازور بأستخدام صخور البورسلينات العراقية و شكلها المحور(متعدد البورسلينات – ميلامين – فورمالديهايد)

رسالة مقدمة إلى

مجلس كلية العلوم – جامعة كربلاء

وهي جزء من متطلبات نيل درجة الماجستير في علوم الكيمياء

من قبل

رسل عزيز جعفر الميالي

بكالوريوس علوم كيمياء - 2011 - جامعة كربلاء

بأشراف

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