Removal of P- nitrophenol From Aqueous Solution Using Egg Shell Powder As a very Low Cost Adsorbent

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Abstract

This work deals the removal of p-nitrophenol (PNP) from its aqueous solutions using hens egg shell powder as a very low cost adsorbent. Adsorption experiments carried out by varying the process parameters like contact time, effect of pH, adsorbent dose, initial concentration of adsorbate, particle size and effect of temperature on removal percentage of PNP have been studied. The data of equilibrium adsorption were interpreted using Freundlich, Langmuir, and Temkin models. The adsorption of PNP was best represented according to the Langmuir model.

Key Words: Adsorption, PNP, egg shells, Langmuir model, Freundlich model, Temkin model.

الخلاصة

يتناول هذا البحث إزالة البارانيتروفينول من المحاليل المائية وذلك باستخدام مسحوق قشور بيض الدجاج كمادة مازة رخيصة جدا. أجريت تجارب الامتزاز بدراسة تأثير بعض العوامل على عملية الامتزاز مثل زمن الاتصال، وتأثير درجة الحموضة، جرعة المادة المازة، الحجم الحبيبي، تركيز المادة الممتزة وتأثير درجة الحرارة على النسبة المئوية للإزالة. ان نتائج الامتزاز تم تطبيقها على كل من معادلة فرندلش، لانكماير وتمكن الايسوثرمية ووجد ان نتائج الامتزاز تطيع بصورة جيدة معادلة لانكماير.

الكلمات المفتاحية: الامتزاز، بارانيتروفينول، قشور البيض، موديل لانكماير، موديل فرندلش، موديل تمكن.

Introduction

Aromatic nitrocompounds are widely used as insecticides, herbicides, fungicides, and explosives. Nitrophenols can accumulate in the soil as a result of the decomposition of several organophosphorous insecticides, such as parathion, or from the use of herbicide nitrophenols (Douglas, 1976). These are carcinogenic and toxic in nature, and thus found on the priority list of pollutants for the Environmental Protection Agency of the United States of America (EPA). They pose a threat to plant and animal life in the biosphere, and thus, it is necessary to eliminate these compounds from liquid wastes before getting rid of surface water (Arinjay *et al.* 2007). These compounds are found not only in industrial effluents but also in ambient freshwater in marine biologist (Lypczynska-Kochany, 1992) (El Mhammedi *et al.* 2009). These contamination factors affect the natural and human environment directly through the creation of conditions that limit the use of water for a particular purpose. Where possible, for pollutants that degrade in water, indicators documenting the effects of deterioration of water determines the water quality. The indicators include deterioration of water quality chemical and physical and biological parameters. Examples of chemical and physical factors involve pH, turbidity and temperature. Examples of biological factors involve the diversity and abundance of species. There are different methods to purify water eliminate pollution including adsorption, filtration, precipitation, coagulation, membrane separation and oxidation by using a strong oxidizing agent such as ozone (Ozacar, *et al.*, 2003)

Adsorption technique is used to achieve many of separation methods especially those that cannot be made according to traditional methods such as distillation and absorption methods. The most important applications of adsorption are the purification and treatment of water especially that are used in industrial processes (Ahmed, 2008).

Egg shell has large porous structure, therefore it has been selected as a good adsorbent (Tsai *et al.,* 2008). The chemical composition (weight %) of hens egg shell consists of calcium carbonate (96.48), Sulfur (2.31), magnesium (0.404), Phosphorus (0.501) and Strontium (0.073) (Arunlertaree *et al.* 2007). In addition, egg shell contains great ratios of amino acids and minerals (Tsai *et al.*, 2006). So the treated or untreated egg shells have many applications in bioremediation areas, therapeutic or metallurgy (Pundir *et al.*, 2009). Due to the high nutrition contents for egg shell like magnesium, calcium and phosphorus it may as well be used as a soil conditioner or fertilizer (Tacon, 1982). There are several distinguishing properties of egg shell such as great porosity, anti-inflammatory and antibacterial properties. (Arami *et al.*, 2006; Tembe *et al.,* 2008; Pundir *et al.,* 2009). In addition in last few years the egg shell used as low cost adsorbents has slightly increased.

The aim of this work is to achieve the capability of hen eggshell wastes as inexpensive and environment-friendly adsorbent for the removal of para-nitrophenol (PNP) from waste water in different conditions.

Materials and methods

Preparation of Eggshell Powder

Hens' egg shells were collected, washed by distilled water many times then dried in the oven at 105 C° for 2 hours to remove moisture (Norzita N., et al. 2013). The dried egg shells were grinded and sieved to (53 - 500) μm particles size that were kept in closed containers to be used later as an adsorbent.

Preparation of adsorbate

The pure crystalline *p*-nitrophenol (PNP) used in the adsorption studies was dissolved in a hot deionized water to prepare a stock solution (100 mg/L), and then a series of diluted solutions were prepared from a stock solution in suitable concentrations from 10 into 50 (mg/L), Which was used throughout the experimental work. The maximum absorbance wave length of (PNP) was (317 nm) where it is measured using optima UV- visible spectrophotometer.

Adsorption procedure

For each experimental run, 0.2 g of Hens' eggs shells powder (53) μm particle size was taken, put in a conical flask then 25 mL of (PNP) aqueous solution (25 mg/L) concentration is added and the flask is tightly closed. These flasks were shaken at 200 rpm at room temperature for a predetermined contact time of (50) min . After that, centrifuged at 3000 rpm for 10 minutes. The pH of solutions in all adsorption processes was (5-6). The p-nitrophenol concentration in the aqueous phase was determined spectrophotometrically by a UV spectrophotometer at 317 nm. the removal percentage of (PNP) was calculated by the following equation :

$$R\% = \frac{C_o - C_e}{C_o} \times 100 \qquad \ldots\ldots\ldots\ldots\ldots (1)$$

Where C_0 (mg/L) the initial concentration and C_e (mg/L) the equilibrium concentration of (PNP).

Results and Discussion

Effect of initial concentration

For this fulfillment, 25 mL of different initial concentrations of (PNP) solution is treated with 0.2 g of egg shells powder. The results obtained in this fulfillment are shown in Figure (1). "The effect of the initial of adsorbed concentration factor depends on the relationship between the concentration of the adsorbed and the binding sites available on surface of the adsorbent" (Bharathi *et al.,* 2013; Salleh *et al.,* 2011).

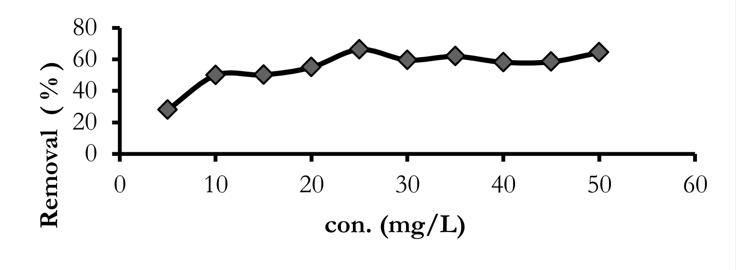

Figure (1): effect of initial concentration on the removal percentage of PNP by egg shells at (25±2 C°) temperature.

Effect of adsorbent dosage

Figure (2) shows the results obtained from this investigation, The removal percentage of PNP increases until it reaches a certain extent and then decreases and stays constant. This increase in the removal percentage with increase amounts of adsorbent may be due to the availability of more effective sites of adsorption due to increased surface area. The decrease of adsorption with increasing the amounts of adsorbent can be attributed to unsaturated absorption sites residual through adsorption procedure (Sathishkumar *et al.,* 2012 ; Thinakaran *et al.,* 2008).

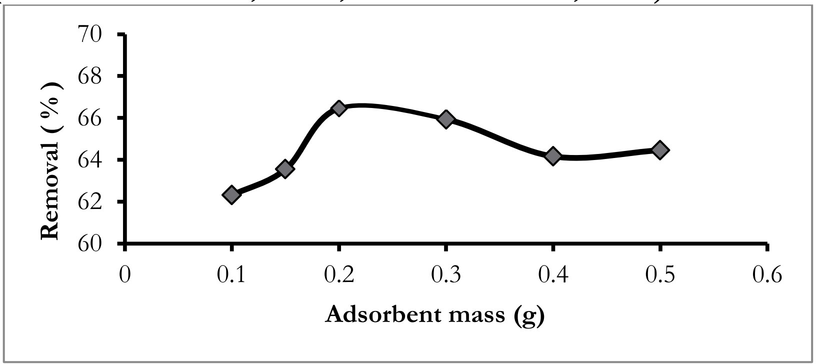

Figure (2) : effect of adsorbent dosage on removal percentage of PNP by egg shells at (25±2 C°) temperature.

Equilibrium contact time

The removal of (PNP) was investigated at time intervals of 5, 10, 20, 30, into 80 minutes from initial time. Results showed that the removal percentage increased with passage time, and reached equilibrium point at (50 min). Figure (3) shows the equilibrium contact time of adsorption.

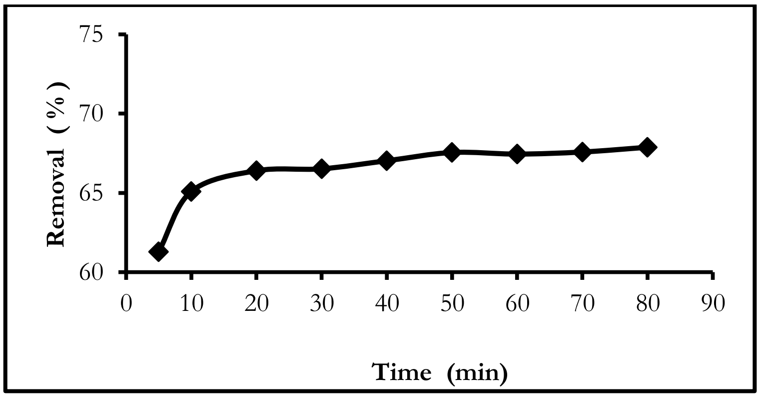

Figure (3): Effect of equilibrium contact time on the removal percentage of PNP by egg shells at (25±2 Cº) temperature

Effect of pH on adsorption

studied The effect of pH solutions on the removal percentage of PNP from aqueous solutions with range of pH (3-9). Natural pH of (PNP) was (5.5). Using 0.1M of (NaOH and HCl) solutions to adjust pH solutions. Figure (4) showed the effect of pH on percentage removal of (PNP).It can be noted that the percentage removal of (PNP) slightly increased with pH increase. This Behavior can be due to the effect of pH solution on the charge of functional group of egg shell, and thus become more effective to adsorption in alkaline pH. The egg shell consisting of protein and polysaccharides containing functional groups like, amine, hydroxyl and sulfonic groups (depending on the aqueous solution pH) can interaction with the adsorbate (Dhuha *et al.,* 2012). In addition, the adsorbate charges may be changed with solution pH.

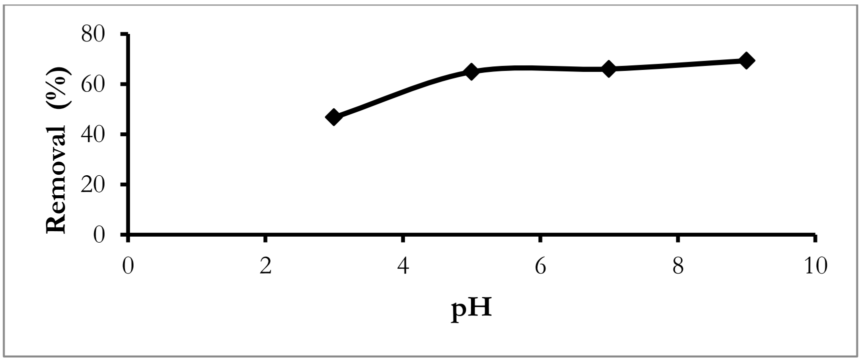

Figure (4): effect of solution pH on removal percentage of PNP by egg shells at (25±2Cº) temperature

Effect of particle size

The adsorption of (PNP) was investigated by using a fixed mass of egg shells by varying the particle size range of (53-300) µm at a room temperature. Figure (5) clarifies that the percentage removal of (PNP) decreases with increased the particle size of egg shells powder from (53 into 300) µm, This is attributed to increasing the activated sites as a result of increasing the surface area of adsorbent with decreasing the particle size.

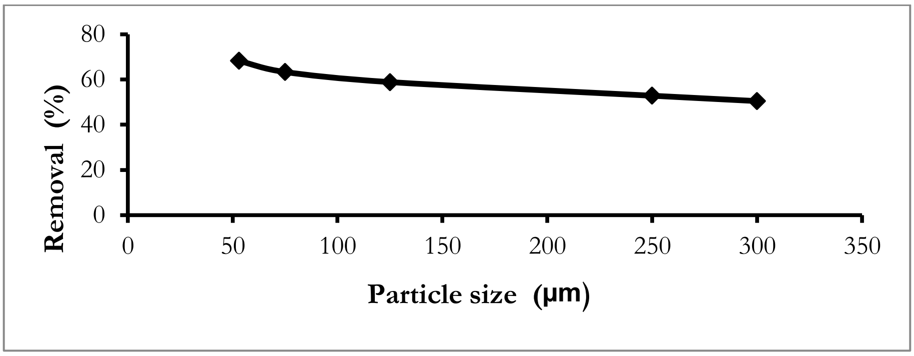

Figure (5): effect of particle size of egg shells powder on removal percentage of PNP by egg shells at (25±2 C°) temperature

Adsorption Isotherm

The adsorption isotherm of PNP was conducted by combining 0.2 g of Hens egg shells with 25 mL of a range of concentrations from (5-50) mg/L of (PNP) solution whose initial pH value is about 5.5 in conical flasks. The flasks were shaken at different temperatures. After centrifuged the Residual PNP concentration was determined As previously reported. The PNP uptake on the egg shells was determined by the following equation:

$$Q_e = \frac{(C_o - C_e)\, V_{(L)}}{m} \qquad \ldots\ldots\ldots\ldots\ldots \ (2)$$

Where: Q_e (mg/g) is the (PNP) uptake at equilibrium, C_o (mg/L) the initial concentration, C_e (mg/L) the equilibrium concentration of PNP, m (g) is the amount of adsorbent and V (L) is the volume of adsorbed solution.

The adsorption isotherm is significant to characterize nature of interaction between the adsorbent and the adsorbed, and gives a notion about the adsorption ability of the adsorbent. As well as can considered the surface phase as a multilayer or monolayer (Bharathi K. S. et ai. 2013; Salleh et al. 2011). There are many adsorption models of isotherm; Freundlich, Langmuir and Temkin models. Figure (6) shows adsorption isotherms at different temperatures.

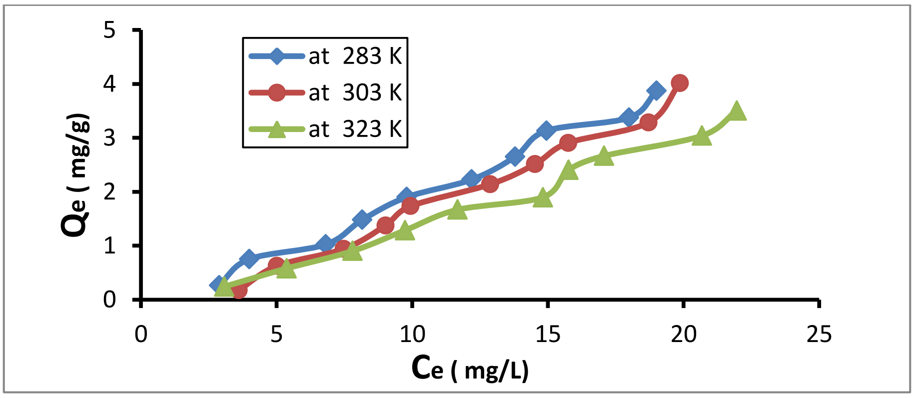

Figure (6): Adsorption isotherm models at different temperatures.

Models of isotherm

Langmuir isotherm model

This model is supposed to be monolayer adsorption and it occurs on a surface which contains a specific homogenous sites of the adsorbent, by supposing that a limited number of effective sites of adsorption is available (Langmuir, 1918). The Langmuir equation has the following general form:

$$q_e = \frac{Q_o\, K_L\, C_e}{1+ K_L\, C_e} \qquad \dots\dots\dots\dots\dots\; (3)$$

The linear form of Langmuir equation is :

$$\frac{1}{q_e} = \frac{1}{Q_o} + \frac{1}{Q_o K_L C_e} \qquad \dots\dots\dots\dots\dots\dots\; (4)$$

Where: q_e (mg/g) is the (PNP) uptake at equilibrium, Q_o(mg/g) is the maximum capacity of monolayer adsorption, C_e (mg/L) the equilibrium concentration of adsorbate, and K_L (L/mg) is constant the Langmuir isotherm.
The slope and intercept from a plot of $1/q_e$ versus $1/C_e$ in equation (4) determines K_L and Q_o values (Langmuir, 1918).

Freundlich isotherm model

This model is supposed multilayer adsorption and it occurs on heterogeneous surface. And adsorption capacity depends on the initial concentration of adsorbed at equilibrium. The equation of Freundlich is an empirical equation that is very valuable as it minutely depicts much adsorption data (Freundlich 1906). This equation is given as:

$$Q_e = K_f C_e^{1/n} \qquad \dots\dots\dots\; (5)$$

The linear form of the equation (5) is written as:

$$\log Q_e = \log K_{f\, +\, 1/n} \log C_e \qquad \dots\dots\dots\dots\; (6)$$

Where Q_e(mg/g) is the (PNP) uptake at equilibrium, C_e (mg/L) the equilibrium concentration of adsorbate, K_f (mg/g) (is an approximate indicator of adsorption capacity) is a constant of Freundlich isotherm and n is the adsorption intensity

The intercept and slope from a plot of log Q_e versus log C_e in equation (6) determines K_f and n values. The extent of slope between zero and one is a scale of adsorption intensity. If value of 1/n is lower than 1 this refers to a natural adsorption, Whenever this value is close to zero it is becoming more heterogeneous. where 1/n being above one indicates cooperative adsorption (Mohan *et al,* 1997; Haghseresht *et al.* 1998).

Temkin Isotherm model

"This model supposes that heat of adsorption of all molecules in the layer would decrease linearly rather than logarithmic with coverage" (Temkin M., 1940; Abdelwahab, N.A. et al., 2014). It is attributed to adsorbate-adsorbent interactions, and the adsorption is Featuring a regular allocation of the energies, even some extreme energy. This equation can be written as:

$$q_e = \frac{RT}{b} \ln(K_T C_e) \quad \ldots\ldots\ldots\ldots (7)$$

$$q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e \quad \ldots\ldots\ldots\ldots\ldots (8)$$

$$B = \frac{RT}{b} \quad \ldots\ldots\ldots\ldots\ldots\ldots (9)$$

$$q_e = B \ln K_T + B \ln C_e \quad \ldots\ldots\ldots.. (10)$$

Where: K_T (L/g) is the Temkin isotherm equilibrium binding constant, B (J/mol) is Constant (affined heat of adsorption), T is the absolute temperature in Kelvin and R is the gas constant (8.314 J/mol/K). The values of B and K_T can be calculated from the slope and intercept of the plot of q_e versus ln C_e

All data of the adsorption isotherm models are illustrated in table (1). The correlation coefficient values were higher for Langmuir than the other correlations. This shows that the Langmuir model is clearly the best fitting isotherm to the empirical data. Figure (7) below showed the plots of the linearized equation isotherm parameters for PNP removal at different temperatures.

Table (1): Langmuir, Freundlich and Temkin Isotherm parameters for the adsorption of PNP onto egg shells powder at different temperatures.

Isotherm models	*Parameters*	*Temperature*		
		283 K	*303 K*	*323 K*
Langmuir	Q_o (mg/g)	68.493	4.133	7.955
	K_L (L/mg)	0.0027	0.026	0.012
	R^2	0.9975	0.9966	0.9861
Freundlich	K_f (mg/g)	0.167	0.067	0.088
	1/n	1.061	1.373	1.141
	n	0.942	0.728	0.876
	R^2	0.9931	0.9856	0.9635
Temkin	K_T (L/mg)	0.315	0.229	0.234
	B (J/mole)	1.955	2.353	1.736
	R^2	0.913	0.867	0.852

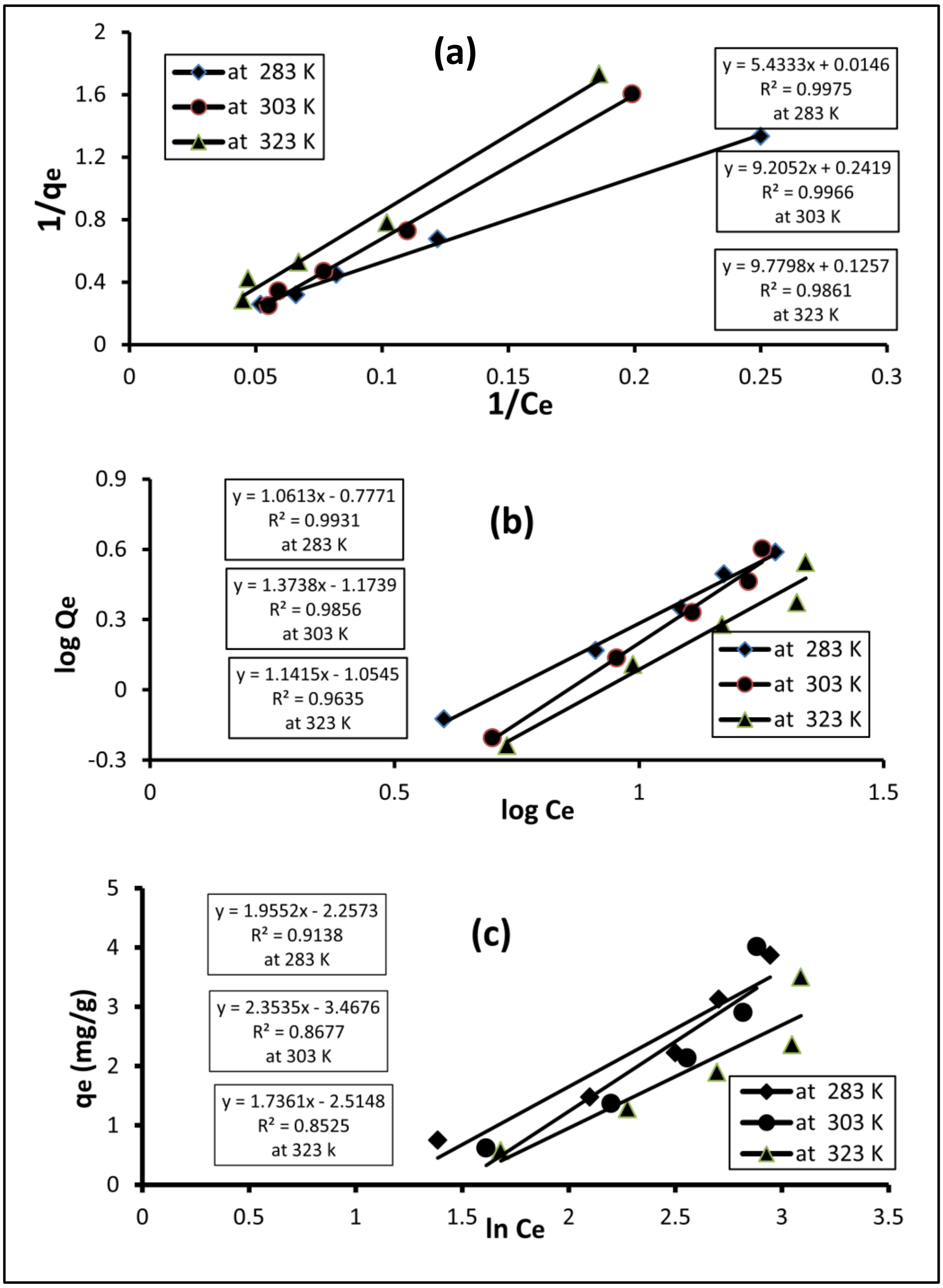

Figure (7): Plots of (a) Langmuir, (b) Freundlich and (c) Temkin isotherms for PNP adsorption onto egg shells at different temperatures.

Effect of temperature

The impact of temperature on the adsorption of PNP on egg shells was investigated at different temperatures range of (10-50 Cº), at fixed concentration was 25 mg/L. Temperature study gives idea for the adsorption nature if it is an endothermic or exothermic adsorption (Salleh et al. 2011). Thermodynamic functions, like enthalpy change (ΔHº), change in Gibbs free energy (ΔGº) and entropy change (ΔSº), were calculated from the following Equations:

$$\log K_d = \frac{\Delta S^\circ}{2.303\,R} - \frac{\Delta H^\circ}{2.303\,RT} \quad \ldots\ldots\ldots\ldots\ldots (11)$$

$$\Delta G = -RT \ln K_d \quad \ldots\ldots\ldots\ldots\ldots (12)$$

Where: K_d is the equilibrium partition constant, T is the temperature in Kelvin and R is universal gas constant (8.314 J/mol/K).
The values of ΔHº and ΔSº can be calculated from the slope and intercept of log K_d versus 1/T in equation (11), as shown in Table (2). See Figure (8).

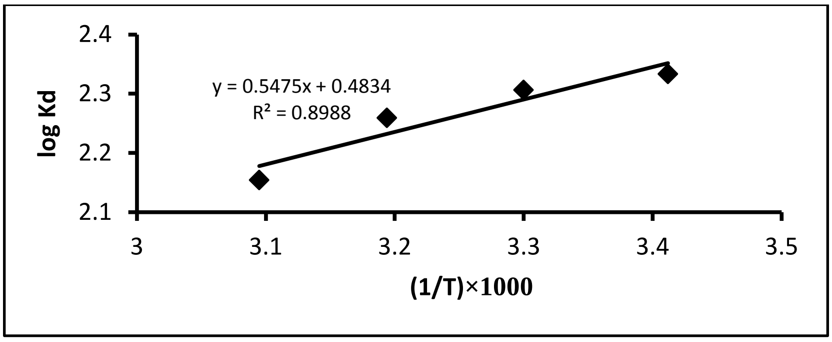

Figure (8): a plot of log K_d versus 1/T for adsorption of PNP onto egg shells powder

Table (2): Thermodynamics parameters for adsorption of PNP on the surface of egg shells powder

T(K)	**ΔH°** (KJ/mol)	**ΔG°** (KJ/mol)	**ΔS°** (J/mol.K)
283	-10.483	-12.392	9.255
293		-13.088	
303		-13.379	
313		-13.534	
323		-13.322	

The thermodynamic parameters indicated in Table 2 shows, the value of ΔG° is negative which asserts the possibility of the process and the sorption process was spontaneous nature, the positive value of Δ*S*◦ indicates the randomness was increasing in the system solid-liquid through the adsorption process and the negative value of ΔH° denotes that the adsorption process is exothermic. The decreasing in adsorption with increases of temperature may be attributed to the relatively high in the immigration tendency of the PNP particles from the solid phase to the bulk phase, or attributed to the fragility of adsorptive forces which Link the active sites of the adsorbents and the adsorbed species and also between the adjacent particles of adsorbed phase.

Conclusion

This study deduces that the hens' eggshell powder can be used as a low cost adsorbent for removal of PNP from Industrial wastewater at low concentration. From the results, it can be concluded that egg shells powder is a somewhat good adsorbent due to its ability to remove PNP from aqueous solution, especially at low concentrations. The experiments explained that the adsorption of PNP is rapid at the beginning and becomes slower near the equilibrium. The percentage removal of PNP increased with increasing the amount of adsorbent dosage due to the increase in adsorbent surface. And slightly increased of adsorption of (PNP) with increase pH this, may be due to surfaces of the adsorbent become negative charged at high pH and therefore an increase of the adsorption of PNP onto eggshell. Equilibrium adsorption data was best fitted with Langmuir isotherm model.

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