Comparison of Synthetic and Natural Adsorbent for Sorption of Ni (II) Ions from Aqueous Solution

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Abstract: Removal of Ni (II) ions from wastewater is obligatory in order to avoid water pollution. In the present study, the sorption of Ni (II) ions from aqueous solution was investigated by using lewatite S-100 (strongly cation-exchange resin) and new sorbent potato peels which are normally discarded as solid waste. In a batch adsorption system as a function of pH, contact time, adsorbent dose, and initial concentration of metal ion was evaluated.The sorption isotherms were studied using Langmuir, Freundlich and Temkin isotherm models. . The date where analyzed on the basis of lagergren pseudo- first order and pseudo – second order models. The results obtained show that the lewatite S-100 strong cation-exchange resin and potato peels char coal (PPC) performed well for the removal of Ni (II) ions. The present study suggest that PPC as a low adsorbent can be used beneficially in treating industrial effluents containing heavy metals. [Nature and Science 2010;8(11):86-94]. (ISSN: 1545-0740).

Keyword: Cation-resin Lewatite S-100, Potato peels, Ni (II) solution,Isotherm and Kinetics

1. Introduction:

Toxic heavy metals in the aquatic ecosystem raise human health risks and cause harmful effects to living organisms in water and also to the consumers of them. Many industries containing oil refining, textile industry,metal plating facilities, electroplating, mining operations,pigments and dyes manufacturing, Fertilizer, and batteries produce heavy metals such as nickel,,cobalt, zinc, chromium, copper, lead and cadmium, etc [1].

Moreover, these heavy metals can contaminate the soil, potable water source, ground water, and crops. Another disadvantage of these contaminants is to be limited reusing of water sources. Nickel and their compounds causing various diseases and disorders including renal edema, skin dermatitis, pulmonary fibrosis and gastrointestinal distress is carcinog, non-biodegradable, and tend to accumulate in living organism. Divalent nickel especially causes cancer of lungs, nose, and bone [2-4].

Traditional methods for recovering heavy metals from effluents are generally expensive or in adequate to treat highly diluted effluents. These methods include: chemical precipitatio and filtration, ,redox reactions, electrochemical treatments, reverse osmosis, ion exchange, adsorption and evaporation.

However, adsorption and ion-exchange methods have been evaluated as promising techniques. In order to find out cost–effective materials, numerous adsorbent and ion exchanging material have been tested for heavy metal removal in last decades.

Ion exchange process is very effective to remove various heavy metals and can be easily recovered and reused by regeneration operation. Ion exchange resins are a varity of different types of exchange materials, which are distinguished into natural or synthetic resin. Furthermore, it can be as well categorized on the basis of functional groups such as cation exchange resins, anion exchange resins, and chelating exchange resins. Depending on the functional groups, ion-exchange resin can deal properly with several heavy metals such as copper, nickel, cobalt, cadmium, zinc and aluminum [5-12].

In recent years, special attention has been focused on the use of natural adsorbents as an alternative to replace the conventional adsorbents, based on both the environmental and the economical points of view. Natural materials that are available in large quantities, or certain waste products from industrial or agricultural operations, may have potential as inexpensive sorbents. Due to their low cast, when these materials the end of their life time, they can be disposed of without expensive regeneration. The abundance and availability of agricultural by – products make them good sources of raw materials for natural sorbents [13-16].

The aim of this work, as a low cont adsorbent (PPC) performance for removal of Ni(II) was investigated against a strongly cation-resin lewatite S-100. Batch technique was used in order to determine the adsorption capacity of these adsorbents for Ni(II) removal from aqueous solutions. After defining optimum reaction conditions (pH, adsorbent

dose, contact time), adsorption isotherms and kinetics were investigated and different adsorption models were used to evaluate the experimental data and to elucidate the possible adsorption mechanism.

2. Materials and Methods:

2.1. Materials
Potato peels (PPC)

The waste potato peels were collected from the local filed of Egypt in the months between January to March.

The adsorbent was developed using these wastes by the method reported else where [17]. These were first washed with water at least five times to remove as and other contaminants. Dried it in an oven at 70-80°C for 2-3 hr, the dried potato peels were ground and this material was then thermally activated (carbonized) at 700°C $\pm$ 5°C in a muffle furnace for 2-3 h in the presence of air. The dried PPC was crushed and sieved be small particle size by 0.355 mm and kept in a desicator for further use.

Ion-exchange resin:

Commercial synthetic Lewatite S-100 cation exchange resin in hydrogen from was kindly obtained from Bayer chemical company. (Germany). Before experiments the cation- exchange resin was acid – conditioned with 2 M to 0.1 M HCl several times to remove impurity from the resin and to convert the exchange sites to the desired H^+ form. Finally washed with deionized water until all chloride ions was removal and dried under vacuum at room temperature for further experimental studies.

Regents

The stock solution of Ni(II) (1000 mg/l) was prepared by dissolving 4.049 gm of analytical grade $NiCl_2$. $6H_2O$ in 1000 ml of double distilled water. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) used for pH adjustment were purchased from Merck.

Apparatus

An atomic absorption spectrophotometer (AAS) "Inductively coupled plasma" ECP, 6500 Duo, thermo-scientific England was used to analyze the concentration of Ni(II) in solutions at 232 nm. The pH measurements were carried out microprocessor, pH meter model (Hanna. 211).

Methods
Determination of optimum conditions

The adsorption of Ni(II) on PPC and Lewatite S-100 resin samples was studied by a batch technique. The optimum conditions were pH, dose, adsorbent amount, contact time and concentration. The batch adsorption experiments were carried out by Shaking known amounts of PPC adsorbent with 50ml aqueous metals solution 100-500 mg/l concentration at various pH, (2-10) and at room temperature 25$\pm$ 2°C in several stoppered bottles for retention times varying from 5-120 min., the pH of the solution were adjusted before adding ion exchange resin and PPC samples well dispersed in aqueous metal solutions. At the end of the pre-determined time interval, the adsorbent was removed by the filtration and the final concentration was determined in the filtrate by atomic absorption spectrophotometry(AAS), optimum conditions were determined for both adsorbents.

Adsorption isotherm

A known volume of Ni(II) solution of varying initial concentrations, take in 50 ml stoppered tubes, was shaken with a fixed dose of adsorbent for a specified contact time. After equilibrium, samples were filtered and the concentration of Ni(II) was analyzed by AAS.

The metal sorption capacity (q_e in mg/g) of adsorbent was calculated according to mass balance in Eq. (1)

$$q_e = \frac{C_i - C_t v}{ms} \quad (1)$$

Where C_i and C_t are the initial and equilibrium concentrations of Ni(II) in solution (mg/l), v is the volume of solution (L) and m is the mass of the adsorbent (g).

In addition, the percentage of Ni(II) ion removed from the aqueous solution was calculated using Eq. (2)

$$\% R = \frac{C_i - C_t}{C_t} \text{ x } 100 \quad (2)$$

The sorption equilibrium date of metal ions onto PPC or Lewatite S-100 were analyzed in terms of Langmuir , Frendlich and Temkin.

The Langmuir isotherm applies to adsorption on completely homogenous surface with negligible interaction between adsorbed molecules [18]. Theoretically, therefore, a saturation value is reached beyond which no further sorption can take place. The saturated monolayer curve can be represented on linearization form :

$$\frac{C_e}{q_e} = \frac{C_e}{Q_m} + \frac{1}{Q_m b} \qquad (3)$$

Where q_e and C_e are the equilibrium concentrations of metal ions in the adsorbed on liquid phase in mg/g and mgl/l, respectively, Q_m and b are Langmuir constants which are related to sorption capacity and energy of sorption, respectively, and can be calculated from the slope and intercept of the linear plot, C_e/q_e vs C_e. The Langmuir equation can also be expressed in terms of a dimensionless constant of separation factor or equilibrium parameter, R_L [19] from the expression:

$$R_L = \frac{1}{1 + bC_o} \qquad (4)$$

Where b is the Langmuir constant and C_o is the initial concentration of adsorptive. For favorable adsorption $0 < R_L < 1$, while $R_L > 1$, 1 and 0, respectively describe unfavorable, linear and irreversible adsorption.

Freundlich isotherm equation can be written in the linear form as given below [10].

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad (5)$$

Where q_e and C_e are the equilibrium concentrations of metal ions in the adsorbed and liquid phases, respectively. K_F and n are the Freundlich constants, associated with adsorption capacity and adsorption intensity respectively. K_F is an important constant used as relative measure for adsorption efficiency. The magnitude of the n shows an indication of the favorability of adsorption. Values of n larger than 1 show the favorable nature of adsorption [21].
Temkin adsorption isotherm equation is expressed as

$$q_e = B \ln A + B \ln C_e \qquad (6)$$

Where A is Temkin constant representing adsorbat-adsorbat interactions and B is another constant related with adsorption heat [22]. Isotherm constants A and B can be determined from plot of q_e vs $\ln C_e$.

Kinetic models

The sorption kinetic data of Ni(II) ions measured using PPC and lewatite S-100 was analyzed in terms of pseudo-first order and pseudo second order sorption equation [23]. The pseudo-first order equation can be written as :

$$\log (q_e - q_t) = \log q_e - \frac{K_1}{2.303} \ t \qquad (7)$$

where K_1 (min^{-1}) is the rate constants of the pseudo-first order sorption, q_t (mg/g) denotes the amount of sorption at time t (min) and q_e (mg/g) is the amount of sorption at equilibrium. The sorption rate constant K_1, can be calculated by plotting $\log (q_e - q_t)$ vs t. The pseudo-second order equation can be written as

$$\frac{1}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \qquad (8)$$

Where K_2 (g/mg min) is the rate constant of the pseudo- second order sorption.
K_2 and q_e can be obtained from the intercept and slope of plotting t/q_t vs t.

3. Results and Discussion:
3.1. Determination of optimum conditions
3.1.1. Effect of pH
The pH of solution played an important role for adsorption of metal ions. To determine the pH effect on adsorption capacity of Ni(II) ions, solutions on PPC and Lewatit S-100 were prepared at different pH levels from (2-10) the results are given in Fig. (1). The adsorption values were increased with increasing pH values for both adsorbent due to lesser number of H^+ and greater number of surface ligands with negative charges. The percentage removal of Ni(II) increases for two adsorbent with an increase in pH of solution from pH 2.2-5.5 $\pm$ 0.5 and still unchanged from pH 5.5-10.0. As seen in Fig. 1, the low adsorption of Ni(II) ions at low pH may be due to sorbate lyophobic behavior [24]. At high pH from 5.5-10.0 values decrease in percentage removal can be described with the formation of Ni(OH)$_2$ during reaction of Ni(II) ions with OH$^-$. In this state, hydrolysis accompanied by precipitation of metal hydroxides may occur [25]. For avoiding precipitation of metal ions, high pH values were not preferable and the optimum pH was chosen between 4.0-6.0 for both adsorbent.

3.1.2. Effect of adsorbent dose
The retention of Ni(II) ions was examined in the relation to the amount of adsorbed. The results of the dependence of Ni(II) adsorption on the amount of PPC and resin are shown in Fig. (2). The percentage removal values were increased with increasing amount of adsorbents upto (0.12, 0.05 gm) for PPC and Lewatite S-100 respectively. This result proved

that increasing the amount of adsorbent provides higher removal due to formation of greater adsorption sites [14]. Fig. (2) is evident that the percentage removal of Ni(II) increases to 52.0% with the increasing of PPC, and 56.0% with lewatite S-100. Thus it results in the increment of adsorption efficiency initial saturation. However considering the cost, the optimum adsorbent amount was chosen as 0.12, 0.05gm for PPC and Lewatite S-100 respectively.

3.1.3 Effect of agitation time and initial metal

A Series of Ni(II) solution of different initial concentration ranging from 230 to 450 mg/l with stirred with 0.12 gm of PPC and from 2 to 12 mmol/l with 0.05gm of Lewatite -100 at 25°C for a contact period from 5 to 120 min. Fig. (3) shows that the percentage removal of Ni(II), increased with the increase in agitation time and equilibrium was attained within 20-30 min for all concentration range of Ni(II). On the basis of these results a 20 min shaking period was selected for all further studies.

3.2. Adsorption isotherms

Results obtained for the sorption of Ni(II) have been subjected to different isotherms namely, Langmuir , Freundlich and Temkin, are given in Fig. 4-6.

In order to as certain whether the adsorption is chemisorptive in nature with chemical forces binding Ni(II) to the surface of adsorbents, the experimental data are tested with respect to Langmuir isotherm. As seen in Fig. (4). from the linear relation between C_e/q_e and C_e. The adsorption equilibrium constant b and maximum adsorption capacity Q_m of adsorbents were calculated and these are shown in Table 1. The adsorption isotherm of Ni(II) exhibit Langmuir behavior, which indicates as monolayer adsorption.

The Freundlich isotherm is known as earliest empirical equation and is shown to be consistent with exponentil distribution of active center, characteristic of heterogenous surface [15].

Plots of log q_e vs log C_e are shown in Fig. 5 the slope and intercept give the values of 1/n and K_F. Table 1 shows the valued of K_f and 1/n obtained by regression analysis. Freundlich values of 1/n between 0.58,0.11 for PPC and Lewatite S-100 indicate the favorable adsorption of Ni(II) on to PPC and resin. Temkin adsorption isotherm models described in section 2. As can be seen from the isotherms in Fig. (6) and regression coefficient (R^2) in Table 1, the Langmuir and Freundlich isothems show the best fit compared to Temkin isotherm.

Table 1 also supports favorable adsorption of the metal ions on the PPC and Lewtite S-100.

3.3. Adsorption kinetics

The prediction of kinetics is necessary for the design of sorption systems. Measurement of sorption rate constants and order of the reaction are important physico-Chemical parameters to evaluate the basic qualities of a good sorbent. In order to observe the sorption proess of Ni(II) ions on to PPC and Lewatite S-100, pseudo-first order and pseudo-second- order kinetic models, which are described in earlier section 2 were implemented.

The constants of kinetics models for the adsorption of Ni(II) onto PPC and Lewatite S-100 are listed in Table 2. It can be concluded from Table 2 that pseudo-second order equation provides the best correlation coefficient, where as the pseudo-first order do not give a good fit to the experimental data for the adsorption of Ni(II) ions. This suggests the chemical adsorption is the rate limiting step.

Table (1): comparison the sorption isotherms between Lewatite S-100 and PPC on Ni(II).

Ni-adsorbent Parameter	Langmuir			Freundlich		
	Q_m	b	R^2	K_f	1/n	R^2
Ni-Lewatite	10.40	5.04	0.999	8.360	0.115	0.990
Ni-PPC	140.8	4.8×10^{-3}	0.988	2.980	0.579	0.986

Table (2) comparison rate constants for pseudo- first and second- order between Lewatite S-100 and PPC on Ni(II).

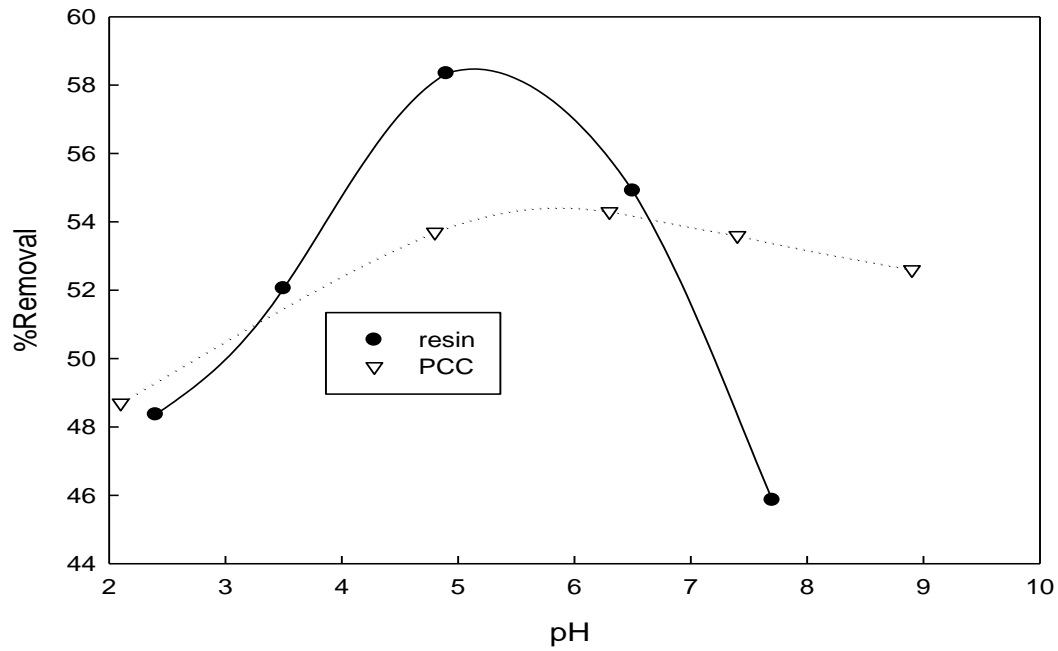| Ni -adsorbent	Pseudo first order		Pseudo second order	
	K_1	R^2	K_2	R^2
Ni-Lewatite -100	0.706	0.950	o.858	0.992
Ni-PPC	o.124	0.921	0.027	0.983

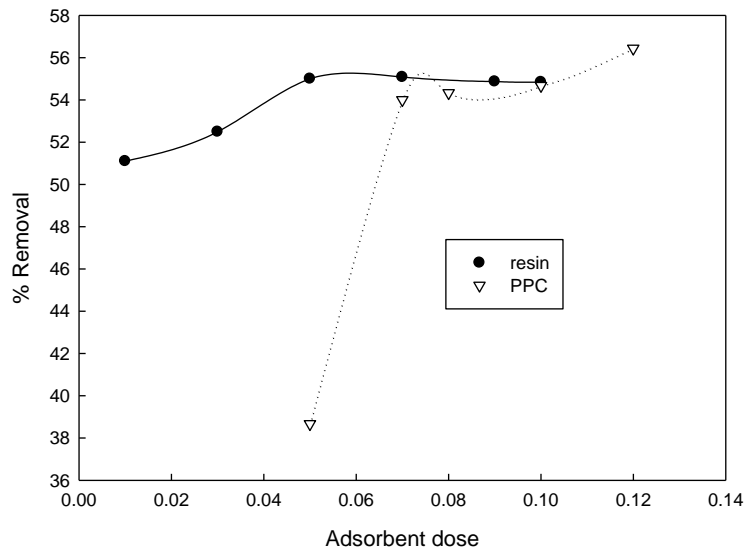**Fig (1) The effect of pH on removal of Ni(II)** ions on PPC and Lewatite S-100

Fig. (2) The effect of adsorbent dose on removal of Ni(II) ions on PPC and Lewatite S-100
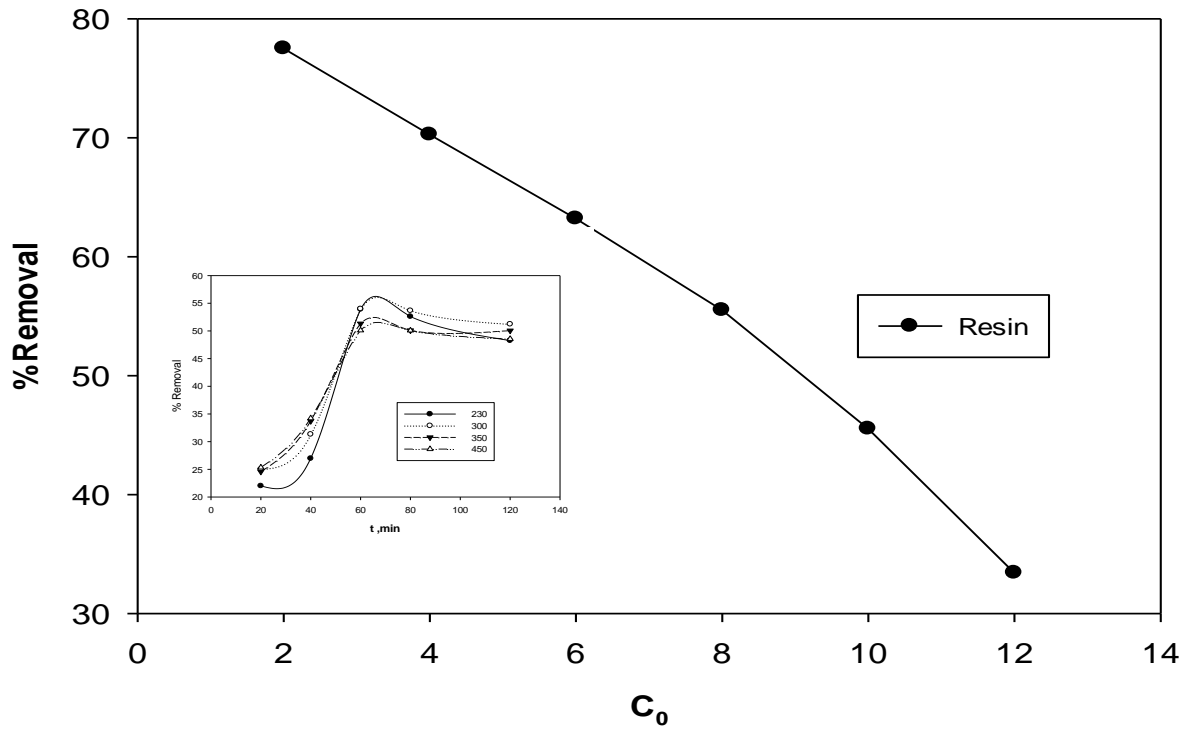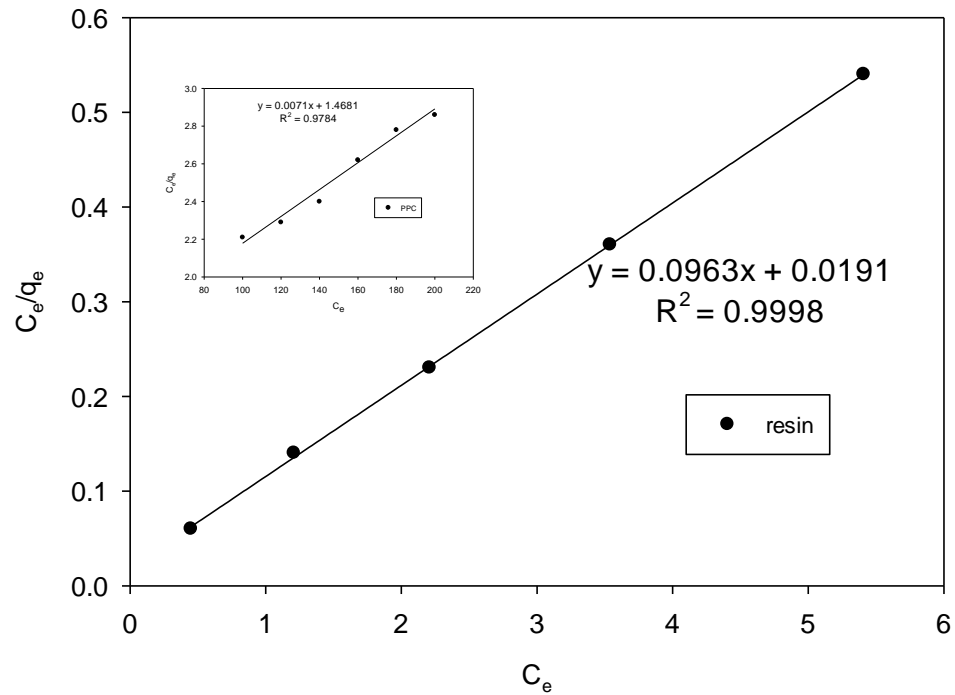
Fig. (3) The effect of different concentration on removal of Ni(II) ions on PPC and Lewatite

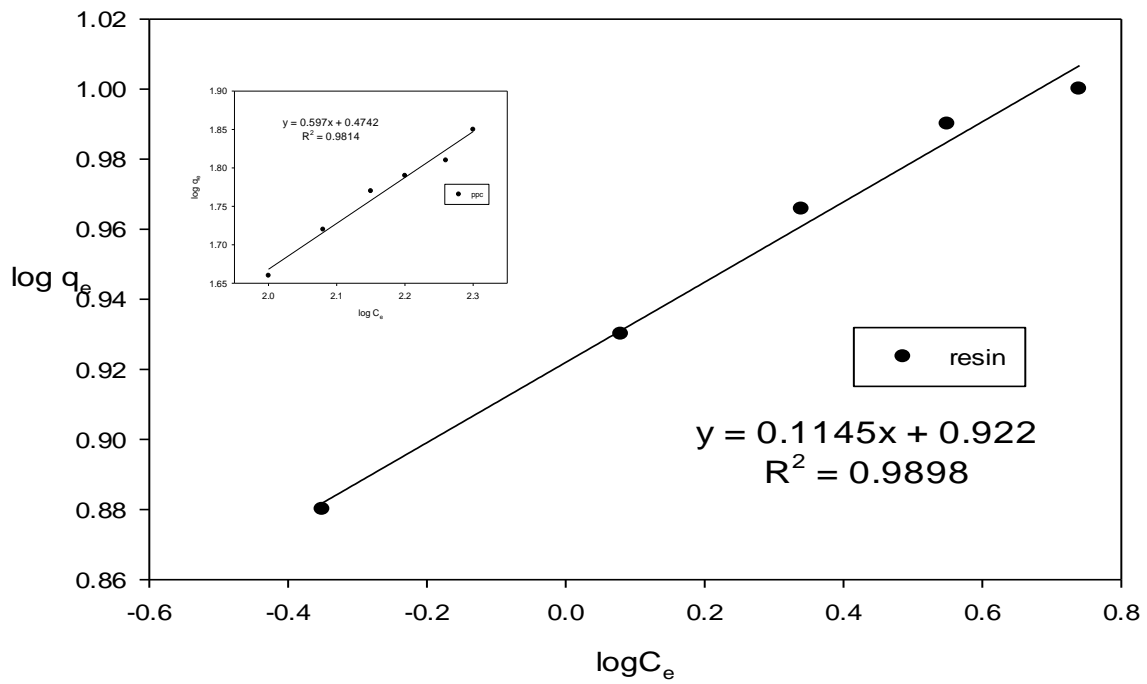Fig(4) Langmuir isotherm on removal of Ni(II) ions on PPC and Lewatite S-100

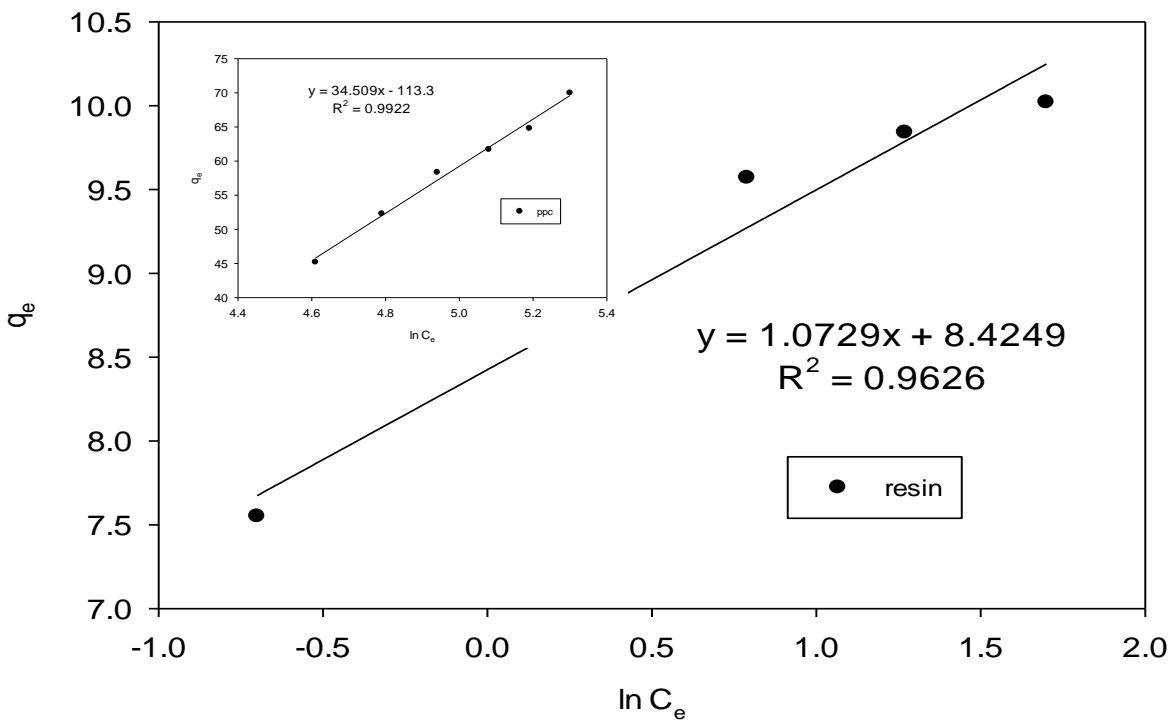Fig (5) Freundlich isotherm on removal of Ni(II) ions on PPC and Lewatite S-100

Fig (6) Temkin isotherm on removal of Ni(II) ions on PPC and Lewatite S-100

4. Conclusion

The aim of this work was to investigate sorption of Ni(II) from aqueous solutions by using PPC as natural adsorbent and Lewatite S-100 cation exchange as synthetic adsorbent. Optimal removal conditions for both adsorbents were determined with batch experimental. For both adsorbents, pH has a great influence on adsorption efficiency. At low pH value, the adsorption efficiency was relatively low, when pH value was 4.0-6.0 almost 52% and 56% Ni(II) ions were adsorbed for 0.12g/l for PPC and 0.05 gm for Lewatite S-100. Adsorption of Ni(II) reached equilibrium faster within 20-30 min). Experimental results were evaluated with Langmuir, Frendlich and Temkin isotherms. In addition to higher values of correlation coefficients, monolayer capacities (Q_o) determined from Langmuir isotherm and adsorption intensities (n) determined from Freundlich isotherm indicate appropriateness of Langmuir and Freundlich isotherms for both adsorbents. In Temkin isotherm, it was stated that adsorbate/adsorbate interactions are weaker for Ni(II) removal due to smaller values of Temkin constant (A).

Kinetic studies suggest that Ni(II) adsorption could be described more favorably by the pseudo-second order kinetic model. According to these experimental results and all previous works with Lewatite S-100 cationic resin and natural adsorbent (PPC), it was demonstrated Lewatite S-100 cation-exchange resin and PPC as a new adsorbent which is in expensive and easily available material have good capability and efficiency for the removal of Ni(II) contained from aqueous solutions.

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