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Using Of Carbon Soot For Nickel (II) Removal By Adsorption; Kinetic Study.

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ABSTRACT

The removal of nickel ions from aqueous solutions, using carbon soot, a very cheap industrial byproducts, and bentonite, natural ore, compared with commercial activated carbon was investigated. The adsorption isotherms (Langmuir, Freundlich, and Brauner-Emmett-Teller) were applied. The rate constant of adsorption, rate constant for intraparticle diffusion, pore diffusion coefficient, overall reaction rate, equilibrium constant and the thermodynamic parameters ΔG, ΔH and ΔS were estimated. Also the effect of time, sorbent dose, initial concentration and the pH at different temperatures were studied. The comparative study indicates that carbon soot and bentonite nearly have the same adsorption ability as commercial activated carbon but they are cheaper than it.

Keywords: Adsorption, Carbon Soot, Bentonite, Thermodynamic Functions, Activated Carbon, Kinetics.

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INTRODUCTION

The relation between trace elements and environmental quality is based upon the need to safeguard man's health. Trace elements are linked to health because of the function they fulfill in physiological processes. Heavy metals differ from alkali-earth, and specially alkali metals, as the latter are mobile and participate in more dynamic activities such as muscle function and nerve conduction. A number of these metals such as nickel, chromium, copper, tin, and vanadium have been shown in trace amounts to produce important beneficial effects in the animal body, but have not been classified generally as nutritionally essential, but if they increased more than the allowed limits they will be pollutants and toxic [1].

Environmental concern has caused a lot of research to concentrate on the effects of toxic metals on the environment, since they ultimately reach and accumulate into animal and human tissues. Efforts are being made, therefore, to remove metal ions from wastewaters in order to clean water before it is eventually either rejected or reused. Nickel is one of the metals found in various raw wastewaters, e.g. of non-ferrous metals mineral processing plants, steam-electric power generating plants, paint formulation and porcelain enamelling [2,3]. It is considered as toxic -e.g. in concentrations of 15 mg/l [4]-especially to activated sludge bacteria [5] and its presence is detrimental to the operation of anaerobic digesters used in wastewater treatment plants[6,7]. Nickel is also known to be highly mobile, hence it is generally sorbed only to a small extent [8]: natural polymeric organic acids (e.g. fulvic or humic acids) are capable of re-mobilising it from solid phases, increasing its solubility [9].

Several efforts have been made to remove nickel ions from wastewaters, either by sorption on wollastonite (α-calcium metasilicate)[10], MnO_2[11], activated carbon[12], various oxides: Fe_2O_3[13], Al_2O_3[14,15], TiO_2[16], SiO_2[17], goethite (α-FeOOH)[14], using ion-exchange resins (Dowex 50WX8)[18], by filteration of precipitate [10]or even by crystallization of nickel carbonate[19].

Maros et. al.[2] showed that the removal of nickel ions from wastewater using flyash, a cheap industrial by-product, was investigated. The addition of flyash to the solution raised the pH, effectively removing all of the nickel ions.

Nickel, copper, cadmium, lead, and zinc may be more or less toxic to aquatic life depending on other water quality conditions, such as pH, temperature, hardness, turbidity, and carbon dioxide content. At certain dosage levels of some heavy metals carcinogenic effects have been observed. The presence of excessive heavy metals in a water supply thus may eliminate its usefulness for some of a community's needs [20].

Gardea et.al. [21] showed that the silica-immobilized African alfalfa shoots were effective for removing metal ions from solution and over 90% of the bound Ni(II), Pb(II), Cu(II), and Zn(II), and over 70% of Cd(II), were recovered after treatment with 4 bed volumes of 0.1M HCl. The results from this study will be useful for a novel phytoremediation technology to remove and recover heavy metal ions from aqueous solution.

Gardea et. al.[21] carry out batch experiments which were performed to determine the optimum binding pH, time dependency for Ni(II), Cu(II), and Pb(II) desorption by inactivated cells of synechoccos PCC7942 (cyanobacteria). The biomass studies showed a high affinity for all metal ions as the pH increased from 2 to 6 with optimum binding occuring at pH 5 . The dependency studies showed that this cyanobacteria had rapid binding to all three metals. More than 90% of Ni(II), Cu(II), and Pb(II) metal ions were recovered when treated with 0.1M HCl.

Activated carbon which is frequently used in the adsorption of pollutants, is costly both to use and to regenerate. Therefore, there is a need for the development of low cost, easily available materials which can adsorb divalent nickel economically. Carbon in the form of carbon soot is produced from the partial oxidation of natural gas in fertilizer industry at , Talkha Fertilizer and Chemical Plant, (SEMADCO, EGYPT) in amount of about 4.5 g/m3 of natural gas used. Previous works conducted by many researchers[22,23] indicated that carbon soot is a promising material for different industrial applications as a substitute for commercial powdered activated carbon.

Bentonite (montmorillonite) is a colloidal clay (aluminum silicate)[24] is found in Koum Oushim, Fayoum, Egypt in economic cost. Chegrouche et.al.[25] indicated that the use of natural bentonite in treating aqueous waste containing heavy metals and organic matter has been previously reported in many works [26,27]. A major part of them deal with water demineralization by means of cationic resins or zeolites. Recently , the substitution of these materials by low cost natural clays (e.g. montmorillonite) was of increasing interest. This is mainly due to their chemical instability in acid media which generally cause pronounced dealumination and subsequent crystallinity loss. Nevertheless, natural clays present a major advantage of giving low cost recovery processes, making them suitable for use in water purification. Moreover, their regeneration does not present any problem and, when needed, the recovering of the fixed element could be reached even by leaching the loaded material. The undertaken work is devoted to study the kinetics and thermodynamics of nickel adsorption onto carbon soot, bentonite and commercial PAC.

MATERIALS AND METHODS

Materials:-

Carbon soot used in this study was produced from the partial oxidation of natural gas at Talkha Fertilizer and Chemical Plant, (SEMADCO, EGYPT). Carbon soot was investigated for adsorption studies against a commercial Activated Charcoal in the form (PAC) supplied from El-Nasr Co. for Pharmaceutical Industry, Egypt and also against bentonite supplied from Koum Oschim, Fayoum, Egypt by the National Research Center (NRC), Egypt. The adsorbent were dried in an oven at 105°C for one hour and then screened through a sieve 30 mesh/inch (0.1 - 0.315 mm) openings to remove any large solids. This was done to produce a uniform material for the complete set of adsorption tests. All the chemicals used were of analytical grade and were obtained from BDH and E.Merck. A stock aqua nickel (II) solution (1000 mg Ni/L) was prepared using nickel nitrate hexahydrate $Ni(NO_3)_2.6H_2O$.

Analytical Procedures:-

The adsorbents used were chemically analysed[22,28,29] and the chemical compositions were listed in Table (1). The determination of divalent nickel in solution was carried out by 902 GBC double beam atomic absorption spectrometer (Australia), with air-acetylene burner-head provided with integrated readings in absorbance or concentration.

The optimum instrumental conditions for determination were: lamp current 4 mA, observation height (slit width) 0.2 cm and wave length 232 nm.

Effect of Contact Time (Equilibrium Time)

0.2 g of adsorbent was placed in a series of stocked glass tubes containing 25 mL of nickel nitrate solution (50 ppm Ni) at a temperature of 20°C in a water bath shaker (150) rpm. After different time intervals, one tube was removed, filtered with Whatman No.1 filter paper. The remaining nickel concentration was determined in the filterate.

Effect of Initial Concentration

0.2g of adsorbent was placed in a series of stocked glass tubes containing 25 mL of nickel nitrate solution (10 - 200 ppm Ni) at temperature of 20°C in a water bath shaker (150 rpm), then filtered and nickel concentrations were determined in the filterate.

Effect of Adsorbent Dose

A series of 0.1g - 0.5g adsorbent were placed in a series of glass tubes containing 25 mL of nickel nitrate solutions (50 ppm Ni) at a temperature of 20°C in a water bath shaker (150 rpm), then filtered and nickel concentrations were determined in the filterate.

Effect of pH of Solution

0.2 g of adsorbent was placed in a series of stocked glass tubes containing 25 mL of nickel nitrate solution (50 ppm Ni) of pH (2-11) at a temperature of 20°C in a water bath shaker (150 rpm), then filtered and nickel concentrations were determined in the filtrate. These all steps were repeated at temperatures 30°C, 40°C, 50°C, and 60°C for each adsorbent type.

Determination of adsorption isotherms and dynamics of adsorption:

Adsorption Isotherms:

Application of Langmuir [36], Freundlich [37], and Brunaur-Emmett-Teller (BET) [38] isotherms and then the constansts associated with these models are determined.

Adsorption dynamics :

Determination of rate constant for adsorption:

Application of Lagergren's equation[39] in the form:

$$\log (Q_e - Q) = \log Q_e - (k_{ad} / 2.303)\ t \qquad \ldots\ldots\ldots\ldots\ldots(1)$$

where,

Qe: amount of metal adsorbed at equilibrium
Q : amount of metal adsorbed at time t
kad : rate constant for adsorption vary according to the temperature, then, plotting the relation between **log (Qe - Q)** against **(t)** the slope will be equal to **(- kad / 2.303)**

b) Determination of the rate constant for intraparticle diffusion kp:

Plotting the relation between the amount adsorbed against the square root of time, the slope will be equal to the kp(40,41)

c) Determination of pore diffusion coeffecient D:

Application of Bhattacharya and Venkobachar equation(42) in the form:

$$t_{1/2} = 0.03\ r_{20}\ /\ D \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

where,

t1/2 : time for the adsorption of half amount of metal
r0 : radius of the adsorbent, which was calculated by an electronic microscope for bentonite, and r0 for both PAC and carbon soot as determined elsewhere(42)
D : pore diffusion coeffecient.

Detremination of overall reaction rate constant K:

Application of the equation(43)

$$\text{Ln} (1 - X_a / X_{ac}) = (- K)\ t \qquad \ldots\ldots\ldots\ldots\ldots\ldots(3)$$

where,

Xa: fraction of solute adsorbed onto the sorbent at any time

Xac: fraction of solute adsorbed at equilibrium condition

K: overall rate constant

t: time (min.)

e)Determination of activation energy (43)*:*

The experimental activation energy was determined using different values of overall rate constant (K) against their corresponding temperatures values in kelvin from Arhenius' equation

$$K = A e^{-E/RT}$$

Where,

A: is a temprerature-independent factor called "frequency factor"

K: is a specific rate constant

E: is the activation energy, representing the minimum energy that the reacting system must have for the reaction to proceed.

The equation can be written in logarithmic form:

$$\text{Ln (K)} = \text{Ln (A)} - (E / R)(1/T) \quad \ldots\ldots\ldots(4)$$

The values of **(E)** can be calculated by plotting the relation between **Ln (K)** against the **reciprocal of the temperature** in Kelvin, the slope will be equal to **(-E/R)**.

Estimation of thermodynamic parameters ΔG, ΔH, & ΔS

Considering the following relations(43):

$$\Delta G = \Delta H - T\Delta S \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

where,

ΔG : change in free energy, cal/mol

ΔH : change in enthalpy, cal/mol

ΔS : change in entropy, cal/mol

T: absolute temperature,(K)

$$\ln Kc = \Delta S /R - (\Delta H /R)(1/T) \quad \ldots\ldots\ldots\ldots\ldots(6)$$

where,

R: gas constant=1.986 cal/mol K

Kc: equilibrium constant

plotting the relation between **ln(Kc)** and **(1/T)** finding ΔS and ΔH from the slope and the intercept, hence ΔG can be calculated, where,

$$Kc = CBO + CAO . XAC / CAO - CAO . XAC \quad \ldots\ldots\ldots\ldots(7)$$

where,

CAO: initial concentration of solute at time, t

CBO: initial concentration of solute on sorbent at time, t

XAC: fraction of solute adsorbed on sorbent at equilibrium

RESULTS AND DISCUSSION:

The chemical analysis of used adsorbents are listed in Table (1). Two important physico-chemical aspects for the evaluation of the sorption process as a unit operation are the equilibria of sorption and the kinetics. Sorption equilibrium is established when the concentration of metal in a bulk solution is in dynamic balance with that of the interface.

Sorption equilibrium:

Effect of time and initial nickel concentration on adsorption:

The results shown in Fig (3) indicate that the remaining concentration of nickel in solution decreases with time up to 25,20 and 30 min. in case of carbon soot, PAC, and bentonite respectively and thereafter it becomes constant somewhile. This shows that equilibrium is attained at 25,20 and 30 min. in case of carbon soot, PAC, and bentonite respectively. However, the results shown in Figs.(4-6) indicate that the increasing in the initial nickel concentration is accompanied with increasing in the remaining nickel concentration in the solution at various intervals of time, and there is no dependence on temperature change in this case.
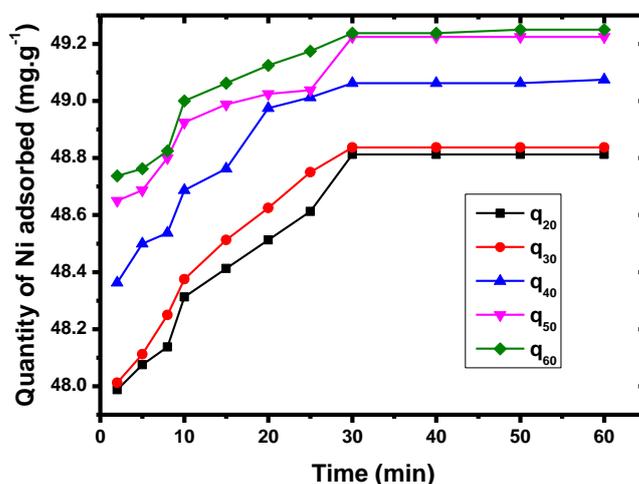

Fig (3): Equilibrium time of nickel adsorption by bentonite pH=8.0   Bentonite dose=0.2g/25mL Initial concentration=50ppm

Effect of adsorbent dose and pH of the solution on nickel adsorption:-

The effect of the adsorbent doses added to the solution (keeping the Ni(II) concentration, pH, and time of agitation constants) is illustrated in Figs.(7-9) indicating the decreasing in the remaining nickel concentration by the increasing in the adsorbent doses. Isothermal data have been used to calculate the ultimate sorption capacity of the adsorbents by substituting the required equilibrium concentrations in the Langmuir, Freundlich and Brauner, Emmit&Teller (BET) equations.

Table (2) summarize the Langmuir, Freundlich and BET parameters of nickel adsorption at different temperatures. The data demonstrate that the adsorption of nickel is effetive in neutral solution in (pH 7.5-8.5). With increasing the temperatures, the Langmuir constant, a (which is an indicative of maximum adsorption capacity) Figs.(10-12), was found to increase whilst the Langmuir constant, b (which is a measure of adsorption energy), show a small decrease trend. On the other hand, Freundlich constant, K (which is a measure of adsorption capacity) Figs.(13-15), showed an increasing trend with increasing the temperature. This result seems to be conflicted with the basic knowledge concerning the increase of desorption with increasing medium temperature, but considering that , the temperature at which an adsorption is conducted will affect both the rate of adsorption and the extent to which adsorption occurs. The rise of temperature affects the solubility and the chemical potential of the adsorbate, the latter being controlling factor for the adsorption. If the solubility of the adsorbate increases with increase in temperature the chemical potential decreases and

both the effects i.e solubility and normal temperatures, wotk in the same direction, causing a decrease in the adsorption. On the other hand if temperature has the reverse effect on the solubility then both effects will act in the opposite direction and the adsorption may increase or decrease depending upon the predominant factor(44). At the same time, the Freundlich constant, n, (a measure of adsorption intensity), show a slight increase with increasing the temperature. In case of Brunaur- Emmett-Teller (BET) constant, A, (describe the energy of interaction between the solute and adsorbent surface) Figs.(16-18), showed an increasing trend with increasing the temperatures indicating the increasing in the interaction between the nickel ions and the adsorbents.

The effect of pH change on nickel adsorption at different temperatures is illustrated in Figs.(19-21), indicating that below pH=7.5, practically the Ni removal was increased with increasing the pH, whereas above pH=7.5-8.5 the Ni removal increased sharply and was practically 100% at pH=10-11. The results indicated that chemical precipitation occurs after approximately pH=8 and is completed by pH>10. Similar results were also obtained by Theis and Richer(14), where it is obvious that above pH=10 practically very little nickel exists in its Ni2+ form. Above pH=9-10, on the other hand Ni(OH)2 only slightly soluble; in this case, its removal is due not to adsorption anymore but to precipitation and adsorbents may be regarded as a more filtering aids.
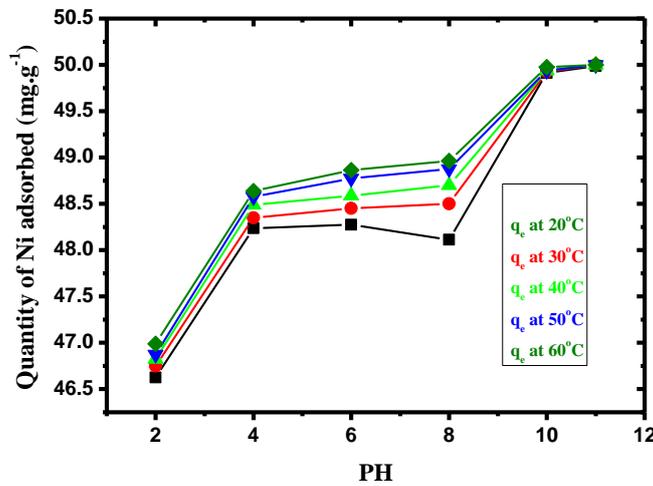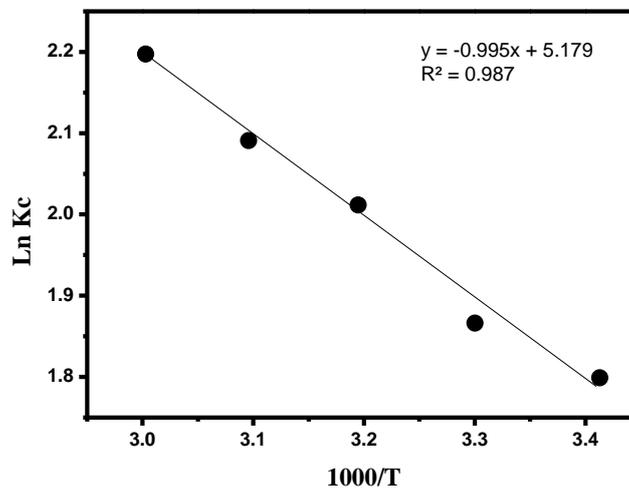

Fig(21): Effect of pH on nickel adsorption by bentonite Initial concentration = 50 ppm Time of shaking = 20 min. Bentonite dose = 0.2 g/25mL
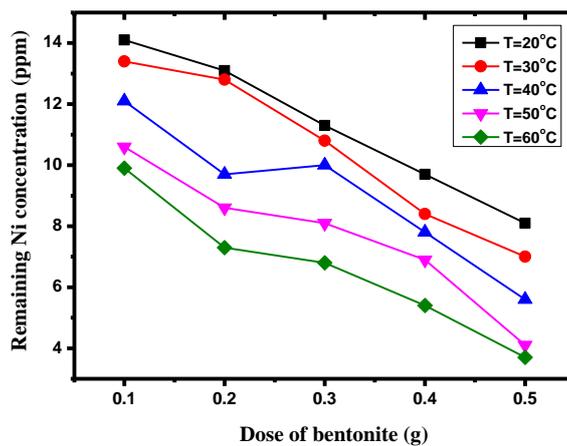
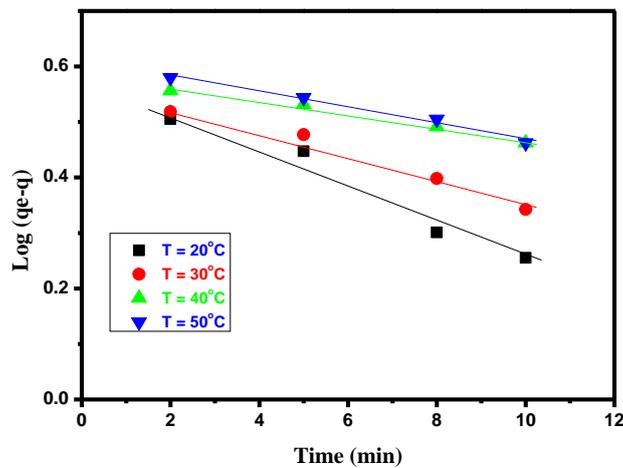

Fig(9): Effect of bentonite dose in nickel adsorption pH=8.0 Time of shaking = 20min. Initial concentration = 50ppm
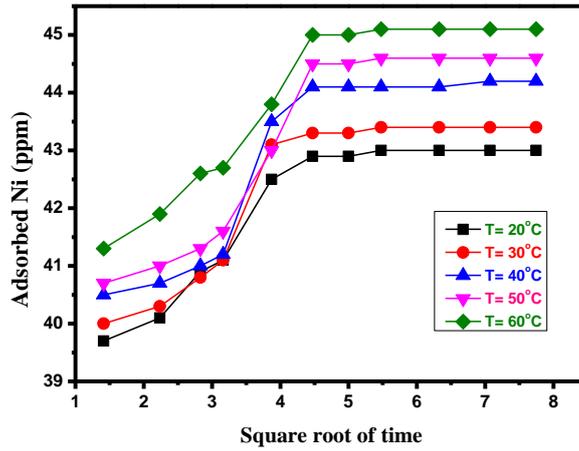
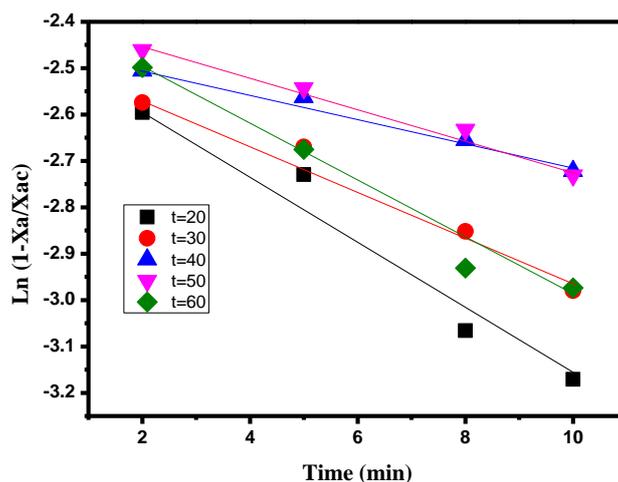**Fig(26): Rate constant of intraparticle diffusion(Kp) in nickel adsorption by PAC**

$y = -0.995x + 5.179$
$R^2 = 0.987$

Fig(35): Thermodynamic parameters of nickel adsorption by PAC

Fig(23): Rate constant of nickel adsorption by PAC (Lagergren's equation)

Fig(29): Overall reaction rate constant (K) of nickel adsorption by PAC

Table (1) : Chemical Composition Of Used Adsorbents

Analyte %	Bentonite	Carbon Soot	PAC
SiO2	54.27	6.39	2.14
CaO	8.54	0.80	0.51
MgO	2.54	0.73	0.60
Na2O	1.02	2.90	1.65
K2O	0.42	0.12	0.90
Al2O3	13.39	0.24	0.14
SO2-4	7.65	0.00	0.00
Cl-	0.15	0.38	0.00
P2O5	0.00	0.00	0.00
Fe	1.98	0.74	0.60
Ni (ppm)	00.00	00.00	0.00
Zn (ppm)	00.04	00.02	0.01
Mn (ppm)	94.01	46.08	21.29
pH	7.9	8.1	7.80
Loss of weight at			
100°C	8.3	3.15	2.10
1000°C	16.53	89.50	94.96

Sorption kinetics:-

Determination of rate constant for nickel adsorption

The rate constant for adsorption of the nickel on different adsorbents were determined using Lagergren's equation. The values of Kad at different temperatures were calculated from the slopes of the respective lines plots Figs.(22-24) and listed in Table (2). It may be concluded from the values of Kad that the reaction taking place is of first order.

b) Determination of rate constant for intraparticle diffusion k*p*:

In a batch reactor with rapid stirring, there is also a possibility that the transport of adsorbate ions from a solution into the pores of the adsorbent is the rate conrolling step(45,46). This possibility was tested in terms of a graphical relationship between the amount of nickel adsorbed and the square root of time Figs.(25-27). The double nature of these plots may be explained as: the initial curved portions are attributed to boundary layer diffusion effects(47).

While the final linear portions are due to intraparticle diffusion. The rate constant for intraparticle diffusion Kp, at different temperatures was determined from the slopes of the linear portions of the respective plots and are given in Table (2).

Table (2): Adsorption parameters of nickel by carbon soot, powdered activated carbon (PAC) and bentonite

Para-meter	Powdered Activated Carbon (PAC)					Bentonite				
	T=20°C	T=30°C	T=40°C	T=50°C	T=60°C	T=20°C	T=30°C	T=40°C	T=50°C	T=60°C
L a	0.077	0.580	1.86	5.39	7.30	-0.046	-0.036	-0.031	-0.003	-0.027
b	13x10-3	7.5x10-3	6.5x10-3	6.7x10-3	7.1x10-3	-3x10-3	-6x10-3	-9x10-3	-0.157	-0.019
F n	1.23	2.20	2.66	2.87	3.24	0.424	0.546	0.588	0.725	0.676
k	0.813	2.51	3.67	5.30	5.84	0.013	0.054	0.098	0.261	0.274
BET A	2.0	22.60	32.94	64.10	65.30	-1.602	-0.664	-0.846	-0.058	-1.070
Kad	0.157	0.090	0.131	0.070	0.085	0.085	0.085	0.104	0.088	0.094
K	0.156	0.228	0.247	0.303	0.341	0.072	0.086	0.107	0.119	0.129
Kc	6.04	6.46	7.47	8.09	9.00	3.85	4.49	5.67	6.04	7.19
Kp	0.84	0.63	0.39	0.49	0.85	1.32	1.61	1.33	1.48	1.04
ΔG	-1.035	-1.138	-1.240	-1.343	-1.446	-0.660	-0.919	-1.048	-1.177	-1.307
ΔH	1.977					2.998				
ΔS	0.01					0.013				
E	4.83					2.921				
D	1.2x10-9					38x10-9				
ro	6.24x10-4					4.35x10-3				

L a: Langmuir constant (mg/g) Kp: Rate constant of intraparticle diffusion (min-1)
  b: Langmuir constant (l/mg) ΔG: Free energy change (kcal/mol)
F n: Freundlich constant ΔH: Enthalpy change (kcal/mol)
  k: Freundlich constant (mg/g) ΔS: Entropy change (kcal/mol)
BET A: Brunaur-Emmet-Teller constant E : Activation energy(kcal/mol)
Kad : Lagergren' rate constant (min-1) D : Pore diffusion coeffecient (cm2 s-1)
K : Overall reaction rate (min-1) ro : Radius of adsorbent (cm)
Kc: Equilibrium constant (min-1)

c) Determination of pore diffusion coeffecient D:

The pore diffusion coeffecient D, at different temperatures was determined and displayed in Table (2). D were found to be 3.8x10-8, 1.2x10-9, and 1.6x10-9 cm2 s-1 for bentonite, PAC, and carbon soot respectively, from the values of Kp and D , it may be indicated that the process is governed by diffusion but pore diffusion is not the only rate limiting step(49).

d) Determination of overall reaction rate K:

The kinetics of nickel adsorption by different adsorbents were investigated during this phase of the experiment. Kinetic experiments were conducted at various temperatures ranging between 20°C and 60°C. The results of the overall rate constant (K), calculated from the negative value of the slope of the relation between Ln(1-Xa/Xac) versus time (t) in Figs.(28-30) and the results are summarized in Table (2) indicating that the adsorption rate increase with the increasing of temperature.

e) Determination of avtivation energy E:-

The values of E can be calculated by plotting the relation between LnK against the reciprocal of the Kelvin temperature in Fig.(31). The activation energy summarized in Table (2) for different adsorbents indicating that these values are small. Low activation energy values are characteristic of a diffusion-controlled process(50).

f) Determination of thermodynamic parameters:-

The kinetic model that was used in the research to describe this reaction rate was based on the assumption that the adsorption of nickel onto the used adsorbents is a diffusion controlled and first-order process. The thermodynamic parameters such as free energy change ΔG, enthalpy change ΔH, and entropy change ΔS, were determined by plotting the logarithmic values of the equilibrium constant Kc versus the inverse temperature in Kelvin(1/T) in Fig.(32), revealed the values of the ΔH, and ΔS, from the slope and the intercept respectively and hence ΔG can be calculated, summarized in Table (2). The positive values of differential heat of adsorption ΔH, suggests that the adsorption of nickel onto the different used adsorbents is an endothermic process. The negative values of the free energy change ΔG, suggest the spontaneous nature of the adsorption process. However, the negative ΔG value decreased with an increase in temperature, indicating that the spontaneous nature of adsorption is directly proportional to the temperature(51).

CONCLUSIONS

* Nickel is a metal considered as being toxic, hence its presence is undesirable in wastewater treatment plants. Its removal is therefore important before the wastewater may be biologically treated.
* Both carbon soot, a by-product produced from partial oxidation of natural gas in fertilizer industry, and bntonite, a natural ore are cheap and abundant. Its use for the removal of nickel(II) from aqueous solutions was investigated as an alternative for the more costly adsorptive powdered activated carbon. Based upon the results of this research, the following conclusions may be drawn:
* Carbon soot and bentonite are capable of removing nickel(II) from an aqueous solution, the equilibrium time for nickel(II) adsorption is of the order bentonite > carbon soot > powdered activatd carbon.
* The kinetics of adsorption of nickel ions onto the sudied adsorbents were investigated as first order diffusion controlled process.
* Thermodynamic functions ΔH, ΔG and ΔS were evaluated indicating that the process of adsorption is endothermic, exergenic, and spontaneous.
* The effect of temperature on the adsorption is conflicted with the basic knowledge concerning the increase of desorption with increasing the medium temperature, but the exerogenicity of the process reflect that adsorption capacity may increase with rise in temperature.
* Ni adsorption onto the studied adsorbents is pH dependent, at pH > 10 the removal of nickel from the medium seems to be due chemical precipitation, reflecting that the used adsorbents may be effectively used as a precipitating aid for nickel removal from aqueous medium.
* Fitting of different adsorption models for the adsorption of Ni on the different adsorbents reveals an anamolus values (negative values) for Langmuir and BET models.

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