Recovery of Mn(II), Ni(II) and Co(II) from aqueous-organic acid complexes: Adsorption mechanisms of metal-organic complexes onto Resinex™K-8 resin

M.M. Wassel, A.A. Swelam, A.M.A. Salem and A.S. El-Fekey

Department of Chemistry, Faculty of Science, Al-Azhar University, Cairo, Egypt.

ABSTRACT

This study examined the recovery of manganese Mn(II), cobalt Co(II) and nickel Ni(II)from aqueous-organic acid complexes using a strong cation exchange of **RESINEX™K-8** (H^+-form) resin, and the possible steric hindrance imposed by the larger bulky metal species on the resin loading capacity. Equilibrium adsorption tests of various low molecular weight organic acids (LMWOAs) concentrations at different temperatures were measured and analysed by fitting the experimental adsorption data to three empirical isotherm models: Langmuir, Freundlich and Temkin. The uptake of Mn(II), Co(II) and Ni (II) based on the stability and formation quotient constants of these metal complexes were used in examining the roles of steric hindrance in the adsorption of metal complexes on **RESINEX™K-8**. Analysis of the mechanism of adsorption of these complexes suggests the size and the nature of the type of metal complexes have a significant influence on the metal uptake. The metal loading capacity of the resin changed with the size of the metal complexes. The type and the number of anions which coordinated with the metal as ligands dictated the size of the complexes. The data obtained indicated that steric hindrance was not only the dominant factor governing the adsorption of these metals. The kinetic data were analyzed using first-order and pseudo-second order kinetic models. The results indicated that adsorption fitted well with the pseudo first-order for Ni(II) and Mn(II) and pseudo-second order kinetic model Co(II). Activation energy, Ea was determined as well as the thermodynamic parameters at different temperatures (25, 35 and 45^0C). Gibbs free energy analysis shows that Mn(II) and Ni(II) adsorption was spontaneous and it exhibited endothermic properties while Co(II) shows opposite trends.

Key words: Resinex™ K-8, Organic acids, Thermodynamic, Kinetic, Temperature

Introduction

Divalent metals in the environment are posing significant threats to human health and the environment. Soils are an important sink for these metals due to soils' highmetal retention capacities. Therefore, the behavior of divalent metals in soils is of increasing scientific concern. Many studies have demonstrated that adsorption–desorption is the most important process affecting the behavior of divalent metals in soils, hence their bioavailability and potential toxicity (Shan *et al.,* 2002). A variety of factors such as organic acids in soils can affect the metal release from soil and speciation in soil solution (Sarkar *et al.,* 2014). Increasing evidences have suggested that the anions of LMWOAs may play an important role in the fate of metals (Malandrino *et al.,* 2006). LMWOAs can form soluble complexes with metal cations (Lackovic *et al.,* 2004), thus modify the fixation of metals by soil organic matter, oxides, clays, and enhance their release (Iklas *et al.,* 2013). Such properties can be used in phytoremediation to increase metal bioavailability and hence the bioaccumulation of metals into plants, minimizing the environmental risk. There were several reports on the effect of LMWOAs on adsorption of metals (Anastopoulos and Ehaliotis, 2013 and Ma *et al.,* 2013).

Metal recovery from solution is typically achieved by techniques including chemical precipitationd (Calzado *et al.,* 2005), solvent extraction (Devi *et al.,* 1998) and adsorption (Virolainen*et al.,* 2014;Mayssa and Damien,2014 ;Katrina and Boyer, 2013 and Wanga *et al.,* 2014). Adsorption is conducted using adsorbents including activated carbon (Yadav *et al.,* 2014) and ion-exchange resins (Virolainen *et al.,* 2014). Although activated carbons are useful in removing organic solutes from solution, they are often not as effective in recovering metals from solutions in comparison to ion-exchange resins. Various types of ion-exchange resins are commercially available and are differentiated by their surface functional groups and nature of adsorption. These include cationic, anionic and chelating resins. Adsorption using chelating resins has found wide use in industry, in particular for divalent metal ion removal (Mayssa and Damien, 2014). Chelating resins are specially oriented ionic and non-ionic groups that are capable of exhibiting high adsorption selectivities and operating capacities. It is therefore not unusual to find that chelating resins have greater success in recovering metals from complex solutions in comparison to cation-exchange resins (Katrina and Boyer, 2013). Commercial chelating resins, for example Dowex M4195, Amberlite IRC748, Ionac SR-5 and Purolite S930, have been used to recover nickel and cobalt successfully from sulfate solutions (Wanga *et al.,* 2014).

Corresponding Author: A.A.Swelam, Department of Chemistry, Faculty of Science, Al-Azhar University, Cairo, Egypt.
E-mail: abdelsamihswelam@yahoo.com

41

Curr. Sci. Int. 3(1): 40-50, 2014

To date, the recovery of nickel, manganese and cobalt from bioleaching solutions by adsorption, has been hampered by the stability of metal-organic complexes. Basically this means the metal-organic complexes will adsorb on the resin surface without dissociating. Some work has examined the recovery of metals from organic acid complexes using ion-exchange resins, however, most have been conducted in-house in industry. Most of these results have been reported only in patents (Duyvesteyn *et al.,* 1997) and a few results have reached the open literature. Often the limited results that been reported provide little basis to understand the fundamental aspects of the adsorption process. An understanding of equilibrium and kinetics of adsorption is essential in design of adsorption units suitable for recovering metals from leaching operation of interest in this study. In this study, the role of steric hindrance in the uptake of metals on **RESINEX**[TM]**K-8** resin was examined.

A series of adsorption tests were therefore conducted to establish the equilibrium adsorption isotherms of Ni-, Mn- and Co-complexes on **RESINEX**[TM]**K-8**. The effects of variables including the type of complexing agents, organic acid concentrations and temperatures on the adsorption capacity, selectivity, adsorption mechanism of the resin were considered. To investigate the mechanism of adsorption, the adsorption data were fitted to different adsorption models such as the Langmuir, Freundlich and Temkin models.

Materials and Methods

Materials:

All the materials and chemicals (Aldrich, USA) were used as received with analytical grade. Stock solutions of cobalt, manganese and nickel were prepared by dissolving its chloride (AR Grade) in distilled water. The stock solution was diluted with distilled water to obtain the desired concentrations.Strong cation exchange of **RESINEX**[TM]**K-8** (H^+-form) used in this work from Jacobi Swedish Company. Prior to use, the resin was converted to the hydrogen (H^+) form by washing it in (1.0) M HCl followed by further washing in deionised water. The resin regeneration procedures follow the recommendations provided by the manufacturers. The resin-H was dried and kept at room temperatu**r**e in a desiccators until it was used.

The adsorption capacity in mg/g of the adsorbent (q_e) and the metal ion adsorption percentage (Ad%) were obtained by Eqs. (1) and (2),

$$q_e = \frac{(Co - Ce)V/1000}{W} \tag{1}$$

$$Ads\% = \frac{(Co - Ce)x100}{Co} \tag{2}$$

where (C_0) and (C_e) are the initial and final metal ion concentrations (mg/l), respectively, V is the volume of metal-organic complex solutions (L) and W is the weight of adsorbent used (g). The data of isotherms were obtained after an equilibrium time of (24 h). After the equilibrium time, the concentrations were determined by AAS varion 6 (Analytik Jena AG Konrad-Zuse-StraBe 1 07745 Jena)

Batch adsorption studies:

Adsorption studies were carried out in a batch mode by shaking (0.5 g) resin in (50 ml) solution of Co(II), Ni(II) and Mn(II) onto the water bath shaker at 100 rpm stirring speed. Effect of low molecular weight organic acids (LMWOAs) on the Co(II), Ni(II) and Mn(II) adsorption onto **RESINEX**[TM]**K-8**was conducted through varying the concentration in the range (0.01–0.1 M) . Furthermore the adsorption studies were also carried out by varying time interval (5–210 min) at 7.7mmol/L of Co(II), Ni(II) and Mn(II) to optimize the time required for the removal of these metal ions.

Results and Discussion

1-Effect of contact time on removal of metal ions:

These studies were carried out at metal ion concentration of (7.7mmol/L) at 25^0C in aqueous-low molecular weight organic acids solutions, the time taken at constant manganese concentration (7.7mmol/L), 25^0C and organic acid concentration of (0.01M) for the uptake of the manganese ions in both aqueous-acetic, tartaric and citric acid solutions. From the data obtained and illustrated in (Fig. 1) as for kinetic studies the preliminary results show that the time taken for manganese equilibrium uptake is obtained within (5–210 min). Then no appreciable changes in sorption were noticed after (210 min). Therefore the phase contact time of (210 min) was used for the other batch tests. In general, the ion exchange rate of Mn(II) follows the order; Citric >Acetic >Tartaric acid solution. It is therefore likely that the size of the ligands played a little role in the order of the manganese Mn(II)-complex adsorption, where the adsorption capacities was influenced not only by the steric

hindrance but also on the crowding effect and the stability constants of manganese-complexes,while for cobalt and nickel uptake within (5–150 min). Then no appreciable changes in sorption were noticed after (150 min).
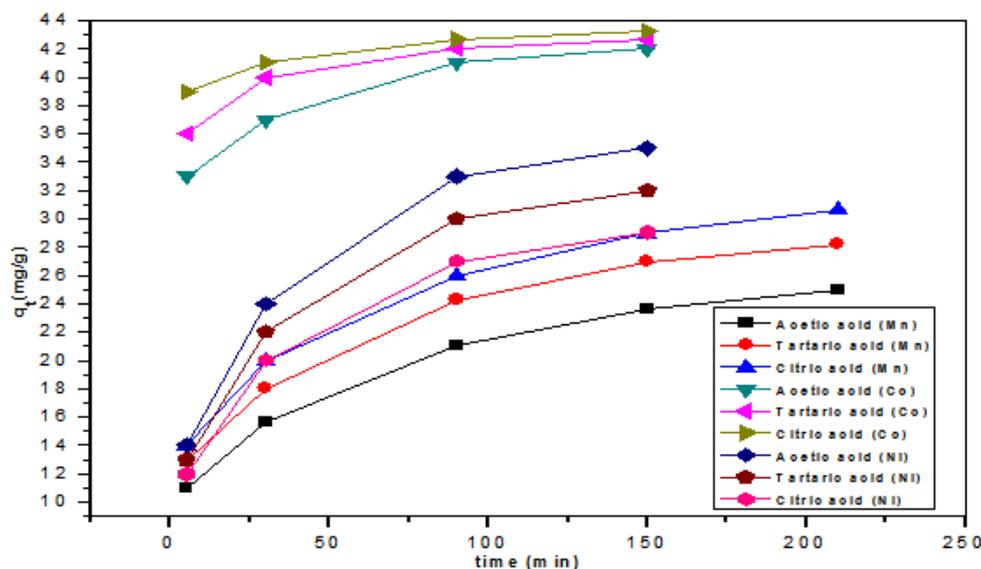

Fig. 1: Contact time on the adsorption of Mn (II). Co (II) and Ni (II) in aqueous-organic acids at 25^0C.

Among the three aqueous- organic acid complexes solutions taken for the study, the order of the manganese percentage uptake (%) is follows; Acetic acid (59%) < Tartaric acid (66.7%) < Citric acid (72.3%), for cobalt follows; Acetic acid (92.6%) < Tartaric acid (94.1%) < Citric acid (95.4%) and Acetic acid (77.4%) > Tartaric acid (70.87%) > citric acid (64.13%) for nickel percentage uptake (%).The order of metals uptake from solution with LMWOAs also provides good evidence that complexation processes were controlling the uptake of metal from solution as it reflects the complex stability of organic ligands with metals.

This dominant role of LMWOAs may be interpreted by the following reasons: (a) This complexation would induce a decrease in the concentration of metal ions in solution, leading to a shift in the right direction in the chemical adsorption (b) The introduction of LMWOAs to the adsorption system may cause the change of the surface characteristics of the resin, competitive distribution of metal ions between resin surface and organic ligands in the solution (Martell and Smith, 1997 and Qin and Wei,2004).

Effect of organic ligands and its concentrations on adsorption processes:

From the data obtained and illustrated in (Figs. 2-4) we can observed that, when the concentration of organic ligands in adsorption solution is low (0.01M), Co(II) in adsorption solution would be bound by organic ligands adsorbed to the adsorbent(Huangand Bethelin, 1995 and Yanzheng*et al.,* 2003), which, on the whole, will lead to the reduction of Co(II) adsorption in the presence of low concentrations of each acetate, tartrate or citrate. However, with the continuous enhancement of organic acid concentration in adsorption solution, the ratio of organic ligands concentration in solution to the organic ligands adsorbed by the resin becomes larger. An increased competition ability of organic ligands in the solution for binding Co(II) led to inhibition of adsorption, as a result lower Co(II) uptake with increments of organic acid concentration. In opposite trend when the concentration of LMWOAs changed from (0.01to 0.1M) Mn(II) adsorption was enhanced directly, and no inhibition was shown for the given citrate concentration, for this reason, the uptake of manganese increased when initial concentration of LMWOAs increased from (0.01to 0.1M) indicating that steric hindrance was not only the dominant factor governing the adsorption of metals. Compared with Ni(II), the uptake of Ni(II) in these three types of acids with varied initial concentration values. It first increased, when the initial concentration of LMWOAs increased from (0.01 to 0.05M) then decreased at (0.1M). These may be arise because the crowding effects and steric hindrance.
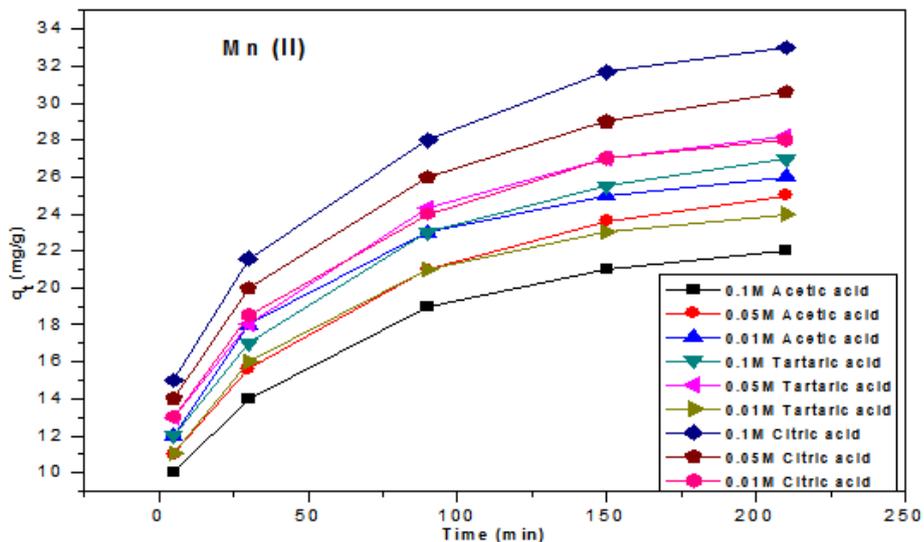
Fig. 2: Mn(II) adsorption by Resinex[TM] K-8 at different concentrations in aqueous-organic acids at 25^0C.
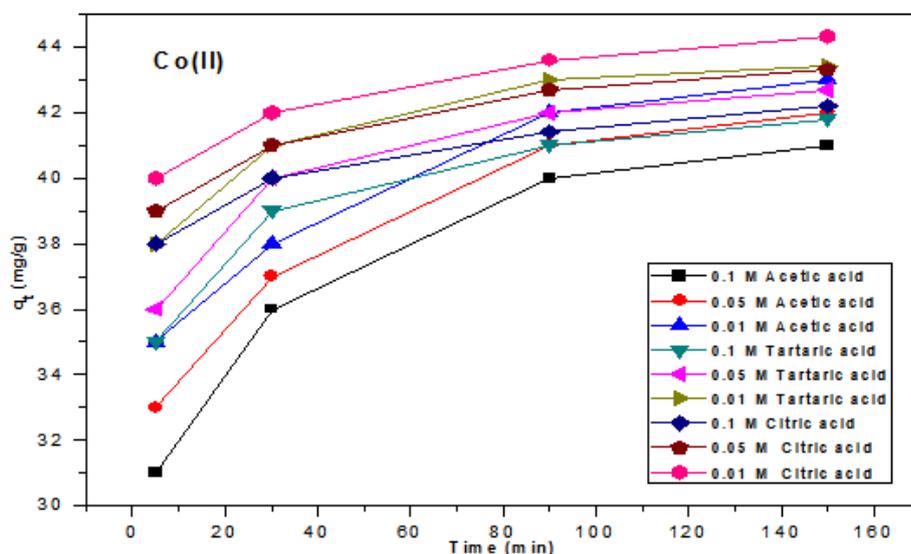

Fig. 3: Co(II) adsorption by Resinex[TM] K-8 at different concentrations in aqueous-organic acids at 25^0C.
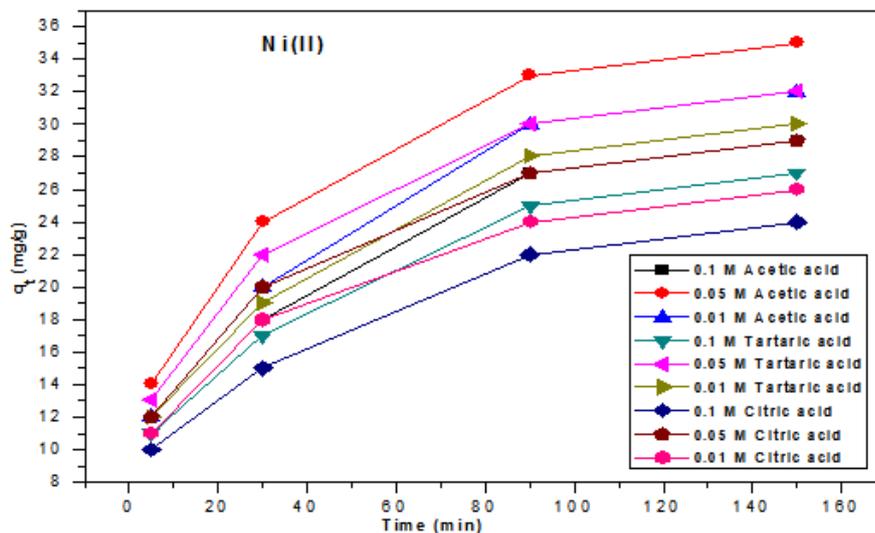

Fig. 4: Ni(II) adsorption by Resinex[TM] K-8 at different concentrations in aqueous-organic acids at 25^0C.

3-Adsorption mechanisms and effect of steric hindrance:

To examine the effect of steric hindrance imposed by the bulkiness of the organic anions coordinated with cobalt Co(II), manganese Mn(II) and nickel Ni(II). The metal complexes adsorption data were fitted to the empirical correlations; Freundlich,1907, Langmuir (El Qada *et al.,* 2006), and Temkin (Mane *et al.,* 2007) isotherm models.

The Freundlich isotherm is applicable to highly heterogeneous surfaces, and an adsorption isotherm lacking a plateau indicates a multi-layer adsorption. The linear form of the Freundlich isotherm is given by the following equation (Mane *et al.,* 2007):

$$\log q_e = \log K_F + (1/n)\log C_e \tag{3}$$

Where (q_e) is the amount of the metal adsorbed (mg/g), (C_e) is the equilibrium concentration of the metal solution (mg/L). (K_F) and n are the Freundlich constants which indicate the capacity and the intensity of the adsorption, respectively. Thus a plot of ($\log q_e$)Vs. ($\log C_e$) should be a straight line with a slope of (1/n) and an intercept of $\log K_F$ (Figs. are not shown). The values of the Freundlich constant (n) (Table 1) showing that the adsorption process may be favorable. (R^2) value (<0.99) for Ni(II) and Mn(II) ions in aqueous-acetic acid solutionsas well as Ni(II), Mn(II) and Co(II) ions in aqueous-tartaric acid solutions also, Mn(II) and Co(II) ions in aqueous-citric acid solutions obtained from Freundlich isotherm indicated that Freundlich model is not suitable.

Langmuir isotherm model. Langmuir adsorption isotherm was applied to equilibrium adsorption assuming monolayer adsorption onto the surface with a finite number of identical sites. The following Langmuir sorption isotherm equation was used:

$$C_e/q_e = 1/K_L Q_m + C_e/Q_m \tag{4}$$

Where (q_e) is the amount of the metal adsorbed on adsorbent (mg/g) at equilibrium(C_e) is the equilibrium concentration (mg/L) of the metal in solution, (Q_m) is the monolayer adsorption capacity (mg/g) and (k_L) is the Langmuir constant (L/mg) related to the free energy of adsorption. The values of (Q_m) and (k_L) were calculated from the slopes ($1/Q_m$) and intercepts ($1/k_L Q_m$) of the linear plots of (C_e/q_e) Vs. (C_e) (Figs. are not shown) and are given in (Table 1). The linearity of plots revealed that the adsorption followed Langmuir isotherm model. The essential characteristic of the Langmuir isotherm can also be evaluated by dimensionless adsorption intensity (R_L)given by Nasir *et al.*(2007)

$$R_L = 1/1 + K_L C_o \tag{5}$$

Where (C_o) (mg/L) is the initial concentration of the metal adsorbed and (k_L) (L/mg) is the Langmuir constant. (R_L) values represent the type of isotherm and its value between 0 and 1 indicates favorable adsorption. The (R_L) values evaluated from the (k_L) values for Co(II), Ni(II) and Mn(II) ions at various temperatures were found to be between (0 and 1.0), further suggesting that the adsorption of Co(II), Ni(II) and Mn(II) onto **RESINEX[TM]K-8**was favorable. The lower (R_L) values implied that the interaction of Co(II) and Ni(II) ions with **RESINEX[TM]K-8** is stronger than Mn(II) ion.

The Temkin isotherm can be expressed by the following equation:

$$q_e = (RT/b_T)\ln A_T + (RT/b_T)\ln C_e \tag{6}$$

Where $B_T = RT/b_T$, (b_T) is the Temkin constant (J/mol) related to adsorption heat, (T) is the absolute temperature (K), (R) is the gas constant (8.314 J/mol K), and (A_T) is the Temkin isotherm constant (L/ g). B_T and (A_T) can be calculated from the slopes (B) and intercepts (B ln A_T) of the plot of (q_e) Vs. (ln C_e) (Figs. are not shown). The Temkin constants (B), (b_T) and (A_T) together with the (R^2) values are shown in (Table 1). The heat of adsorption of the three divalent metal ions in the layer would decrease linearly with coverage due to adsorbate/adsorbate interactions.

However, the values of (R^2) from Langmuir isotherm for Ni(II) and Mn(II) ions in aqueous-Acetic acid solutions as well as Ni(II), Mn(II) and Co(II) ions in aqueous-tartaric acid solutions, also, Mn(II) and Co(II) ions in aqueous-citric acid solutions are greater than those from other isotherms (Freundlich and Temkin), indicating the adsorption process of these metal ions onto **RESINEX[TM]K-8**is better described by Langmuir isotherm.

45

Curr. Sci. Int. 3(1): 40-50, 2014

Table 1: Adsorption isotherm parameters of Mn(II), Co(II) and Ni(II) on Resinex[TM] K-8 in organic acids.

Metal ions	Langmuir parameters				Freundlich parameters			Temkin parameters		
	Q_o	k_L	R_L	R^2	n	K_f	R^2	k_T	B_T	R^2
	(mg/g)	(L/mg)				mg/g		L/g	J/mol	
ACETIC ACID										
Mn(II)	19.00	0.023	0.106	0.9901	2.10	291.4	0.9895	9.1×10^{-4}	13.35	0.9879
Co(II)	35.71	0.190	0.011	0.9980	9.69	60.30	0.7245	3.34×10^{-6}	4.62	0.9858
Ni(II)	32.30	0.110	0.020	0.9949	6.70	70.80	0.9286	2.5×10^{-5}	5.96	0.9481
TARTARIC ACID										
Mn(II)	20.60	0.026	0.833	0.99936	2.20	263.7	0.9835	7.03×10^{-4}	12.20	0.9884
Co(II)	38.36	0.360	6.1×10^{-3}	0.99874	13.65	54.35	0.9774	3.9×10^{-7}	3.70	0.9811
Ni(II)	28.27	0.060	0.038	0.99203	4.54	96.09	0.9368	1.7×10^{-4}	8.50	0.9779
CITRIC ACID										
Mn(II)	25.40	0.049	0.046	0.9972	4.20	96.20	0.9597	3.4×10^{-4}	9.36	0.9998
Co(II)	39.60	1.800	1.2×10^{-3}	0.9999	10.00	59.20	1.0000	2.1×10^{-8}	2.95	0.9812
Ni(II)	22.99	0.029	0.083	0.9928	2.49	222.8	0.9958	5.7×10^{-4}	12.29	0.9891

4-Adsorption kinetics:

The adsorption kinetics of Co(II), Ni(II) and Mn(II) ions onto **RESINEX[TM] K-8**, was investigated with the aid of three kinetic models, namely Lagergren's pseudo-first order (Lagergren,1998), Ho and McKay's pseudo-second order (Ho and McKay, 2000) and Weber-Morris's intraparticle diffusion(Weber, and Morris,1963) models to analyze the experimental data. The pseudo-first-order rate model of Lagergren is based on solid adsorbent capacity and generally expressed as follows:

$$\text{Log}(q_e-q_t)=\log q_e-\frac{k1}{2.303} t \qquad (7)$$

Where (q_e) is the amount of solute adsorbed at equilibrium per unit weight of the adsorbent (mg/g), q_t is the amount of solute adsorbed at any time (mg/g) and k_1 (min/1) is the adsorption rate constant. Values of (k_1) calculated from the plots of Log ($q_e - q_t$) Vs. (t) at different temperatures (Fig. is not shown) are summarized in (Table 2). The correlation coefficient values were high and the calculated (q_e) values obtained from this kinetic model show good agreement with the experimental one. These results suggest that the pseudo-first-order model describe the adsorption kinetics of Ni(II) and Mn(II) ions onto **RESINEX[TM]K-8**. However, for Co(II) uptake the correlation coefficient values were low and the calculated q_e values obtained from this kinetic model did not show good agreement with the experimental one. These results suggest that the pseudo-first-order model does not describe the adsorption kinetics of Co(II) onto**RESINEX[TM]K-8**.This behavior is predominates for all aqueous-organic acids solution.The pseudo-second order model can be expressed as:

$$(t/q_t)=(1/k_2 q_e^2)+(1/q_e)t \qquad (8)$$

Where (k_2) (g/mg min) is the rate constant of the pseudo-second-order equation (q_e) (mg/g) is the maximum adsorption capacity, and q_t (mg/g) is the amount of adsorption at time t (min). The plot of (t/q_t) Vs. (t)(Fig. is not shown)shows a linear relationship. The value of (q_e) (mg/g) and (k_2) (g/mg min) are determined from the slope and intercept of the plot. The results are summarized in (Table 2). It can be seen that the calculated coefficient of determination (R^2) for Co(II) is very close to unity and that q_e (cal) values agree approximately with the experimental values. These results suggest that the pseudo second-order model describes the adsorption kinetics of the present system. k_2 values decreased with the increased temperatures. This decrease in k_2 values at higher temperatures seems due to the repulsion between the adsorbed and the non-adsorbed Co(II) ions.

To gain insight into the mechanisms and rate controlling steps affecting the kinetics of adsorption, the intra-particle diffusion plays an important role in the extent of adsorption and can be expressed as:

$$q_t=k_i t^{0.5}+C \qquad (9)$$

where (k_i) is the intraparticle diffusion constant (mg/g min) and the intercept (C) reflects the boundary layer effect. The values of (k_i) were calculated from slopes (k_i) of the plots of (q_t) Vs. ($t^{0.5}$) (Fig. is not shown) and are presented in (Table 2). The plot of (q_t) Vs. ($t^{0.5}$) should be linear if intraparticle diffusion is involved in the adsorption process and if these lines pass through the origin then Intraparticle diffusion is the rate controlling step. When the plots do not pass through the origin, this is indicative of some degree of boundary layer control and further shows that the intraparticle diffusion is not the only rate limiting step, but also other kinetics models

may control the rate of adsorption, all of which may be operating simultaneously. In the present workthe plots of q_t vs. $t^{0.5}$do not pass through the origin, showing that intra-particle diffusion is not the only rate controlling step.

In order to study the thermodynamics of adsorption studies were performed at (25, 35 and 45^{0}C).

Table 2: Kinetic parameters for of Ni(II), Co(II) and Mn(II) on Resinex^{TM} K-8 in organic acids.

		Pseudo first-order model			Pseudo second-order model				Intraparticle diffusion model		
		$q_{e,1,cal}$	K_1	R^2	$q_{e,2,cal}$	K_2	h	R^2	K_{int}	C	R^2
		(mg/g)	(min^{-1})		(mg/g)	(g/mg min)	(mg/g min)		(mg/g min$^{-0.5}$)	(mg/g)	
ACETIC ACID											
Mn(II)	Temp.K										
	298	15.3	0.016	0.9973	27.00	1.77 x10^{-3}	1.3	0.9913	1.17	8.99	0.9786
	308	19.9	0.017	0.9705	30.20	1.8 x10^{-3}	1.6	0.9881	1.42	8.83	0.9829
	318	23.1	0.016	0.9681	33.00	2.2 x10^{-3}	2.4	0.9834	1.68	8.68	0.9908
Co(II)											
	298	10.46	0.026	0.9978	42.60	7.8 x10^{-3}	13.60	0.9993	0.918	31.49	0.9496
	308	11.25	0.024	0.9981	41.10	6.5 x10^{-3}	10.98	0.9991	1.03	28.48	0.9400
	318	12.4	0.021	0.9797	39.80	5.4x10^{-3}	8.60	0.9985	1.18	25.32	0.9423
Ni(II)											
	298	25.01	0.028	0.9997	37.60	2.15x10^{-3}	3.04	0.9955	2.13	10.79	0.9332
	308	20.70	0.014	0.9402	45.50	2.21x10^{-3}	3.81	0.9944	2.16	14.31	0.9471
	318	24.70	0.027	0.9881	47.00	2.39x10^{-3}	4.71	0.9949	2.08	18.20	0.9954
TARTARIC ACID											
Mn(II)											
	298	16.97	0.0173	0.9958	29.8	2.2 x10^{-3}	1.95	0.9939	1.28	10.85	0.9687
	308	17.60	0.0168	0.9989	30.5	2.3 x10^{-3}	2.1	0.9947	1.37	10.51	0.9579
	318	19.10	0.0160	0.9989	32.0	2.4 x10^{-3}	2.5	0.9924	1.46	10.74	0.9699
Co(II)											
	298	6.86	0.026	0.9675	43.12	0.01300	24.2	0.9999	0.653	5.37	0.8656
	308	9.76	0.033	0.9987	42.10	0.01100	19.5	0.9997	0.84 3	2.16	0.8599
	318	13.21	0.039	0.9984	41.20	8.2 x10^{-3}	13.9	0.9997	1.04	28.91	0.8602
Ni(II)											
	298	21.94	0.027	0.9998	34.30	2.4x10^{-3}	2.82	0.9953	1.92	10.08	0.9379
	308	21.21	0.026	0.99863	7.90	2.79x10^{-3}	4.00	0.9959	1.83	14.98	0.9496
	318	22.82	0.022	0.9987	40.03	3.00x10^{-3}	4.80	0.9962	2.38	14.75	0.9992
CITRIC ACID											
Mn(II)											
	298	17.90	0.0160	0.9967	32.4	2.9 x10^{-3}	2.00	0.9933	1.37	11.9	0.9723
	308	19.20	0.0151	0.9989	34.6	1.97 x10^{-3}	2.40	0.9927	1.48	12.6	0.9755
	318	19.90	0.0154	0.9985	36.5	2 x10^{-3}	2.70	0.9939	1.55	13.7	0.9676
Co(II)											
	298	4.69	0.0230	0.9987	43.6	0.01800	34.2	0.9999	0.43	38.3	0.9522
	308	4.50	0.0245	0.9985	42.5	0.01700	30.7	0.9999	0.41	37.4	0.9377
	318	4.67	0.0248	0.9998	41.6	0.01400	24.2	0.9999	0.42	36.4	0.9417
Ni(II)											
	298	19.12	0.025	0.99990	30.70	2.3x10^{-3}	2.2	0.9826	1.72	9.37	0.9434
	308	19.12	0.025	0.99090	35.96	2.55x10^{-3}	3.3	0.9932	1.72	13.37	0.9434
	318	21.21	0.026	0.99875	37.9	2.79x10^{-3}	4.0	0.9959	1.841	4.98	0.9496

5-Temperatures and Thermodynamics of Ni(II), Co(II) and Mn(II) adsorption:

Effect of temperature on the adsorption of Ni(II), Co(II) and Mn(II) from aqueous-organic acids (acetic, tartaric and citric acid) solutions onto the **RESINEX^{TM}K-8**was performed at (25, 35 and 45^{0}C). As can be seen from (Figs. 5-7) in general, the Ni(II) and Mn(II) uptake tended to increase with the increase of temperatures from 25-45^{0}C for all aqueous-organic acids solutions studied. Enhancement of the adsorption capacity at higher temperatures may be attributed to the enlargement of pore size and/or activation of the adsorbent surface (Jhaa*et al.,* 2008). Opposite trend was also observed for Co(II) adsorption. This may be due to low stability constant of Co(II) complex with the **RESINEX^{TM}K-8**.
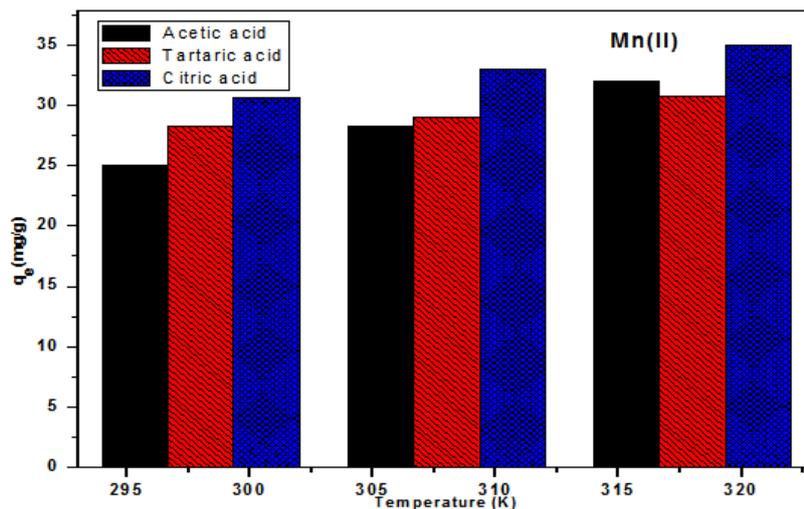
Fig. 5: Effect of temperature on the adsorption uptake of Mn(II) in aqueous-organic acids at 25,35, and 45 ^{0}C
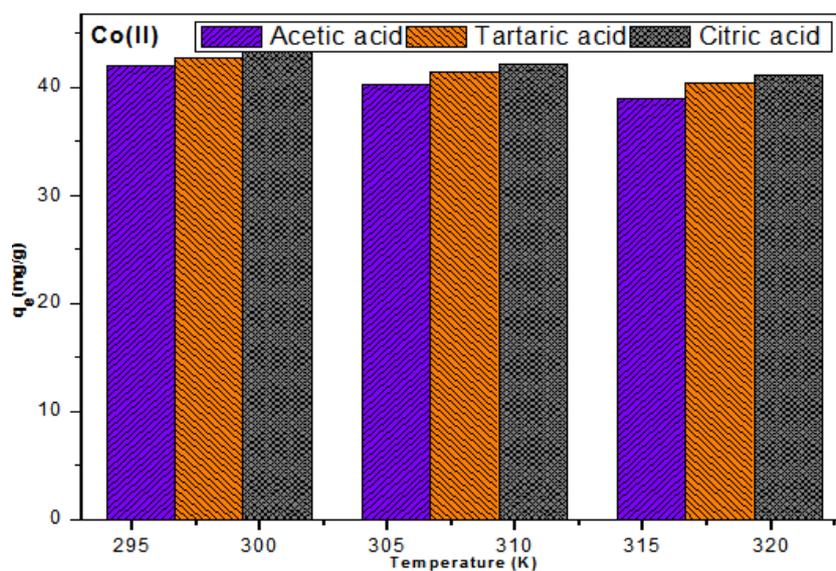

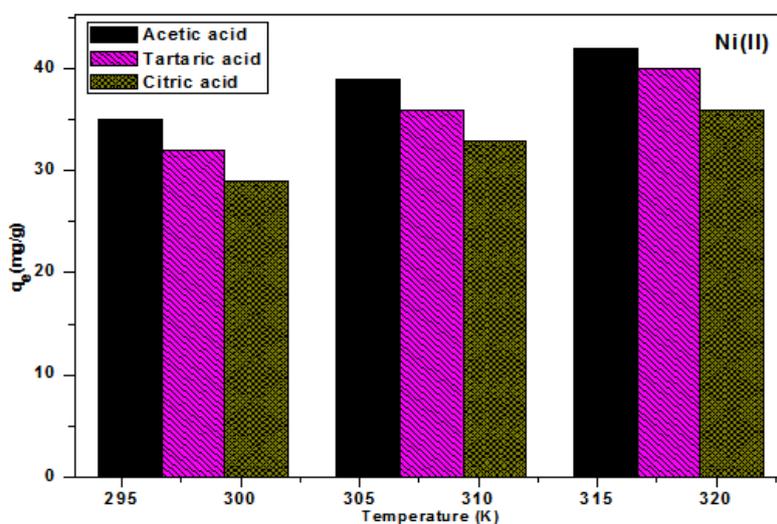**Fig. 6:** Effect of temperature on the adsorption uptake of Co(II) in presence of organic acids at 25,35, and 45 ^{0}C

Fig. 7: Effect of temperature on the adsorption uptake of Ni(II) in presence of organic acids at 25,35, and 45 ^{0}C

48

Curr. Sci. Int. 3(1): 40-50, 2014

From (Figs.8) thermodynamic parameters were determined for temperatures ranging from (25 to 45^{0}C) using the equilibrium constant $K_D= (q_e/C_e)$.The parameters of enthalpy (ΔH) (kJ/mol) and entropy (ΔS) (J/mol) related to the adsorption process were calculated from the following equation:

$$logK_D=\Delta S/R−\Delta H/RT \tag{10}$$

The parameters of enthalpy (ΔH) and entropy (ΔS) can be calculated from the slope and the intercept of the linear plot of (lok$_D$) Versus (1/T). The data obtained from the thermodynamic plots and the related parameters are collected in (Table 3). From the data obtained in (Table 3) we can observed that the values of $\Delta H°$ were positive for Ni(II) and Mn(II) indicating that the adsorption process is endothermic in nature, while the negative $\Delta H°$ values confirmed the exothermic nature of Co(II) adsorption.

However, the positive values of (ΔS)for Ni(II) and Mn(II) showed the increased randomness at the solid/solution interface during the adsorption process. The adsorbed water molecules, which were displaced by the adsorbate species, gained more translational energy than was lost by the adsorbate ions, thus allowing the prevalence of the randomness in the system. Moreover negative (ΔS) value showed reduction in affinity of Co (II) onto the **RESINEX^{TM}K-8**.In addition, The change in free energy ($\Delta G°$) was determined as follows:

$$\Delta G°=−RTlnK_D \tag{11}$$

Where (ΔG) is the standard free energy (kJ/mol), (R) is the ideal gas constant (8.314J/mol K). Depending on types of the metal ions. The values of standard free energy change (ΔG) were negative under the conditions applied, the ion exchange of the metal ions was spontaneous. The values of (ΔG) becomes more negative with the increase of temperature for Ni(II) and Mn(II) indicated more efficient adsorption at high temperature and hence its adsorption become more favorable. While for Co(II) values of ΔG becomes less negative or positive with the increase of temperature indicated lower efficient adsorption at high temperature and hence its adsorption become less favorable at high temperature (Arias and Sen, 2009; Samiey and Toosi, 2010; Sepehra *et al.,* 2013; Franco *et al.,* 2013 and Sharma *et al.,* 2013). The result derived from the references and this work indicates that the thermodynamic parameters are related to the nature of metal ions.
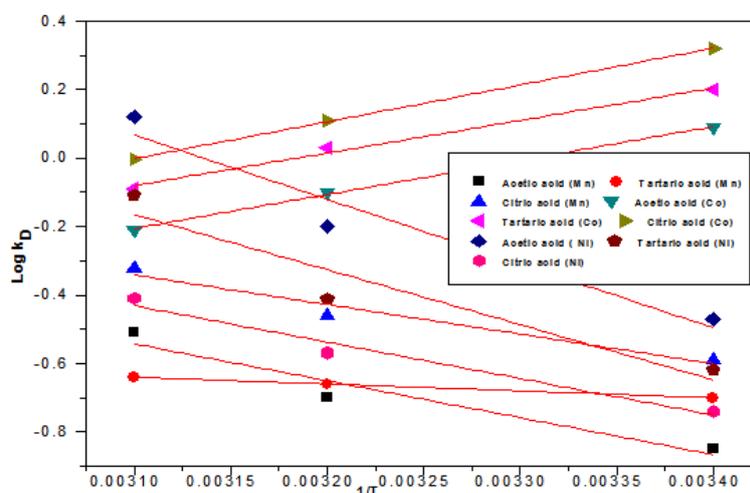

Fig. 8: Van't Hoff plot for Mn (II), Co(II) and Ni(II) adsorption by Resinx^{TM} K-8 in aqueous-organic acids at different tem pretures (25,35 and 45 ^{0}C)

The activation energy, Ea (kJ mol^{-1}) can also be calculated using the following equation:

$$logk_2=lnA−Ea/RT \tag{12}$$

The positive values of activation energy in (Table 3)(fig. 9) indicated that the minimum energy is required to facilitate the forward (M^{2+}–H^+) ion-exchange process and endothermic process. The order of activation energy to facilitate the ion exchange processes for the divalent metal ions was observed to be Ni(II) > Mn(II) for Tartaric and Citric complex solutions. While for acetic complex solution opposite trend were observed since Mn(II) > Ni(II). The higher activation energy for M^{2+}–H^+ exchange as compared to other M^{2+}–H^+ exchange may be considered due to higher ionic radii even though ionic mobility for the metal ions is same (Alothman *et al.,* 2012).
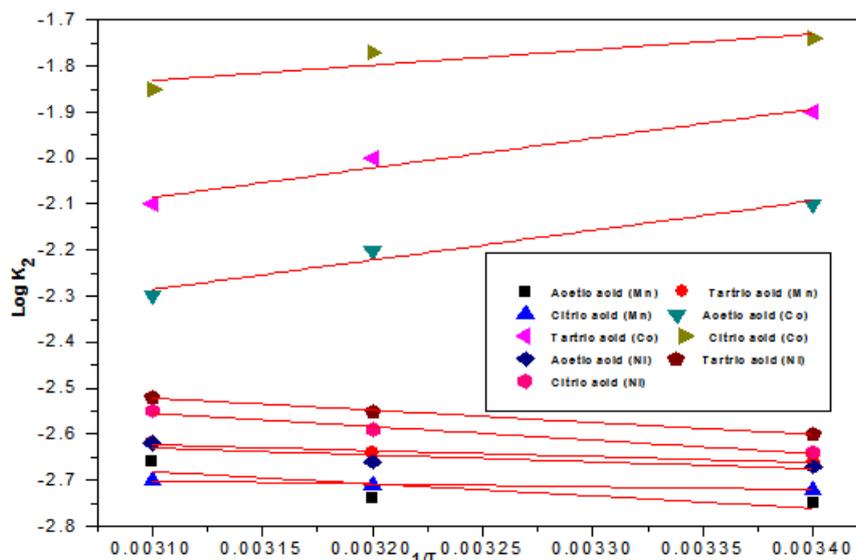
Fig. 9: Arrhenius plot for Mn(II), Co(II) and Ni(II) adsorption by resinx K-8 in aqueous-organic acids at different tem pretures (25,35 and 45 ^{0}C)

Table 3: Thermodynamic parameters for of Ni(II), Co(II) and Mn(II) on Resinex^{TM} K-8 in organic acids.

	ΔG (KJ/mol)	ΔS (J/mol k)	ΔH (KJ/mol)	A	Ea (kJ/mol)
ACETIC ACID					
Ni(II)					
Temp.K					
298	-2.67	112.8	35.97	6.8×10^{-3}	1.25
308	-1.18				
318	-0.719				
Co(II)					
298	0.53	-62.87	-19.01	5.3×10^{-5}	-5.34
308	0.60				
318	1.27				
Mn(II)					
298	-4.87	53.6	20.65	0.0137	2.20
308	-4.12				
318	-3.10				
TARTARIC ACID					
Ni(II)					
298	-3.54	92.2	30.77	0.0199	2.20
308	-2.41				
318	-0.691				
Co(II)					
298	1.14893	-62.9	-19.01	8.3×10^{-5}	-5.34
308	0.173.3				
318	0.557.1				
Mn(II)					
298	-3.99	-0.38	3.83	5.97×10^{-5}	1.07
308	-3.88				
318	-3.89				
CITRIC ACID					
Ni(II)					
298	- 4.25	54.9	20.38	0.023	2.43
308	- 3.35				
318	- 2.49				
Co(II)					
298	1.81	-63.9	-20.60	1.3×10^{-3}	-2.79
308	6.32				
318	26.6				
Mn(II)					
298	-3.34	44.8	16.55	3.1×10^{-3}	0.54
308	-2.69				
318	-1.94				

References

Alothman, Z.A., M.M. Alam and M. Naushad, 2012. J. Indust. Eng. Chem. in press.

Anastopoulos, I.M. and C. Ehaliotis, 2013. Chem. Eng. J. 231: 245-254.

Arias, F. and T.K. Sen, 2009. Colloids Surfaces A: Physicochem. Eng. Aspects., 348: 100-108.

Calzado, L.E., C.O. Gomez and J.A. Finch, 2005. Miner. Eng., 18(5): 537-543.

Devi, N.B., K.C. Nathsarma and V. Chakravortty, 1998. Hydrometallurgy, 49(1-2): 47-61.

Duyvesteyn, W.P.C. and M. Omofoma, 1997. U.S. Patent 5: 626-648.

El Qada, E.N., S.J. Allen and G.M. Walker, 2006. Chem. Eng. J. 124: 103-110.

Franco, P.E., M.T. Veit, C.E. Borba, G.C. Gonçalves, M.R. Fagundes-Klen, R. Bergamasco, E.A. Silva and P.Y.R. Suzaki, 2013. Chem. Eng. J., 221: 426-435.

Freundlich, H., 1907. Ueber dye adsorption in loesungen, Z. Phys. Chem., 57: 385-470.

Ho, Y.S. and G. McKay, 2000. Water Res., 34: 735-742.

Huang, P. and J. Bethelin, 1995. Florida: CRC Press, 2: 376-84.

Iklas, S., S. Smiljanic, A. Peric´-Grujic, M. Šljivic´-Ivanovic and D. Antonovic, 2013. Chem. Eng. J., 214: 327-335.

Jhaa, M.K., R.R. Upadhyay, J.C. Lee and V. Kumar, 2008. Desalination, 228: 97-107.

Katrina, A.I., and T.H. Boyer, 2013. Sep. and Purif.Technol., 118: 112-119.

Lackovic, K., M. Angove, D.W. John and B.B. Johnson, 2004. J. Colloid and Interf. Sci., 269: 37-45.

Lagergren, S., 1998. kungliga svenska vetenskap sakademiens, Handlingar, 24(04): 1-39.

Ma, L., Y. Peng, B. Wua, D. Lei and H. Xu, 2013. Chem. Eng. J. 225: 59-67.

Malandrino, M., O. Abollino, A. Giacomino, M. Aceto and E. Mentasti, 2006. Journal of Colloid and Interf. Science, 299: 537-546.

Mane, V.S., I.D. Mall and V.C. Srivastava, 2007. J. Environ. Manage., 84: 390-400.

Martell, E.A. and M.R. Smith, 1977. Plenum Press, 3 New York.

Mayssa Y., and R. Damien, 2014. Surf. Sci., 619: 10-18.

Nasir, M.H., R. Nadeem, K. Akhtar, M.A. Hanif and A.M. Khalid, 2007. J. Hazard. Mater., 147: 1006-1014.

Qin, F., X. Shan and B. Wei, 2004. Chemosphere, 57: 253-263.

Samiey, B. and A.R. Toosi, 2010. Journal of Hazard. Mater., 184: 739-745.

Sarkar, D., D. Kumar, R. Das and B. Mandal, 2014. Geoderma, 214-215: 213-216.

Sepehra, M.N., M. Zarrabia, H. Kazemianb, A. Amranec, K. Yaghmaiand and H.R. Ghaffarie, 2013. Appl. Surf. Sci. in press.

Shan, X., J. Lian and B. Wen, 2002. Chemosphere, 47: 701-710.

Sharma, P., M. Sharma and R. Tomar, 2013. J. of the Taiwan Institute of Chem. Eng. in press in press.

Virolainen, S., I. Suppula and T. Sainio, 2014. Hydrometallurgy, 142: 84-93.

Wanga, J., K. Zhang and L. Zhao, 2014. Chem. Eng. J., 239: 123-131.

Weber, W.J. and J.C. Morris, 1963. J. Sanit. Eng. Div. ASCE., 89: 31-59.

Yadav, S.K., D.K. Singh and S. Singh, 2014. J. Environm.Chem. Eng., 2: 9-19.

Yanzheng, G., J. Heb, W. Ling, H. Hub and F. Liub, 2003. Environ.Internat., 29: 613-618.