ADSORPTION OF Cr(VI) FROM AQUEOUS SOLUTION USING A LOW COST ACTIVATED CARBON PREPARED FROM POMEGRANATE PEEL

M. Jambulingam, N. Renugadevi*, S. Karthikeyan[†] and J. Kiruthika[††]
Department of Chemistry, PSG College of Arts and Science, Coimbatore, Tamil Nadu
*Department of Chemistry, Avinashilingam Deemed University, Coimbatore, Tamil Nadu
[†] Department of Chemistry, Erode Sengunthar Engineering College, Erode, Tamil Nadu
[††]Department of Biotechnology, Karpagam Arts and Science College, Coimbatore, Tamil Nadu

ABSTRACT

Studies on removal of Cr(VI) from aqueous solution using activated pomegranate peel carbon have been carried out at 32°C. Various parameters such as initial concentration of adsorbate, pH, adsorbent dosage and agitation time were studied by conducting batch mode experiments. The experimental adsorption data fitted reasonably well to Langmuir and Freundlich adsorption isotherms. The adsorption follows Lagergren first order kinetic model. The thermodynamic parameter enthalpy change (ΔH) suggests exothermic nature of adsorption of Cr(VI) on to activated pomegranate peel carbon.

INTRODUCTION

The treatment of wastewater containing metals is a challenging problem. Chromium, in particular, has received a great deal of attention. The increased environmental burden of Cr(VI) may come from various industrial sources like those from electroplating, leather tanning, textiles and metal-finishing industries (Udy 1956). In solutions, it is found in its different oxidation states, for example, the electroplating and metal finishing wastes contain Cr(VI), while textile and tanning wastes may contain either trivalent or hexavalent chromium (Thackston 1973). Chromium enters into water resources through discharge of untreated industrial effluents. Cr(III) is less toxic than Cr(VI) (Udy 1956). Cr(VI) has been reported to be a potent carcinogen producing cancer of various parts of the body (Mukherjee 1986). Various technologies available for the removal of Cr(VI) from aqueous solutions include ion-exchange, solvent extraction and chemical precipitation etc. (Dean et al. 1972). But these methods are cost intensive and are unaffordable for large scale treatment of wastewater rich in Cr(VI) for developing countries like India. Adsorption using activated carbon is one of the efficient process for treatment of wastewater. But, the high cost of activated carbon limits its use for removing metals from waste water. Therefore, the production of low cost alternatives has been the focus of researchers in the area for the last few years. Efforts made in this direction for the removal of metals from aqueous solution using agricultural and industrial wastes are well documented. Several low cost and non-conventional adsorbents have been used for heavy metal removal.

Adsorbents used include fly-ash (Nagarnaik et al. 2003, Brain et al. 2002) wollastonite (Swamy et al. 1998, Sharma 2001, Saravana et al. 2002) sawdust and rice husk with coir pith carbon (Namasivayam & Kadirvelu 2000).

This technique has an added advantage of having no sludge disposal problems as compared with the conventional precipitation technique. The objective of this investigation is to study the effect of initial concentration of Cr(VI) solution, pH, adsorbent dose and agitation time on the extent of Cr(VI) adsorption and to fit the adsorption data to Langmuir and Freundlich adsorption isotherms and

M. Jambulingam et al.

Lagergren first order kinetic model and also to evaluate thermodynamic parameters like change in free energy, enthalpy and entropy.

MATERIALS AND METHODS

Preparation of adsorbent: Pomegranate peel was collected from local juice factory in Coimbatore city. It was cut into small pieces, dried, powdered and activated using concentrated sulphuric acid.

Preparation of hexavalent chromium solution: Hexavalent chromium solution was prepared by dissolving 28.28mg of $K_2Cr_2O_7$ (AR grate) to one litre of metal free doubly distilled water.

(1 mL = 100 mg of Cr(VI))

The batch adsorption studies were performed at 32°C. A predetermined amount of adsorbent is mixed with known initial concentration of Cr(VI) solution and agitated for desired time. The adsorbent and the adsorbate was separated by filtration and the filtrate was analyzed for residual Cr(VI) concentration spectrophotometrically. pH was adjusted using 2N H_2SO_4.

RESULTS AND DISCUSSION

Effect of initial concentration of Cr(VI) solution: The initial concentration of Cr(VI) solution was varied (0.04, 0.06, 0.08 and 0.1 mg/100mL) and batch adsorption experiments were carried out with 100mg of the adsorbent at 32°C and at pH 6.3. An increased percentage removal of Cr(VI) from 64 to 75 was observed with 100 mg of the adsorbent in agitation time of 180 minutes when the initial concentration of the Cr(VI) solution was varied from 0.1 to 0.04 mg/100mL. The higher uptake of Cr(VI) at low concentration may be attributed to the availability of more active centres on the surface of the adsorbent for lesser number of adsorbate species. Cr(VI) adsorption curves are single, smooth and continuous (Fig. 1) suggesting the possible monolayer coverage of metal ion on the surface of the adsorbent. Mise & Rajamanya (2003) also reported a similar result in the removal of Cr(VI) using activated carbon from dried jowar.

Effect of pH on Cr(VI) removal: The pH is an important controlling parameter in the adsorption process and thus the role of hydrogen ion concentration was studied for the adsorption of Cr(VI) at different pH, covering a range of 2 to 5 at 32°C. Batch experiments were conducted. The initial
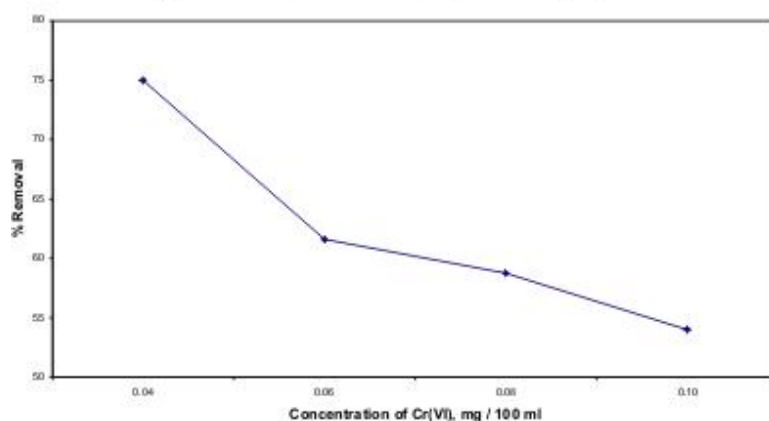

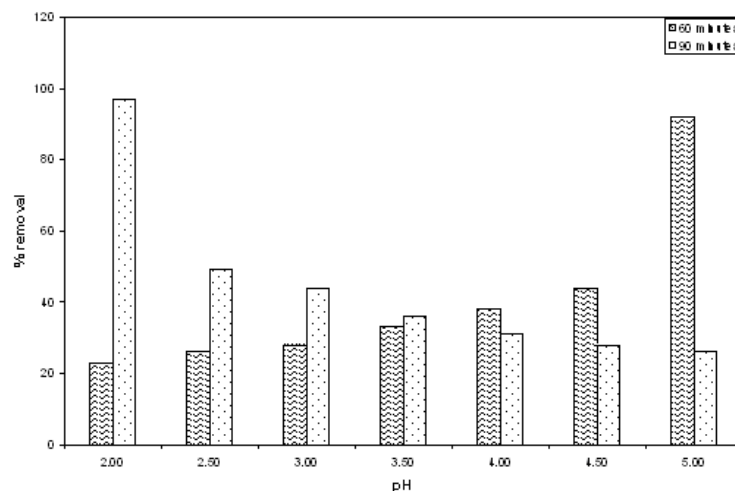Fig. 1: Effect of initial concentration on Cr (VI) removal.

Fig. 2: Effect of pH Cr (VI) removal.

concentration of the Cr(VI) solution used was 0.1mg/100mL with 50 mg of the adsorbent. The removal of Cr(VI) increased from 23 to 92% in 60 minutes of agitation time and 26 to 97% in 90 minutes of agitation time when the pH is varied from 5 to 2 as shown in the Fig. 2. At lower pH the large number of H^+ ions neutralize the negatively charged coal surface or convert a neutral group to a positively charged group and enhanced the adsorption of Cr(VI) species. The equilibrium is attained in 90 minutes of agitation time at pH 2. A similar result was reported on the extent of hexavalent chromium removal using iron bearing industrial sludge by Singh & Singh (2001).

Effect of adsorbent dosage: Increase in adsorbent dosage increased the adsorption of Cr(VI) species batch adsorption studies were carried out at 32°C and at pH 2.5. The initial concentration of the Cr(VI) solution was maintained to be 0.1 mg/100mL and the adsorbent dosage was varied from 20mg to 100mg. The removal of Cr(VI) increased from 33 to 77% for the adsorbent dosage variation of 20 to 100mg in 120 minutes of agitation time. This is to be expected because for a fixed initial solute concentration, increasing total adsorbent doses provides a greater surface area or adsorption sites, and thus the adsorption increases with adsorbent dosage as given in Fig. 3. Namasivayam & Yamuna (1999) reported a very similar result in the removal of Cr(III) using biogas residual slurry.

Effect of agitation time: The uptake of Cr(VI) from water by activated pomegranate peel carbon increases from 41 to 97% when the agitation time was varied from 10 to 90 minutes and attains equilibrium in 90 minutes at 32°C and at pH 2, when the initial concentration of the Cr(VI) solution used was 0.1mg/100mL and the adsorbent dosage 50mg. The increase in adsorption of Cr(VI) with increase in agitation time may be attributed to the increased intraparticle diffusion occurring at long shaking time (Fig. 4). A similar result was observed by Rao & Bhole (2001) in the removal of Cr(VI) by fly ash and bagasse.

Kinetic modeling: The study of kinetics of adsorption describes the solute uptake rate, which in turn controls the residence time of adsorbate uptake at the solid-solution interface. The adsorption kinetics of Cr(VI) adsorption on activated pomegranate peel carbon follows first order rate expression given by Largergen as quoted by Singh et al. (1988).
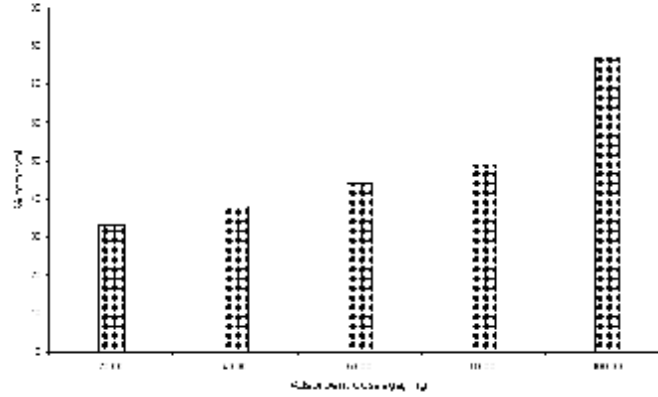
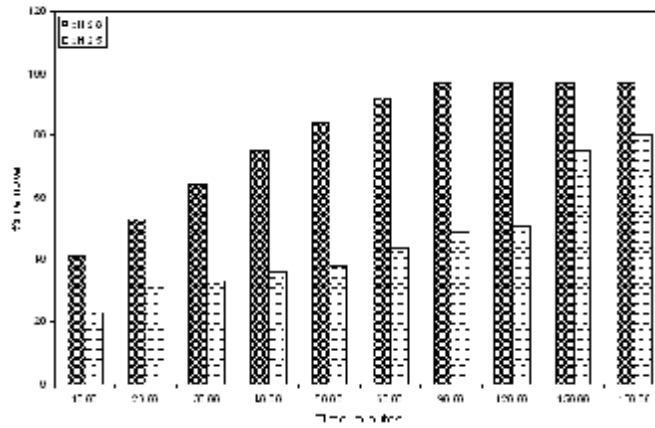Fig. 3: Effect of adsorbent dossage on Cr (VI) removal.

Fig. 4: Effect of agitation time on Cr (VI) removal.

Log $(q_e-q) = \log q_e - K_a t/2.303$. Where K_a (min^{-1}) is the rate constant of adsorption, q and q_e are the amount of Cr(VI) adsorbed (mg/g) at time 't' and equilibrium time respectively. When log (q_e-q) versus 't' is plotted (Fig. 5) the linear plots show the applicability of Langergren equation for Cr(VI) adsorption. The K_a values at different initial concentrations are calculated from the slope of the linear plots and are given in the Table 1.

Table 1: Kinetic modeling for the adsorption of Cr(VI) on to activated pomegranate peel carbon using Legergren equation.

Conditions		
Adsorbate dosage	: 100mg	pH: 6.3 ± 0.02
Temperature	: 32°C	

Initial concentration of Cr(VI) solution in 100mL	Ka, ×10^{-4} (sec^{-1})
0.04 mg	3.0883
0.06 mg	2.4497
0.08 mg	1.8216
0.10 mg	1.5744

Adsorption isotherm: The studies of adsorption isotherms are helpful in determining the adsorption capacity of an adsorbent. Langmuir and Freundlich adsorption isotherm models were applied for Cr(VI) adsorption.

The Langmuir equation correlates the amount of adsorbate adsorbed with the equilibrium aqueous concentration. The linear transformation of the Langmuir equation (Rao & Bhole 2001) is given as:

$1/x/m = 1/b + 1/abC_e$

Where 'x' is the amount of Cr(VI) adsorbed in mg/100mL, 'm' is the weight of the adsorbent (g), C_e is the residual concentration of Cr(VI) at equilibrium in mg/100mL. Langmuir constants 'a' and 'b' are the measures of maximum adsorption capacity and the energy of adsorption given in the Table 2.

$R_L = 1/1 + bC_o$

Where C_o is the initial concentration of the adsorbate and 'b' the langmuir constant.

R_L Value	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

The values of $R_L < 1$, obtained in this study indicate the applicability of Langmuir adsorption isotherm. The Langmuir adsorption isotherm obtained in 60 minutes of agitation time is shown in the Fig. 6.

The linear form of Freundlich equation (Sumanjit & Prasad 2001) is represented as:

$Lng \ x/m = \log K_f + 1/n \log C_e$

Where 'x' is the amount of Cr(VI) adsorbed in mg/100mL 'm' is the weight of adsorbent (g) and C_e is the residual concentration of Cr(VI) at equilibrium in mg/100mL.

K_f and $1/n$ are Freundlich constants related to the adsorption capacity and adsorption intensity respectively and are evaluated by least square fitting of the data by plotting log x/m vs log C_e with a slope of $1/n$ and intercept of log K_f (Fig. 7). The values of adsorption intensity $1/n \ll 1$ reveal the applicability of this adsorption isotherm. The values of K_f are given in Table 2.

Thermodynamic parameters: Any chemical system tends to attain a state of equilibrium from one of non-equilibrium. The thermodynamic parameters, which characterize the equilibrium of a system are the Gibbs free energy change ∆G, the enthalpy change ∆H and the entropy change ∆S. These parameters were determined using the following relations as quoted by Stephen Inbaraj & Sulochana (2002).

Table 2: Parameters of Langmuir and Freundlich adsorption isotherms for Cr(VI) adsorption calculated for 60 minutes of agitation time onto activated pomegranate peel carbon.

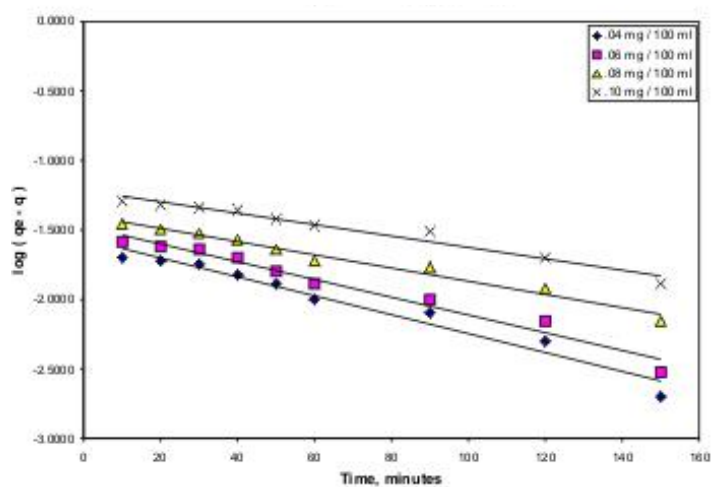| Langmuir			Freundlich		
a	b	Correlation Coefficient (r)	K_f	1/n	Correlation coefficient (r)
0.0469	4.05	0.9719	73.706	0.3326	0.9967

M. Jambulingam et al.
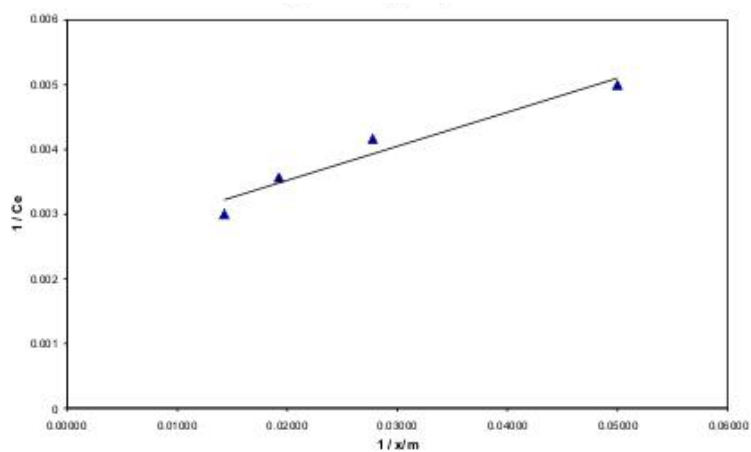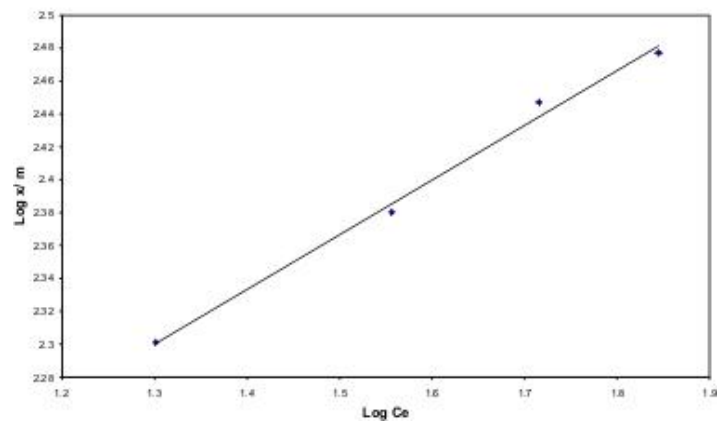

Fig. 5: Lagergren plot.

Fig. 6: Langmuir plot.

Fig. 7: Freundlich plot.

Table 3: Thermodynamic parameters for the adsorption of Cr (VI) on to activated pomegranate peel carbon.

Conditions				
Initial concentration of Cr(VI) : 0.1mg/100mL Adsorbent dosage :100 mg				
pH	Temperature in Kelvin	ΔG J mole^{-1}	Δ S J mole^{-1}	Δ H KJ mole^{-1}
6.3 ± 0.02	305	-1458.828	81.130	-23.317
2.5	305	-2785.797	815.788	-243.909

$$K_c = CA_e/C_e$$
$$\Delta G = RT \ln K_c$$
$$\text{Log } K_c = \Delta S/2.303 R - \Delta H/2.303 RT$$

Where K_c is the equilibrium constant, CA_e is the solid phase concentration of Cr(VI) at equilibrium, C_e is the residual concentration of Cr(VI) at equilibrium, R is the gas constant (J mole^{-1}) and T is the temperature in Kelvin. ΔH and ΔS were obtained from the slope and intercept of Vant Hoff plot (1/T vs. $\ln K_c$) as given in the Fig 6. Batch adsorption studies were carried out with Cr(VI) solution at pH ≈ 6.3 and at pH 2.5 by varying the temperature (300K, 305K and 310K). The initial concentration of Cr(VI) solution used was maintained to be 0.1mg/100mL with 100mg of the adsorbent. Table 3 gives the value of ΔG, ΔS and ΔH for the adsorption of Cr(VI). The negative values of free energy change (ΔG) indicate the feasibility and spontaneous nature of the adsorption of Cr(VI) species (Singh & Shukla 2000). The negative ΔH values of the process suggest the exothermic nature of adsorption of Cr(VI) on to activated pomegranate peel carbon (Gupta et al. 1999). The positive value of ΔS is due to the increased randomness during adsorption of Cr(VI) (Murugan & Subramaniam 2003). The free energy change values ΔG indicate more favourable adsorption at pH 2.5 (Table 3).

CONCLUSION

In the present study adsorption of Cr(VI) on activated pomegranate peel carbon has been investigated. The data obtained through this work support that the pomegranate peel carbon is an effective low cost adsorbent for the removal of Cr(VI) from aqueous solution. The adsorption of Cr(VI) ions is dependent on the initial concentration of the metal ion, pH, amount of adsorbent and agitation time. Maximum removal of Cr(VI) is noted at pH 2. Langmuir and Freundlich adsorption isotherms correlate the equilibrium adsorption data. The adsorption of Cr(VI) follows Lagergren first order kinetics. The adsorption of Cr(VI) onto activated pomegranate peel carbon is an exothermic reaction.

REFERENCES

Brian, P. Kelleheri, Marguerite, N.O., Callaghan, Martin J. Leahy., Thomas, F.O Dwyer and Leahy, J.J. 2002. The use of flyash from the combustion of poultry litter for the adsorption of chromium (III) from aqueous solution. Journal of Chemical Technology Biotechnology, 77: 1212-1218.

Gupta, Vinod, K., Dinesh Mohan, Sharma, Saurabh and Kuk, T. Park. 1999. Removal of chromium (VI) from electroplating industry waste water using bagasse flyash, a sugar industry waste material. The Environmentalist, 19 :129-136.

Murugan, M. and Subramaniam, E. 2003. Biosorbent *Cupressus* female cone in the efficient treatment of effluent containing Cr(VI). Journal of Scientific and Industrial Research, 62: 1071-1078.

Nagarnaik, P.B., Bhole, A.G. and Natarajan, G.S. 2003. Adsorption of arsemic on flyash. Indian Journal Environmental Health, 45: 1-4.

Namasivayam, C. and Kadirvelu, K. 2000. Agricultural by product as metal adsorbent sorption of lead (II) from aqueous solution on to coir pith carbon. Environmental Technology, 21: 1091-1097.

Namasivayam, C. and Yamuna, R.T. 1999. Studies on chromium (III) removal from aqueous solution by adsorption onto biogas residual slurry and its application to tannery waste water treatment. Water, Air and Soil Pollution, 113: 371-384.

Rao, M. and Bhole, A.G. 2001. Chromium removal by adsorption using flyash and bagasse. Journal of Indian Water Works Association, 97: 997-1000.

Saravanam, R., Sundararajan, T. and Sivamurthy Reddy, S. 2002. Efficiency of chemically modified low cost adsorbents for the removal of heavy metals from waste water. A Coparative Study. Indian Journal Environmental Health, 44: 78-87.

Sharma, Y.C. 2001. Adsorption of Cr(VI) on to wollastenite: Effect of pH. Indian Journal of Chemical Technology, 8: 186-190.

Mise, Shashikant R. and Rajamanya, V.S. 2003. Adsorption studies of Cr(VI) on activated carbon derived from *Sorghum vulgare* dried stem. Indian Journal Environmental Health, 45: 49-58.

Singh, Anju and Shukla, Rami 2000. Removal of alizarin red containing effluents on to chitin based adsorbents. Poll. Res., 19: 179-184.

Singh, I.B. and Singh, D.R. 2001. Hexavalent chromium removal using iron bearing industrial sludges. Indian Journal of Chemical Technology, 8: 487-495.

Singh, D.B., Prasad, G., Rupainwar, D.C. and Singh, V.N. 1988. As(III) removal from aqueous solution by adsorption. Water Air Soil Pollution, 42: 373-386.

Stephen Inbaraj and Sulochana, N. 2002. Basic dye adsorption on a low cost carbonaceous sorbent kinetic and equilibrium studies. Indian Journal of Chemical Technology, 9: 201-208.

Sumanjit and Prasad, N. 2001. Adsorption of dyes on rice husk ash. Indian Journal of Chemistry, 40A : 388-391.

Swamy, M.M., Mall, I. D., Prasad, B. and Mishra I. M. 1998. Sorption characteristics of O-cresol on bagasse flyash activated carbon. Indian Journal of Environmental Health, 40: 67.

Thackston, E.L. 1973. Secondary waste treatment for small diversified tannery. Environmental Protection Technology Series, Environmental Protection Agency, Project 12120 EFM, Caldwell Lace leather Co, Auburn.

Udy, M.J. 1956. Chromium. Reinhold, Newyork, USA.