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Research Article

APPLICATION OF SILICA GEL/POLYPYRROLE COMPOSITE AS AN EFFICIENT SOLID PHASE ADSORBENT FOR SEPARATION OF ASCORBIC ACID FROM AQUEOUS SOLUTIONS

***Ansari R. and Shademan S. M.**
Department of Chemistry, University of Guilan, Rasht, Iran, POB: 41635-1914
**Author for Correspondence*

ABSTRACT

In the present study, the adsorption behavior of ascorbic acid (AA) from aqueous solutions onto silica gel and silica gel chemically modified with polypyrrole represented as PPY/SiO_2 were investigated. The nature of the possible interactions of ascorbic acid with PPY/SiO_2 was examined using FTIR technique. Adsorption experiments were carried out using both batch and column systems at room temperature. In batch system, the effect of some important parameters such as sorbent dose, contact time, initial concentration and temperature were studied. Based on isotherm analysis, it was found that the equilibrium adsorption data for ascorbic acid onto SiO_2 were best fitted to the Freundlich adsorption model and for the PPY/SiO_2 composite, the equilibrium adsorption data conformed well to Langmuir isotherm. The kinetic experiments indicated that the adsorption of AA on both adsorbents follows pseudo-second order kinetic. The thermodynamic studies also revealed that the process of ascorbic acid sorption onto PPY/SiO_2 is endothermic with spontaneous nature. Based on the desorption study, it was found that using dilute NaOH solution as washing solution it is possible to elute the adsorbed ascorbic acid from uploaded adsorbent.

Keywords: *Silica Gel, Polypyrrole, Composite, Ascorbic Acid, Adsorption*

INTRODUCTION

Inherent conductive polymers (ICP) have attracted a great deal attention owing to their useful physical and chemical properties. Polypyrrole is one of the most important ICP due to its comparative stability but bulk Polypyrrole is intractable and insoluble in common solvents because of partial cross–linking through hydrogen bonding, so the polymer has poor process ability and inferior mechanical properties. To overcome these restrictions, many researcher concentrated on the prepartion of conducting PPy-based composite materials. Formation hybridization of polypyrrole with silica deserves special attention due to its composite nature. The advantage of such composite is the synergistic blending of properties of both the components, thus with using these composites, we can achieve required mechanical strength of silica as well as high ion exchange properties of polypyrrole (Mondal *et al.,* 2011; Perruchot *et al.,* 2000; Ansari & Khoshbakht, 2007a).

Ascorbic acid (or vitamin C) is one of the most important vitamins that commonly exist in numerous vegetables and fruits. Furthermore, ascorbic acid has been frequently used in large scale in the cosmetic, pharmaceutical, chemical and food industry as antioxidant but ascorbic acid is chemically very unstable under the exposure to air, light, moisture, heat, metallic ions and oxygen (Ping *et al.,* 2012; Lee *et al.,* 2008; Yilmaz *et al.,* 2008). So, its determination via solid phase extraction and subsequent elusion is in great importance especially in trace analysis. In this paper, the silica gel and chemically modified silica gel with polypyrrole (PPY/SiO_2) were used for sorption of ascorbic acid from aqueous solutions in order to find out the possibility of the introduced composite material for extraction and preconcentration of AA for subsequent elution and analysis.

Polypyrrole was selected for coating of silica gel because of its ease of direct in-situ synthesis by chemical rout from aqueous media. The adsorption capacities of SiO_2 and PPY/SiO_2 were compared in both batch (equilibrium) and column (dynamic) systems. In order to find out optimum sorption conditions, the effects of some important chemical and physical parameters such as initial concentration, adsorbent dosage, contact time, and temperature on the ascorbic acid sorption was investigated. For treatment the obtained data and plotting the adsorption isotherms, two popular equations of Langmuir and

Freundlich were employed. In batch investigation, pseudo-first and second order equations were used for determination of kinetics parameters as well as sorption mechanism. Vant, Hoff equation was used for determination of thermodynamic parameters and then compared with results obtained for untreated SiO_2 under the same experimental adsorption conditions.

MATERIALS AND METHODS

All chemicals used were analytical reagent grade. Pyrrole was purchased from Merck Chemical Company. All experiments were performed in aqueous solutions prepared using de-ionized water. Determination of ascorbic acid was carried out by iodometric coulometric titration. Platinum and silver wires were used as working (anode) and counter (cathode) electrodes in, respectively. Excess of potassium iodide was used as auxiliary electrolyte and starch was used as indicator helping to detect the endpoint. A Digital coulometer (ZAG Chemie Co.) was used for recording of the charge consumed during titration. The measurements were performed based on Faraday Law ($q = nNF$). Infrared spectra were obtained using Shimadzu FTIR Spectrometer.

Preparation of Adsorbent (PPY/SiO_2)

Silica gel (50-80 mesh size) particles were first soaked into a 0.20 M of aqueous pyrrole solution for 6 hours. The excess of monomer was removed via simple decantation and then a solution of 0.50 M $FeCl_3$ (as chemical oxidant) was added onto the silica gel particles previously soaked in pyrrole. Polymerization was carried out on the surface of silica gel immediately after addition of oxidant. The reaction was allowed to completion for 30 min. The coated silica gel particles with polymer were then filtered. The prepared PPY/SiO_2 particles were washed with deionized water and dried in an air circulating oven at 50-60 °C. In order to increase reproducibility of the data, the particles were sieved again and stored.

Adsorption Tests

In batch wise experimental process, fixed amounts of adsorbents (0.20 g) were weighed and treated with 100 mL ascorbic acid solutions containing different concentration (100-300 mg L^{-1}) for definite periods of time (1 h). The mixtures were stirred at constant speed of 50 rpm in a shaking water bath (Grant Operation C100196). All experiments were carried out at least for three times and the averages of the values are reported. Sorption efficiency (%Sorption) and the amount of ascorbic acid adsorbed by adsorbents (mg g^{-1}) were calculated using the following equations:

$$\%Sorption = \frac{(C_0 - C_t)}{C_0} \times 100 \tag{1}$$

$$q_e = \frac{(C_0 - C_e)}{m} \times V \tag{2}$$

Where; C_0 is initial acid concentration (mg L^{-1}), C_t is the left out acid concentration in bulk solution at time t (mg L^{-1}), m is adsorbent mass (g), and V is the volume of acid solution (L). The amount of adsorption at equilibrium, q_e (mg g^{-1}), was calculated by replacing the C_t with C_e.

Column Study (Fixed Bed)

For column experiments, glass columns with dimensions of 1.0 cm diameter and 25 cm height were employed. 2.0 g of each adsorbent was packed in the column (bed volume = 5 cm^3), and then ascorbic acid solution with inlet concentration of 200 mg L^{-1} was passed through the column with constant flow rate of 2 mL min^{-1}. The outlet solution was analyzed for residual ascorbic acid and the resulted breakthrough curve was plotted.

RESULTS AND DISCUSSION

Effect of Sorbent Dosage

In this study, accurate known amounts (0.10-0.50 g) of modified and unmodified silica gel (PPY/SiO_2, SiO_2) were treated with fixed volumes of ascorbic acid solutions (100 mL) containing constant initial concentration of 200 mg L^{-1} at pH=3.4 (the natural pH of AA solution). The mixtures were shaken for 1 h at room temperature in a batch mode. As the results obtained show (Figure 1) with increasing of adsorbents dosage at initial stage, sorption (%) of AA onto PPY/SiO_2 increased considerably and became nearly constant after 0.20 g adsorbent dose. The sorption capacity of unmodified SiO_2 was also much lower than PPY/SiO_2 at all adsorbent dosages.

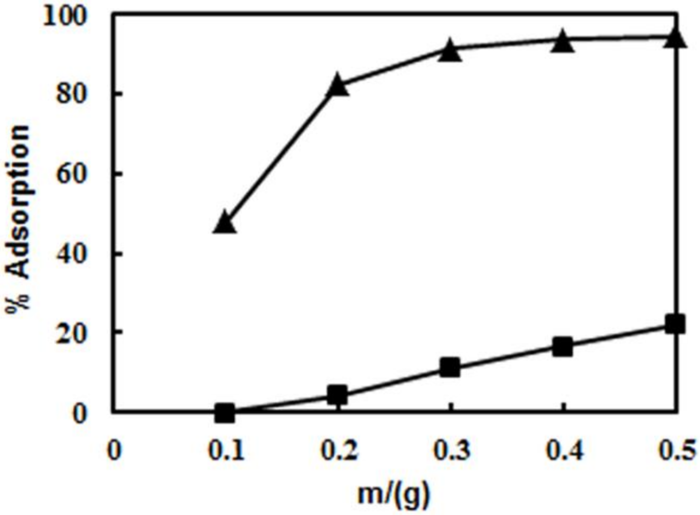

Figure 1: The effect of adsorbent dosage on AA sorption onto PPY/SiO_2 (▲) and SiO_2 (■)

Effect of Initial Concentration

For investigation of initial concentration for driving isotherms, fixed amounts (0.20 g) of adsorbents (PPY/SiO_2 and SiO_2) were treated with constant volumes of AA solutions containing various concentrations (from 100 to 300 mg L^{-1}) at room temperature accompanied by agitation. The results obtained are shown in Figure 2. As the results show with rising initial AA concentration, the AA uptaken by adsorbents is increased. However, the increase in the case of PPY/SiO_2 is much more distinguished. At all investigated concentrations, sorption capacity of PPY/SiO_2 was much more than SiO_2. It could be concluded that AA removal by PPY/SiO_2 is also dependent on the initial concentration of ascorbic acid.

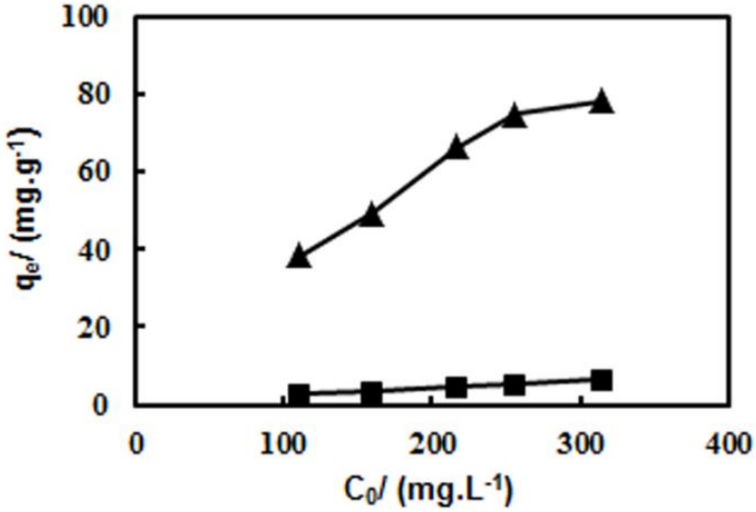

Figure 2: The effect of initial concentration of ascorbic acid on its adsorption onto SiO_2 (■) and PPY/ SiO_2 (▲)

Adsorption Isotherm

The purpose of the sorption isotherms is to express the relation between the equilibrium concentration of adsorbate in the bulk solution and the amount of adsorbate adsorbed at the surface of solid phase. Langmuir and Freundlich isotherm are the most commonly used equations in batch adsorption systems. The Langmuir adsorption model is based on the assumption of monolayer adsorption of adsorbate onto the adsorbent surface with no lateral interaction between the adsorbed molecules (Zheng *et al.*, 2009). The equation is given as:

$$q_e = \frac{q_m k_a c_e}{1 + k_a c_e} \tag{3}$$

The Langmuir equation can be described by the linearized form:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{k_a q_m c_e} \tag{4}$$

where q_e is the amount of acid sorbed (mg g^{-1}), C_e is the equilibrium concentration (mg L^{-1}), q_m is the maximum adsorption capacity for a complete monolayer (mg/g), and K_a is the sorption equilibrium constant related to energy of adsorption (L mg^{-1}). A plot of 1/qe vs. C_e should designate a straight line of slope $1/q_m$ and an intercept of 1/ (K $C_e q_m$). A dimensionless constant, commonly known as separation factor (R_L) defined by Webber and Chakkravorti (Foo & Hameed, 2010) that it can be represented as:

$$R_L = \frac{1}{1 + K_L C_0} \tag{5}$$

where K_L (L mg^{-1}) refers to the Langmuir constant and C_o is devoted to the adsorbate initial concentration (mg L^{-1}). In this context, lower R_L value reflects that adsorption is more favorable. In a deeper explanation, R_L value indicates the adsorption nature to be either unfavorable ($R_L>1$), linear ($R_L=1$), favorable ($0<R_L<1$) or irreversible ($R_L=0$). Freundlich isotherm is the earliest known relationship describing the non-ideal and reversible adsorption (Foo & Hameed, 2010).This important model can be applied to multilayer adsorption, with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface and is expressed by the following equation:

$$q_e = KC_e^{\frac{1}{n}} \tag{6}$$

The Frundlich equation can be described by the linearized form:

$$log q_e = log K_F + \frac{1}{n} log C_e \tag{7}$$

where, q_e is the amount of adsorbate adsorbed per unit of adsorbent (mg/g), C_e is the concentration of adsorbate solution at adsorption equilibrium (mg L^{-1}), K_F (mg $^{(1-\ 1/n)}$ g^{-1} $L^{1/n}$) and n (dimensionless parameter) are the empirical Freundlich adsorption isotherm constants relating to the adsorption capacity and adsorption intensity respectively. The favorable adsorption of this model can be characterized such that if a value for n is above unity, adsorption is favorable and a physical process (Vimonses *et al.*, 2009). The magnitude of the Freundlich constant n gives a measure of favor ability of adsorption. The values of n between 1 and 10 (i.e., 1/n<1) represents a favorable sorption. The Freundlich isotherm is linear if 1/n=1 and, as 1/n decreases, the isotherm becomes more nonlinear (Ho *et al.*, 2002). The values of Langmuir and Freundlich parameters with the nonlinear correlation coefficients (R^2) are concluded in Table 1.

Table 1: Isotherm parameters obtained from adsorption of AA onto SiO_2 and PPY/SiO_2

Adsorbent		***Langmuir parameters***			***Freundlich parameters***		
	q_m (mg g^{-1})	**K_L (L mg^{-1})**	**R_L**	**R^2**	**K_F**	***n***	**R^2**
SiO_2	23.80	0.0011	0.75	0.9860	0.046	1.16	0.9927
PPY/SiO_2	116.27	0.0143	0.18	0.9653	6.657	1.98	0.9427

As the obtained isotherm parameters show (Table 1), PPY/SiO_2 has a relatively large monolayer adsorption capacity of 116.27 mg/g for adsorption ascorbic acid which is about 5 times more than SiO_2. As a result, modification of SiO_2 by polypyrrole (PPY/SiO_2) improves sorption capacity greatly. Based on regressions analysis (R^2 value), adsorption of AA onto SiO_2 and PPY/SiO_2 follows by Freundlich and Langmuir isotherms, respectively. On the other hand, the experimental data for SiO_2 confirms that the adsorption is multilayer whereas the adsorption AA onto PPY/SiO_2 is monolayer.

Effect of Contact Time

In this experiment, 0.20 g of SiO_2 and PPY/SiO_2 were mixed with constant volumes of AA (100 mL) and initial concentration of 150 mg L^{-1}. The solution then stirred on a shaker at room temperature for various time intervals (10-60 minutes). The natural pH of AA solution was about 3.4. The left out AA concentration in the solution was measured at different predetermined contact times. As the results indicate (Figure 3), with increasing of contact duration, more adsorption of AA is observed. The same as previous results, PPY/SiO_2 was found to be much more efficient than SiO_2 for adsorption of AA. Adsorption of AA by PPY/SiO_2 reaches to its maximum amount at equilibrium time (60 min). In the initial stages the adsorption efficiency of AA by the PPY/SiO_2 increased quickly due to the abundant availability of free active binding sites on the adsorbent, and with gradual occupancy of these sites, the adsorption became slow in the later steps (Mansour *et al.,* 2011).

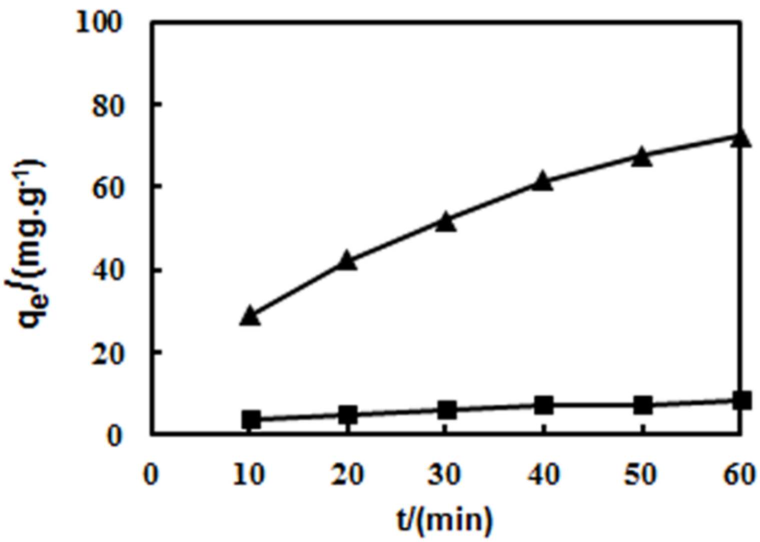

Figure 3: The effect of exposure time on sorption of AA onto PPY/ SiO_2 (▲) and SiO_2 (■)

Kinetics Study

Pseudo-first-order and pseudo-second-order were used to test dynamical experimental data.
The pseudo-first-order kinetic model of Lagergren is given by the following equation (Al-Ghouti *et al.*, 2009; Chiron *et al.*, 2003; Tamezuddin *et al.*, 2009):

$$log(q_e - q_t) = logq_e - \frac{k_1 t}{2.303} \qquad (8)$$

Where q_e and q_t are the amounts of adsorbate adsorbed on adsorbent (mg g^{-1}) at equilibrium and at time t, respectively and K_1 is the rate constant of pseudo-first-order adsorption (min^{-1}). The slopes and intercepts of plots of log (q_{1e} - q_t) versus t were used to determine the pseudo-first-order rate constant K_1 and q_{1e}. Pseudo-second-order rate equation can be expressed in the following form.

$$\frac{t}{q_t} = \frac{1}{K_2 q^2{}_e} + \frac{1}{q_e} t \qquad (9)$$

Where K_2 (g mg^{-1} min^{-1}) is the rate constant of pseudo-second order adsorption. The slopes and intercepts of plots of t/q_t versus t are used to calculate K_2 and q_e. The calculated kinetic parameters of SiO_2 and PPY/SiO_2 and the consistent linear regression correlation coefficients R^2 are given in Table 2. The high value of R^2 for the pseudo second-order kinetic model, clearly represent the AA sorption on PPY/SiO_2 sorbent is mainly happened with chemisorptions process.

Table 2: The Pseudo-first-order kinetic model and Pseudo-second-order kinetic model for adsorption of AA onto SiO_2 and PPY/SiO_2

Adsorbent	***Pseudo-first-order kinetic model***			***Pseudo-second-order kinetic model***		
	q_{e1} (mg g^{-1})	**k_1 (min^{-1})**	**R^2**	**q_{e2} (mg g^{-1})**	**k_2 (g mg^{-1} min^{-1})**	**R^2**
SiO_2	7.27	0.0386	0.943	11.45	0.003	0.970
PPY/SiO_2	86.27	0.0543	0.967	106.38	0.0003	0.992

Effect of Temperature

Thermodynamic experiments were carried out by contacting 0.20 g of each adsorbent (SiO_2 and PPY/SiO_2) with 100 mL of 150 mg L^{-1} ascorbic acid solution at different temperatures (288-318 K) for 60 min. The supernatants in each test solution were analyzed for remaining or unadsorbed AA. As the results show (Figure 4), with rising temperature, adsorption of AA by the selected adsorbents increased which implies the endothermic nature of adsorption process. This effect may be due to the fact that at higher temperatures, an increase in kinetic energy occurs and diffusion rate of molecules through the external boundary layer and internal positions of the adsorbent are increased (Aksakal & Ucun, 2010).

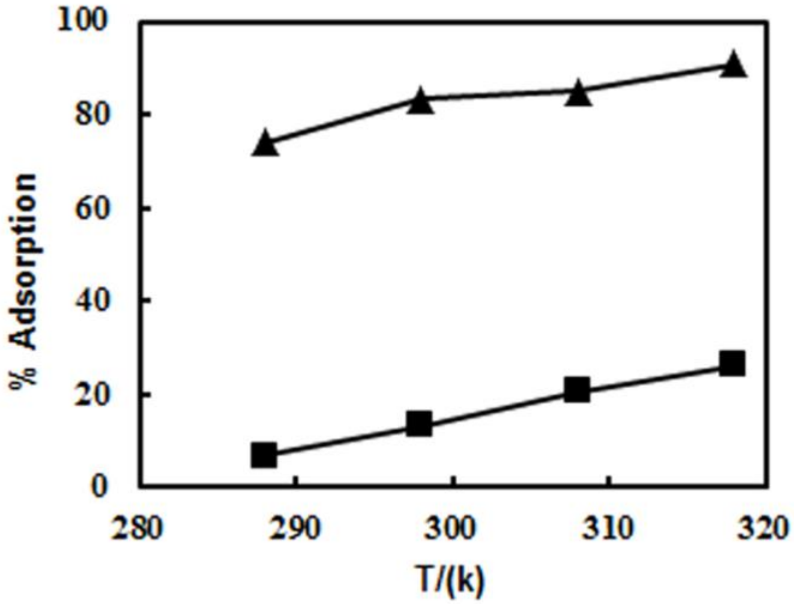

Figure 4: The effect of temperature on sorption of AA onto SiO_2 (■) and PPY/SiO_2 (▲)

Thermodynamic Study

The equilibrium adsorption data obtained from temperature effect was used for calculating of the most important thermodynamic parameters (ΔG°, ΔH° and ΔS°) using the following equations:

$$K_d = \frac{C_{Ad}}{C_e} \tag{10}$$

$$\Delta G^{\circ} = -RTLnK_c \tag{11}$$

$$LnK_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{12}$$

where K_d is the adsorption distribution coefficient, C_{Ad} (mg g^{-1}) is the amount of AA (mg) taken by unit mass of solid adsorbent, C_e is the concentration of unadsorbed or remained AA in the solution (mg L^{-1}), R is the universal gas constant (8.314 KJ/mol K) and T is the absolute temperature (K). The Gibbs free energy shows the degree of spontaneity of the sorption process. The results is showed in table 3, were obtained from the slope and intercept of a plot of ln K_d against 1/T (Ncibi *et al.*, 2007).

Table 3: Thermodynamic parameters for sorption of AA onto SiO2 and PPY/ SiO_2

Adsorbent	*T* (K)	K_c	ΔG^0 (KJ mol^{-1})	ΔH^0 (KJ mol^{-1})	ΔS^0 (J mol^{-1} K^{-1})
SiO_2	288	0.07	6.23	+40.0	117.9
	298	0.15	4.63		
	308	0.26	3.44		
	318	0.35	2.73		
PPY/ SiO_2	288	2.86	-2.52	+39.0	143.5
	298	5	-3.98		
	308	8.66	-5.52		
	318	13	-6.78		

Negative values of ΔG^o obtained for PPY/SiO_2 at various temperatures clearly demonstrate the spontaneous nature of the adsorption process. The positive values of ΔG^o obtained for SiO_2, indicate that the adsorption of AA onto untreated silica gel particles is non-spontaneous and needed some activation energy to be provided. The positive values of ΔS^o for both adsorbent mean that sorption of AA onto PPY/SiO_2 and SiO_2 is mainly determined by entropy factor.

Column Study and Breakthrough Curves

Adsorption ascorbic acid using two selected adsorbents were also performed in continuous mode (fixed bed column system). The continuous adsorption in fixed-bed column is often desired from industrial point of view. It is simple to operate and can be scaled-up from a laboratory process. The data analyzed by the column adsorption can provide valuable information for the design and operation of an adsorption process for preconcentration, separation, purification and pharmaceutical purposes. In order to design and operate fixed-bed adsorption process successfully, the breakthrough curves under specified operating conditions must be predictable. Breakthrough determines bed height and the operating life span of the bed and regeneration times. Breakthrough curve is the plot of effluent solute concentration vs. volume or time of solution usually earnings as S shaped curve. The point of column exhaustion is the time where the effluent solute concentration reaches 95% of its influent value (Ahmad & Hameed, 2010; Zhang *et al.*, 2011; Ansari & Mosayebzadeh, 2010b). It was also interesting to note that untreated silica gel showed not any tendency to uptake AA when a column system was employed. Instead, PPy/SiO_2 column showed high affinity for adsorption of AA even in non-equilibrium column system. There was a great difference between treated and untreated SiO_2 for adsorption of AA in column system. It was also found that the sorption capacity of PPy/SiO_2 column can be further improved upon pretreatment of the column with copper salt (Figure 5).

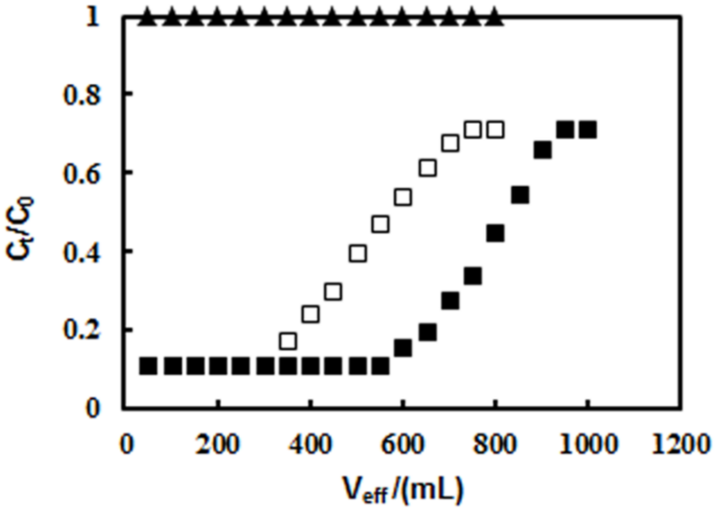

Figure 5: The breakthrough curves for adsorption of AA by SiO_2 (▲), PPY/SiO_2(☐), PPY/SiO_2/Cu(II)(■)

The increase in AA removal after treatment of PPy/SiO_2 column with copper salt can be due to the adsorption of some copper ion by the column and high affinity of copper ion to form stable complex with ascorbic acid (Sachan *et al*., 2011).

Desorption Study

The possibility of desorption with high performance is one of the main factors for selecting a material as a suitable candidate for separation or adsorption of a solute. It was found that regeneration of the PPY/SiO_2 or elution of adsorbed AA is quite possible using dilute alkaline solution (0.01 M NaOH). Upon alkaline treatment of used PPY/SiO_2 column, adsorbed AA molecules are neutralized and leave the polymer or column easily.

Conclusions

It was found that SiO_2 has very negligible tendency for adsorption of ascorbic acid from aqueous solutions. Affinity of SiO_2 particles for uptake of AA improves greatly when coated by polypyrrole. Adsorption AA onto SiO_2 followed the Freundlich isotherm while for absorbent PPY/SiO_2 data were best fitted with Langmuir model. Based on kinetic study, adsorption of ascorbic acid onto PPY/SiO_2 follows pseudo-second order reaction which confirms a chemisorptions mechanism. The negative and positive values for ΔG^o and ΔH^o, respectively implies spontaneous and endothermic nature of AA adsorption by PPY/SiO_2. Treatment of PPY/SiO_2 with copper salt, sorption capacity is improved considerable.

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