

SORPTION OF ARSENIC (V) BY TITANIUM OXIDE LOADED POLY(HYDROXAMIC ACID) RESIN

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ABSTRACT

The sorption process for removal of As(V) by titanium oxide-loaded poly(hydroxamic acid) chelating resin (TiO₂-PHA) was assessed with various parameters including effect of pH, contact times, initial As(V) concentrations, temperatures and existence of foreign anions. The loaded resin was tested for removal of arsenic anions from industrial wastewater samples. The maximum sorption capacity of As(V) was found in acidic conditions at pH 1.5. Kinetics study shows that As(V) sorption followed the second order kinetic rate equation with the rate constant of $2.9 \times 10^{-2} \text{ g mg}^{-1} \text{ min}^{-1}$ at room temperature and increase with increasing temperature. The sorption capacity of As(V) which increases as temperature increases indicates that the sorption was an endothermic process. The free energy change, ΔG° was negative, showing that the sorption of As(V) onto TiO₂-PHA resin is spontaneous and thermodynamically favorable. In addition the values of ΔH° are positive, confirming that the sorption process is endothermic in nature. Negative values of ΔS° indicate the increase of order after the sorption of As(V) on the TiO₂-PHA. Sorption isotherm of As(V) by TiO₂-PHA could be interpreted by Langmuir equation with sorption capacity 12.72 mg/g at room temperature and increase with increasing temperature. The selectivity study showed that the sorption of As(V) was affected by the presence of phosphate but not affected by sulphate, chromate, carbonate, bromide and nitrate anions. The resin was found effective for the removal of arsenic anion in wastewater samples from electronic and wood treatment industries.

ABSTRAK

Proses erapan untuk penyingkiran As(V) oleh titanium oksida terpegun dalam resin pengkelat poli(asid hidroksamik) (TiO₂-PHA) telah dikaji dengan pelbagai parameter termasuk kesan pH, masa sentuhan, kepekatan awal As(V), suhu dan kehadiran anion lain. Resin terubahsuai tersebut telah dikaji keberkesannya untuk penyingkiran ion arsenik daripada sampel air buangan industri. Erapan maksimum As(V) oleh TiO₂-PHA didapati berlaku pada keadaan berasid pH 1.5. Kajian kinetik menunjukkan erapan As(V) mematuhi persamaan kinetik order kedua dengan nilai pemalar kadar $2.9 \times 10^{-2} \text{ g mg}^{-1} \text{ min}^{-1}$ pada suhu bilik, dan meningkat apabila suhu meningkat. Muatan erapan juga didapati meningkat dengan peningkatan suhu menunjukkan proses erapan adalah endoterma. Perubahan tenaga bebas ΔG° adalah negative menunjukkan erapan As(V) pada resin TiO₂-PHA adalah tindakbalas spontan dan sesuai dari segi termodinamik. Sebagai tambahan nilai ΔH° adalah positif mengesahkan proses erapan adalah endoterma. Nilai ΔS° pula didapati negative yang mana menunjukkan erapan As(V) pada TiO₂-PHA telah meningkatkan aturan bahan tindakbalas. Isoterma erapan As(V) oleh TiO₂-PHA mematuhi persamaan Langmuir dengan muatan erapan 12.72 mg/g pada suhu bilik dan meningkat dengan peningkatan suhu. Kehadiran ion fosfat merendahkan erapan As(V) tetapi erapan tidak dipengaruhi oleh kehadiran ion sulfat, kromat, karbonat, bromide dan nitrat. Resin ini juga didapati berkesan untuk menyingkir ion arsenik dari sampel air buangan industri elektronik dan industri perawatan kayu.

Keywords: Titanium dioxide-loaded poly(hydroxamic acid), arsenate sorption, thermodynamic, kinetics, industrial wastewater.

Introduction

In spite of its toxicity, arsenic has been used in medicine, cosmetic, agriculture and industry. It can cause skin, lung and kidney cancer [1]. The USEPA permissible limit of arsenic in drinking water is $10 \mu\text{g L}^{-1}$. Due to its high toxicity the removal of trace arsenic from drinking-water or industrial effluents has been an

increasing importance. The main arsenic species present in surface water are arsenate, As(V) and arsenite, As(III). Usual treatments for arsenic removal include flotation [2], co-precipitation with ferric chloride, sulfide precipitation [3] or lime softening. These techniques involve the production of highly toxic sludge, which must further treated before disposal. As an alternative to these treatment methods, many sorption techniques have been experimented [4] including using oxide of metals such as manganese [5], iron [6], aluminum [7] lanthanum [8], cerium [9], zirconium [10], tin [11] and titanium [12,13]. Titanium dioxide is non toxic semi conductor and is stable over pH range of 2-14 [14]. Although these adsorbents are effective in removing arsenic ions, a common drawback of inorganic ion exchangers is usually very fine and difficult to obtain in spherical beads of suitable size for the required applications. In order to overcome this difficulty, the oxide was incorporated into the pores of a porous polymer resin [15]. Balaji and Matsunaga [16] has incorporated tin dioxide in Amberlite XAD-7 natural polymer resin and use for adsorption of arsenic ions. However the paper did not mention about the stability of the oxide in the polymer. Poly(hydroxamic acid) chelating resin was reported to form stable complex with Ti(IV) [17]. In the present paper we describe the loading of titanium oxide into poly(hydroxamic acid) chelating resin and studied the adsorption characteristic of As(V). Parameters investigated include effect of pH, contact time, temperature and foreign ions. The sorbent was tested for removal of arsenic ion from industrial waste water samples.

Experimental

Chemicals

Titanium (IV) stock solution (4800 mg/L Ti) was prepared by diluting 11.14 mL TiCl_4 (Merck) in 1000 mL 3 M HCl solution. Arsenic (V) stock solution (1000 mg/L) was prepared by dissolving 4.1644 g $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ (Sigma) in 1000 mL distilled water. Ammonium stock solution (0.1M) was prepared by diluting 0.77 mL 13 M ammonium hydroxide (BDH) with 100.0 ml distilled water.

Phosphate stock solution (1000 ppm) was prepared by dissolving 0.1479 g Na_2HPO_4 (Unilab) in 100.0 ml distilled water. Bromide, sulphate, chromate and carbonate solutions were prepared by dissolving their sodium salts. Sodium acetate buffer solution (0.1M) was prepared by dissolving appropriate amount of sodium acetate (BDH) and adjusted to required pH by acetic acid glacial (BDH). Industrial wastewater samples containing arsenic ion were obtained from electronic and wood treatment industries. Poly(hydroxamic acid) chelating resin was prepared by reacting poly methylacrylate-divinyl benzene with hydroxylamine hydrochloride in alkaline medium using method reported elsewhere [18].

Preparation of titanium oxide-loaded poly(hydroxamic acid) chelating resin (TiO_2 -PHA)

About 10.0 g of the PHA resin was shaken in 95 mL acetate buffer solution at pH 2.7 containing 0.1 M TiCl_4 . The Ti(IV)-loaded resin was filtered and rinsed with distilled water and dried. The Ti(IV)-PHA resin was then shaken in 95 mL 0.1M ammonium hydroxide. The product TiO_2 -PHA resin was filtered and dried in oven at 60°C.

Sorption of As (V) by TiO_2 -PHA

About 0.1000 g of TiO_2 -PHA resin was shaken in 20 mL of 80 mg/L As(V) at various pH values for overnight. The resin was filtered and the filtrate was analyzed for As and Ti by inductively couple plasma atomic emission spectrometer (ICP-AES) (Perkin Elmer model Plasma 1000). Intensity of As emission was measured at λ 189.04 nm while Ti emission was measured at λ 334.94 nm. Sorption kinetic and isotherm (at various temperatures 25°, 50°, 70°C) were studied by shaking the resin in the arsenic solutions at various contact time and concentration, respectively. Effect of foreign ions on the sorption was studied by shaking the resin in As(V) solutions (80 mg/L) either containing phosphate, sulphate, chromate, carbonate and bromide anions of various concentrations. Removal of arsenic ion from industrial wastewater samples was carried out by shaking 0.1 g or more TiO_2 -PHA resin in 20.0 mL sample.

Results and Discussion

Sorption of As (V) by TiO_2 -PHA Resin at various pH

The results show that the As(V) sorption by TiO_2 -PHA was depending on pH (Table 1). The data show that the sorption increases from pH 3.0 and maximum at pH 1.5. The results were similar to that of Balaji and Matsunaga [16]. They reported the As(V) maximum sorption by TiO_2 -loaded polymer occurred from pH 1 to 5. Since the pK_{a1} and pK_{a2} values of H_3AsO_4 are 2.24 and 9.96, respectively [19], the predominant arsenic species sorbed should be H_2AsO_4^- . Dutta et al. [12] and Yang et al. [20] reported that the sorption tendency of As(V) under acidic conditions was stronger than at basic condition. The average PZC of TiO_2

was reported at pH 5.9 [21]. The strong sorption of As(V) at pH > PZC indicates that the electrostatic interaction between positive charge of TiO₂ surface and anions H₂AsO₄⁻ contributes to the process [16]. The sorption trend of As(V) is similar to that of Cr(V) on TiO₂ [22]. When the solution pH reduced from 5.0 to 2.5, the Cr(V) sorption capacity of TiO₂ increased from 7.4 to 14.6 mg g⁻¹. These results showed that the solution pH is important factor affecting the arsenic ion sorption on TiO₂. Table 1 also shows that the desorption of TiO₂ from the resin was negligible at all pHs studied. In the present work pH 1.5 was chosen for further study of As(V) sorption by TiO₂-PHA resin.

Sorption kinetics of As (V) by TiO₂-PHA Resin

The kinetics of sorption of As(V) by TiO₂-PHA resin was studied at various temperatures. The sorption is rapid during initial stage and then decreases when approaching equilibrium. The pseudo-second order rate constant, k₂ for the sorption was determined using the following equation

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{1}$$

where q and q_e refer to the amount of sorption at time t and at equilibrium, respectively. The plot of t/q versus t shows a straight line (R² = 0.89) indicating the applicability of the second-order kinetics (Figure 1). The pseudo second order rate constant k₂ for As(V) sorption on TiO₂-PHA is calculated to be 2.9x10⁻² g mg⁻¹ min⁻¹ at 25°C. In addition the equilibrium capacity was calculated to be 2.08 mg g⁻¹ which is closed to the experimental data.

Table 1: Effect of pH on As(V) sorption by TiO₂-PHA. As(V): 20 mL, 80 mg/g; TiO₂-PHA: 0.1 g.

pH	Sorption capacity mg/L	Dissolution of TiO ₂ %
1.0	0.91	0.5
1.5	1.72	0.3
2.0	1.52	0.2
2.5	1.26	0.2
3.0	1.18	0.1

Activation Energy

The activation energy is related to the rate constant by the Arrhenius equation as shown below

$$\ln k_2 = \ln A - \frac{E_a}{RT} \tag{2}$$

with A is the pre-exponential factor and E_a the activation energy of sorption (kJ mol⁻¹). From the plot ln k₂ as a function of 1/T (Figure 2) the value of activation energy was determined from the slope of the straight line and found to be 4.45 kJ mol⁻¹. It is known that when activation energy is low the rate is controlled by intra-particle diffusion mechanism and hence it can be concluded that the process is governed by interactions of physical nature.

Thermodynamic parameters

The amount of As(V) sorption at equilibrium was measured at 298, 323 and 345 K. The equilibrium partition constant K_d is calculated as follows

$$K_d = \frac{q_e}{C_e} \tag{2}$$

The following relationship has been used to evaluated the thermodynamic parameters ΔG°, ΔH° and ΔS° [23,24]

$$\Delta G^\circ = RT \ln K_d \tag{3}$$

$$\log K_d = \left(\frac{\Delta H}{2.303R} \right) \frac{1}{T} + \frac{\Delta S^\circ}{2.303R} \tag{4}$$

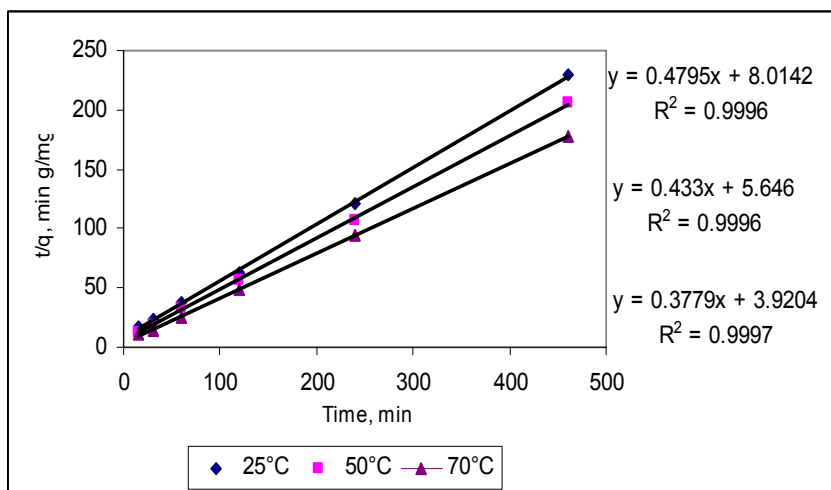


Figure 1 Second order kinetic plots for sorption of As(V) (20 mL, 80 ppm) by (0.1g) TiO₂-PHA resin at various temperatures.

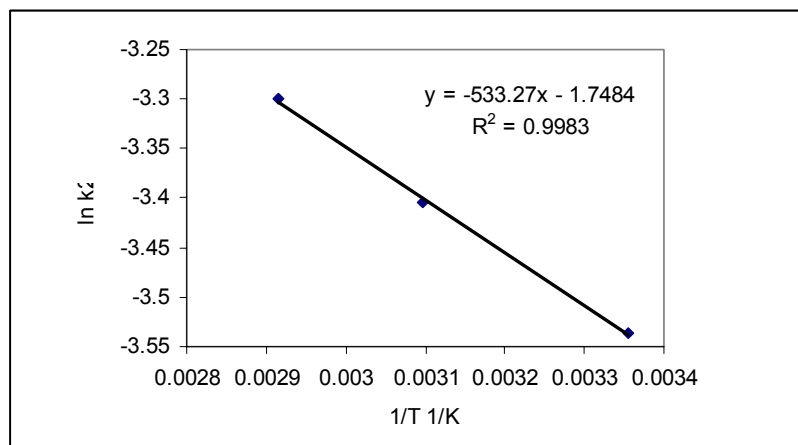


Figure 2 Arrhenius plot for second order rate constant, k₂

The change in the free energy (ΔG°) is calculated to be $-6.99 \text{ kJ mol}^{-1}$ at 25°C . The negative value of ΔG° means the sorption of As(V) on the resin is spontaneous, perhaps due to columbic attraction. As shown in Eq. (4), a plot of $\log K_d$ versus $1/T$ would give ΔH° and ΔS° (Figure 3). The value of ΔH° and ΔS° (25°C) are 8.03 kJ mol^{-1} and -3.48 J mol^{-1} . The positive value of ΔH° confirms that the sorption process is endothermic in nature. The sorption energy lies well within the range of $8\text{-}16 \text{ kJ mol}^{-1}$ which is the sorption energy for ion exchange process [25]. The negative values of ΔS° reflect the affinity of the sorbent towards As(V) which increase the order of the sorbate after the sorption.

Equilibrium Model

Equilibrium data is important to compare the performance of different sorbent materials. Among equilibrium models, Langmuir isotherm is commonly used for sorption data. The equation represents the equilibrium amount of metal sorbed (q_e) as a function of the equilibrium concentration (C_e) is as follows

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \tag{5}$$

By plotting C_e/q_e versus C_e , Langmuir constants, Q_0 (maximum sorption capacity) and b , (related to binding energy) can be determined if a straight line is obtained (Figure 4). The maximum sorption capacity at monolayer Q_0 and equilibrium constant b were calculated as 12.72 mg g^{-1} and $21.73 \times 10^{-4} \text{ L mg}^{-1}$. These values were higher compared to those reported by Balaji and Matsunaga [16] who used TiO₂ loaded Amberlyte XAD-7 polymer resin for As(V) sorption. They reported that maximum As(V) sorption capacity at monolayer Q_0 and equilibrium constant b were 4.73 mg g^{-1} and $7.87 \times 10^{-4} \text{ L mg}^{-1}$, respectively. However the maximum sorption capacity of As(V) by granular titanium oxide was reported to be 41.4 mg/g [13].

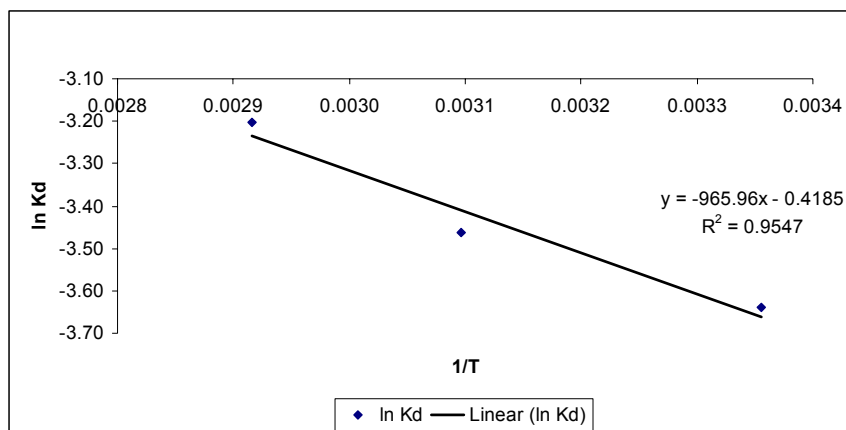


Figure 3: Van't Hoff plot for the sorption of As (V) by TiO₂-PHA.
As(V): 20 mL, 80 ppm, TiO₂-PHA resin 0.1g

Effect of foreign ions

The efficiency of the sorbent for removal of arsenic in the treatment of industrial wastewater is usually affected by selectivity against various common anions. The influence of coexisting ions of various concentrations towards the sorption of As(V) was investigated. Table 2 shows that with the exception of HCrO₄⁻ and H₂PO₄⁻, all other anions studied did not significantly affected As(V) removal present at similar concentration. However the presence foreign anion at a higher anion:As(V) ratio reduced the sorption removal significantly especially phosphate. We also found the unexpected results where the present of chromate ion increase the sorption of As(V) significantly (Table 2).

Removal of arsenic ion from industrial wastewater samples

Two types of industrial wastewater samples were from electronic and wood treatment industries. Appropriate amount of TiO₂-PHA sorbent were shaken in 20 mL of industrial wastewater samples without any pretreatment. Table 3 shows the percentage removal of arsenic ion by the resin. The percentage removal was depending on the initial concentration of arsenic ion in the samples and the dosage of sorbent used. The low percentage arsenic removal could be due to the interference by other anions in the wastewater samples.

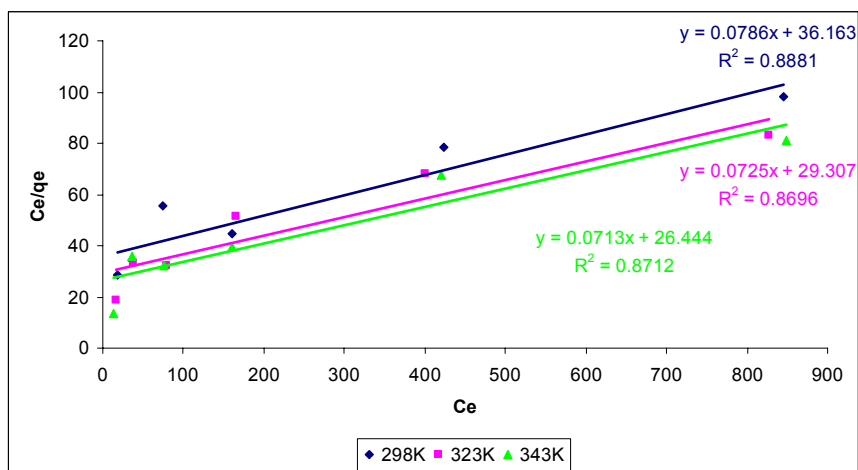


Figure 4 Langmuir plot for sorption of As(V) by TiO₂-PHA.
Resin dosage 0.1g at various temperatures.

Table 2 Variation of percentages of As(V) sorption capacities in the presence of foreign anions at different concentration ratios. As(V) initial concentration 80 ppm, 20 ml; TiO₂-PHA dosage 0.1g

Ratio of Anion:As(V)	HCrO ₄ ⁻	H ₂ PO ₄ ⁻	Br ⁻	CO ₃ ²⁻	NO ₃ ⁻	SO ₄ ⁻
1:1	119	82	97	90	98	99
5:1	142	14	63	58	108	66
10:1	165	9	71	57	82	45

Table 2 Percentage removal of arsenic ion from industrial wastewater samples by TiO₂-PHA sorbent.

Sample	pH	Initial As concentration ppm	Dosage g	Percentage removal
A50	5.89	2.65	0.10	10.90
B	1.57	60.30	0.10	18.52
E	1.88	49.12	0.10	14.75
E	1.88	49.12	0.40	20.66
E	1.88	49.12	0.60	25.48
E	1.88	49.12	1.00	30.81

A50=electronic industry, B and E =wood treatment industry

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References

- 1 C.J. Chen (1992) Br. J. Cancer, 66:8888
- 2 Y. Zhao, A.I. Zouboulis and K.A. Matis (1996). Hydrometallurgy 43:143
- 3 D. Bhattacharyya, A.B. Jumawan Jr and R.B. Grieves (1979) Sep. Sci. Technol. 14:441
- 4 L. Dambies, E. Guibal and A. Roze (2000) Arsenic(V) sorption on molybdate-impregnated chitosan beads. Coll. and Surfaces A 17:19-31
- 5 S. Bajpai and M. Chaudhuri (1999) Removal of arsenic from ground water by manganese dioxide-coated sand. J. Env. Eng. 125(8):782-784
- 6 P.R. Grossl, M. Eick, D.L. Sparks, S. Goldberg and C.C. Ainsworth (1997) Arsenate and Chromate Retention Mechanisms on Goethite. 2. Kinetic Evaluation Using a Pressure-Jump Relaxation Technique, Environ. Sci. Technol. 31:321-326.
- 7 S.K. Gupta and K.Y. Shen (1978) Arsenic removal by adsorption. J. Wat. Pollut. Control Fed. 497-436
- 8 S. Tokunaga, S.A. Wasay and S.W. Park (1997) Wat. Sci. Tech. 35: 71-78
- 9 H. Imai, J. Nomura, Y. Ishibashi and T. Konishi (1987) Anion adsorption behavior of rare earth oxide hydrates. Rare Earth 5:807
- 10 T.M. Suzuki, J.O. Bomani, H. Matsunaga, T. Yokoyama (1997) Chem. Lett. 1119
- 11 D.A. White & R. R. (1997) The sorption of anionic species on hydrous tin dioxide. Chemical Engineering Journal 66(2):85-89
- 12 P.K. Dutta, A.K. Ray, V.K. Sharma and F.J. Millero (2004) Adsorption of arsenate and arsenite on titanium dioxide suspensions. J. Coll. Interfaces Sci. 278:270-275
- 13 S. Bang, M. Patel, L. Lippincott and X. Meng (2005) Removal of arsenic from ground water by granular titanium dioxide adsorbent. Chemosphere 60: 389-397
- 14 K. Esumi, H. Toyoda, T. Suhara and H. Sukui (1998) Colloid and Surfaces A, 145:145
- 15 T.M. Suzuki, Bomani, J.O., Matsunaga, H. Yakoyama, T. (2000) Preparation of porous resin loaded with crystalline hydrous zirconium oxide and its application to the removal of arsenic. Reactive and Functional Polymers 43:165-172
- 16 T. Balaji and H. Matsunaga (2000) Adsorption characteristics of As(III) and As(V) with titanium dioxide loaded Amberlite XAD-7 resin. Anal. Sci. 18:1345-1347
- 17 R.J. Phillips and J.S. Fritz (1980) Synthesis and analytical properties of an N-phenyl hydroxamic acid resin. Anal. Chim. Acta. 121: 225-232
- 18 M. J. Haron, W.M.Z. Wan. Yunus, M.Z. Desa and A. Kassim (1994). Synthesis and properties of poly(hydroxamic acid) from cross linked poly(methacrylate). Talanta 41(5) 805-807
- 19 A.E. Martell and R.M. Smith (eds) (1979) Critical Stability Constants, Plenum Press, N.Y., 4:133
- 20 H. Yang, W.Y. Lin and K. Rajeshwar (1999) Homogeneous and heterogeneous photo catalytic reactions involving As(III) and As(V) species in aqueous media. J. Photochemical. Photobiol A: 123: 137-143
- 21 M.K. Smulski (2002) The significance of difference in the point of zero charge between rutile and anatase. Adv. Coll. Interf. Sci. 99:255-264
- 22 C.H. Weng, J.H. Wang and C.P. Huang (1997) Adsorption of Cr(VI) onto TiO₂ from dilute aqueous solutions. Water Sci. Technol. 35(7) 55-62
- 23 L. Zhu, X. Ren and S. Yu ((1998) Use of cetyltrimethylammonium bromide-bentonite to remove organic contaminants of varying polar character from water, Environ. Sci. Technol 32:3374
- 24 J.I. Huh, D.I. Song and Y.W. Jeon (2000) Sorption of phenols and alkylphenols from aqueous solution onto organically modified montmorillonite and applications of dual-model sorption model, Sep. Sci. Technol. 35:243
- 25 M.A. Rauf, S.M. Hasany, M. Ikram and N. Din (1995) Adsorption studies of arsenic on manganese dioxide using radiometric technique. Ads. Sci. Technol. 12:93-100 ↵