

Application of Hydrothermal and Non-Hydrothermal TiO₂ Nanoporous Materials as New Adsorbents for Removal of Heavy Metal Ions from Aqueous System

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ABSTRACT

Hydrothermal and non-hydrothermal spherical TiO₂ nanoporous with crystalline framework were prepared by sol-gel method. The Crystalline structures, morphologies and surface texturing of materials were determined by X-ray diffraction (XRD), scanning electron microscopy (SEM) and N₂ adsorption-desorption isotherms. The Hydrothermal spherical TiO₂ nanoporous was found to have a narrow and strong pore size distribution peaks with average of 37.8 Å and pore volume of 0.41 cm³/g and the (Brunauer–Emmett–Teller) BET specific surface area of 365 m²/g. Hydrothermal and non-hydrothermal spherical TiO₂ nanoporous have been used as adsorbent to study of the adsorption behavior of Pb(II), Co(II) and Ni(II) ions from aqueous system in a batch system. Effect of equilibrium time on adsorption Pb(II), Co(II) and Ni(II) ions on these adsorbent was studied The results show that the shaking time 0.5 to 10h has no serious effect on the percentage of ions removal, and the adsorption is fast in all cases. The maximum uptake capacities of Hydrothermal and non-hydrothermal spherical TiO₂ nanoporous was calculated. Both hydrothermal and non-hydrothermal TiO₂ nanoporous materials were found to have very good potential as new adsorbents in removal of these ions. In batch systems the maximum uptake capacities of Pb(II), Ni(II) and Co(II) on the hydrothermal and non-hydrothermal TiO₂ nanoporous materials was Co(II) > Pb(II) > Ni(II) and Co(II) > Ni(II) > Pb(II), respectively.

Keywords: Adsorbent; Heavy metals; Nanoporous Materials; Titanium dioxide.

1. Introduction

Although heavy metals are well known for their toxic effect and tendency to accumulate in living bodies [1-2] many industries are responsible for the release of heavy metal ions in the environment through their wastewaters [3]. Metal ion concentrations in the range of mg/L can be easily reduced by electrochemical treatment [4-5], reverse osmosis [6] or chemical treatment [7] of the wastewater. However, these conventional ways are inadequate, expensive or have secondary problems. Moreover, the application of these methods

becomes more costly at lower concentrations of metal ions [8]. Even though the adsorption process is probably the most attractive and efficient method for decontamination of waste water [9-10], the cost of the adsorbent is an importance limiting factor. Thus, the use of new low cost materials able to replace materials such as activated carbon [11-12] and resins [13-16] is importance. Attention has been focused on biopolymers [17], natural zeolites [18-19] clays [20-21], natural oxides [22], and carbonaceous waters [23], which are cheap and able

to remove heavy metal ions from contaminated water [24]. However, lack of model predictability and their inability to remove the pollutants down to very low levels are a drawback of these materials. In contrast, synthetic zeolites and nanoporous materials have well-defined structures, high ion-exchange capacity, selectivity and environmental compatibility [25-27].

TiO₂ nanomaterial is promising with its high potential and outstanding performance in photocatalytic environmental applications, such as CO₂ conversion, water treatment, and air quality control. For many of these applications, the particle size, crystal structure and phase, porosity, and surface area influence the activity of TiO₂ dramatically. TiO₂ nanomaterials with special structures and morphologies, such as nanospheres, nanowires, nanotubes, nanorods, and nanoflowers are thus synthesized due to their desired characteristics [28-29]. The mesoporous TiO₂ with large surface area and narrow pore size distribution, by a modified sol-gel method with phosphorus surfactants as templates has been reported by Antonelli and Ying [30], which has opened many possibilities for its application in catalysis, separation and nanoscience [31].

ETS-10, first synthesized by Engelhard in 1989 [32] is a microporous zeolitic titanosilicate with the basic anhydrous formula Na_{1.5}K_{0.5}TiSi₅O₁₃ [33]. Nanoporous TiO₂ is a mesoporous titanosilicate with framework composed of SiO₄ and TiO₆. The presence of each tetravalent Ti atom in an octahedron generates two negative charges, which are balanced by alkali metal ions Na⁺ and K⁺ [33]. the exchangeable ions (Na⁺, Ca²⁺ and K⁺) present great potential for the purification of metal-polluted waters, Because these ions are relatively harmless [34].

According to our previous paper [35], a mesoporous TiO₂ with crystalline framework was synthesized using a double surfactant system and the potential of these materials in removal of heavy metal ions from aqueous solutions was studied. In the present work, mesoporous TiO₂ was synthesized using a single surfactant system. Then the potential of this products in removal of pollutants mentioned above were studied. Effect of contact time and initial concentration for Pb(II), Ni(II) and Co(II) ions have been described. Furthermore, the adsorption results were compared with those of mesoporous TiO₂ using a double surfactant system.

2. Experimental

2.1. Material

Reagents used in this study were N-cetyl-N, N, N-trimethylammoniumbromide (CTAB), titanium (IV) oxide, and sodium silicate from E. Merck (Germany). All chemicals were used without further purification.

2.2. Synthesis of nanoporous TiO₂

For synthesis of nanoporous TiO₂ by a sol-gel method [36], 10g of sodium silicate solution (27.5 wt. % SiO₂, 8 wt. % Na₂O) was mixed with a solution of 2.25g of NaOH (Merck) in 50ml of distilled water and then 6.65g of CTAB was added. The mixture was stirred for 5min and then 0.773g of TiO₂ was added to the solution. The pH of the gel with 37 wt. % hydrochloric acid (Merck) was adjusted to 13.5. The mixture was stirred at room temperature for 30min to form a homogeneous translucent gel with the composition 5.0 SiO₂: 1.0 TiO₂: 2.4 NaOH: 5.0 CTAB: 2.7 HCl. nanoporous TiO₂ material synthesized without hydrothermal treatment is denoted Tinh.

2.3. Hydrothermal treatment of nanoporous TiO₂ materials

The hydrothermal treatment was carried out with the following procedure: Tinh materials was heated at 80°C for 24h without stirring. The resulting powder was collected by filtration and thoroughly washed with water. Nanoporous TiO₂ material synthesized with hydrothermal treatment is denoted Tih.

2.4. Calcination of nanoporous TiO₂ materials

To removal of the surfactant the material was heated at 550°C for 6h.

2.5. Characterization of nanoporous TiO₂

The morphology of the materials was studied using Scanning Electron Microscopy (SEM JEOLJSM-6330F). The crystalline structures of the materials were investigated by analyzing the X-ray powder diffraction patterns (XRD) obtained with a SIEMENS D5005 diffractometer equipped with Cu K α irradiation and a fixed powder source (40kV, 40 mA). The specific surface area and pore size distribution were measured by analyzing the N₂ adsorption-desorption isotherms obtained at 77K using Micrometric ASAP 2010 equipment. The surface area of the materials were calculated using the Brunauer- Emmett- Teller (BET) equation, and

their pore-size distribution were determined by the Barrett-Joyner-Halenda (BJH) formula from the desorption branch.

2.6. Synthetic wastewater preparation

Synthetic wastewater solutions were prepared by dissolving analytical grade Pb (NO₃)₂, Ni (NO₃)₂·6H₂O, Co (NO₃)₂·6H₂O and copper phthalocyanine powder in distilled water to obtain 1000 mg/L of metal solutions. The solutions were diluted to the required concentrations for experiments. The pH of the solutions was measured and was found as 5.5±0.5.

2.7. Batch adsorption tests

Batch adsorption tests were conducted by mixing 0.05g of Tih and Tinh and 25 ml of solution of known metal ion concentration. Metal ion concentrations used were in the range 50-500 mg/L. The mixture was shaken in a mechanical shaker and filtered at known time intervals. The sample was filtered to remove any fine particles and analyzed for the metal ions. Series of experiments were conducted to determine the effect of initial metal ion concentration and time on adsorption. The solution pH was at 5.5±0.5 and all the experiments were conducted at room temperature 22±2 °C. Atomic absorption spectrophotometer with an air-acetylene flame and hollow cathode

lamps for Pb(II), Ni(II) and Co(II) was used for metal ion analysis. The absorbance of the samples was read in triplicate.

3. Results and discussion

3.1. SEM images

The surface morphology of the Tih nanoporous material was observed by SEM and are shown in Fig. 1a-d. The particles have spherical morphology with a diameter range of 50-200 nm. These fine particles may explain the high surface area of the material.

3.2. XRD Pattern

In order to analyze the crystallite phases and crystallinity of the material, the powder X-ray diffraction (XRD) pattern of the Tih material was investigated (Fig. 2). A diffraction peak due to an anatase phase is present at 2θ= 25°, the average crystallite size was calculated from this peak (1 0 1) with the Scherer equation ($\Phi=k\lambda/\beta\cos\theta$), where Φ is the crystallite size, λ is the wavelength of the X-ray irradiation(0.154nm), k usually taken as 0.89, β is the peak width at half-maximum height and θ is the diffraction angle of the (1 0 1) peak. The average crystallite size for anatase was found to be 22.3nm that indicates high intensity of anatase phase. A crystalline phase of rutile can be seen at 2θ=38°. Crystallinity ratio of anatase and rutile phases is

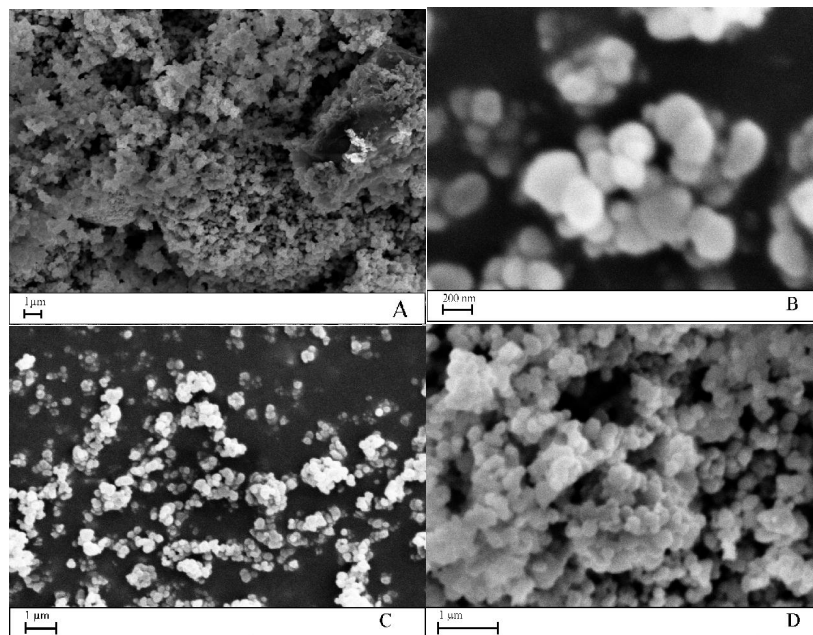


Fig. 1- SEM images of Tih with spherical shape.

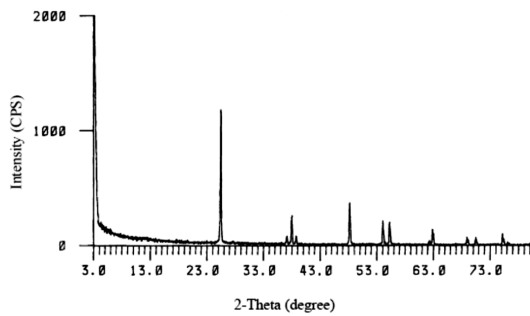


Fig. 2- X-ray diffraction of Tih material.

close to 3:1. The stability of the anatase phase up to 550°C can be attributed to the small crystallite sizes in the inorganic domain. Thermodynamic phase stability is generally dependent on particle size and the anatase structure is more stable thermodynamically than the rutile structure at particle sizes below approximately 14nm.

3.3. N₂ adsorption-desorption isotherms

Nitrogen physisorption is the method of choice to gain knowledge about nanoporous materials. This method gives information on the specific surface area and the pore diameter. Calculating pore diameters of nanoporous materials using the BJH (Barrett, Joyner, and Halenda) method is common. Former studies show that the application of the BJH theory gives appropriate qualitative results which allow a direct comparison of relative changes between different nanoporous materials. Fig.3 shows The N₂ adsorption-desorption isotherms of the nanoporous TiO₂ samples. Here, Tih material has a large surface area than Tinh which is due to hydrothermal treatment for Tih; for this material a hysteresis loop with a stepwise adsorption and desorption branch was observed for a wide range of pressures (P/P₀) and which has a surfactant area of 365 m²/g. The pore size distribution of the

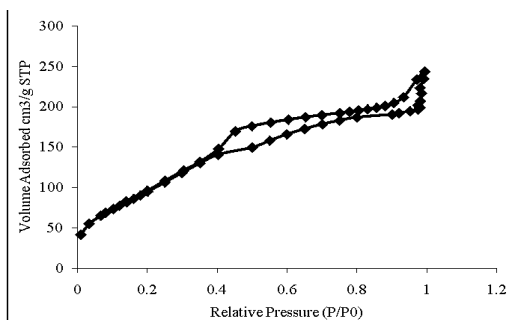


Fig. 3- N₂ adsorption-desorption isotherms of Tih nanoporous material.

material was analyzed by the BJH method for the desorption branch. The Tih material was found to have a narrow and strong pore size distribution peaks with average of 37.8 Å and pore volume of 0.41 cm³/g. Tinh material was found to have a low pore size distribution intensity with an average pore size of 29.1 Å [37-38].

3.4. Adsorption study

The metal ion concentrations obtained for batch experiments were converted to percentage of metal ion removed and amount of metal adsorbed per unit weight of adsorbent after making necessary corrections for errors due to filtration. The results thus obtained are presented and discussed in this section.

3.4.1. Effect of contact time, initial concentration

In order to establish the equilibration time, the effect of contact time on the adsorption of Pb(II), Ni(II) and Co(II) by Tih and Tinh was studied. The studied time range was from 0 to 10 h using 0.05g adsorbent (Tinh and Tih) and 25 mL 50 mg/L, 250 mg/L and 500 mg/L metal ions solution at room temperature and pH of solution 5.5. Figures 4.a, 5.a and 6.a show the removal percentage of metal ions for Tih, and figures 4.b, 5.b and 6.b show same results for Tinh. The results show that the shaking time 0.5 to 10h has no serious effect on the percentage of ions removal, and the adsorption is fast in all cases. Thus, shaking time 0.5 h was used for subsequent experiments. The adsorption rate was related to the content of the active adsorption sites on the matrix of the adsorbent and also on the metal ionic radius [39]. As can be seen in this figure, Pb(II) ions with a greater ionic radius showed the higher adsorption rate than of Ni(II) and Co(II) ions. Also, initial concentration of Pb(II) ion has no effect on removal percentage but for Ni(II) and Co(II) ions showed a increases at removal percentage from initial ion concentration of 50mg/L to 250 and 500 mg/L. However, amount of metal adsorbed per unit weight of adsorbent, q, is higher at high concentrations. The heavy metal ions displayed different adsorption properties on Tih and Tinh. The differences between hydrothermal and non-hydrothermal treatment in terms of their adsorption capacity is mentioned in table 1. As can be seen , the maximum adsorption capacities of Pb(II), Ni(II) and Co(II) on the Tih and Tinh nanoporous was Co(II) > Pb(II) > Ni(II) and Co(II) > Ni(II) > Pb(II), respectively. The order

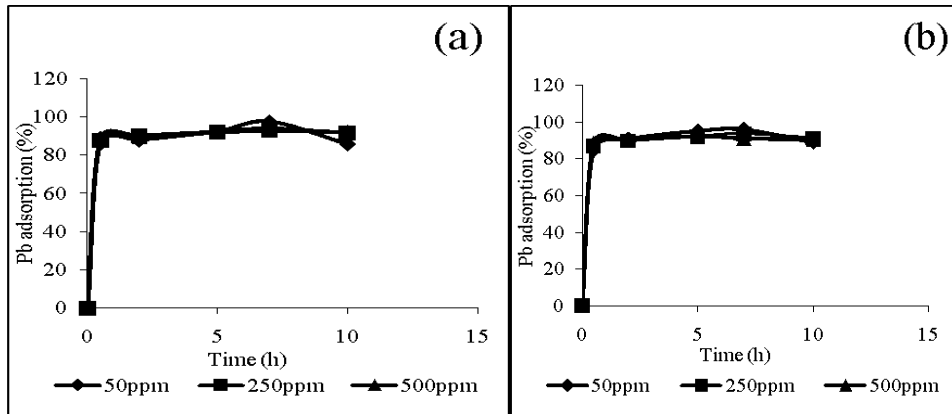


Fig. 4- Effect of equilibrium time on adsorption of Pb(II) ion on (a) Tih, and (b) Tinh.

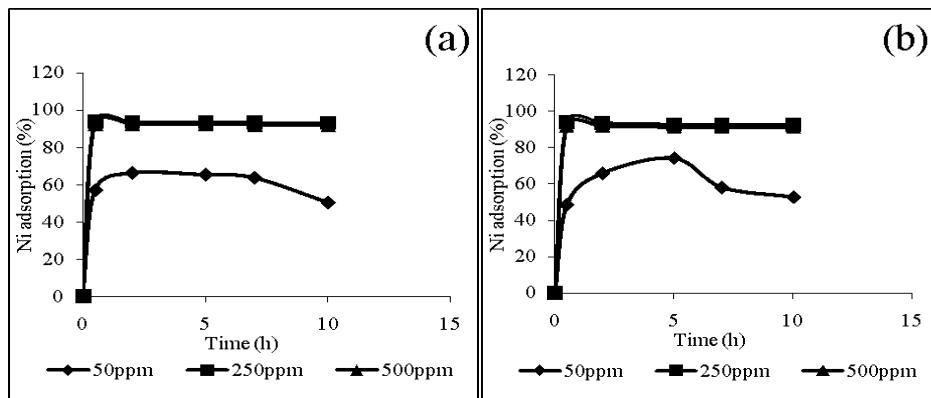


Fig. 5- Effect of equilibrium time on adsorption of Ni(II) ion on (a) Tih, and (b) Tinh.

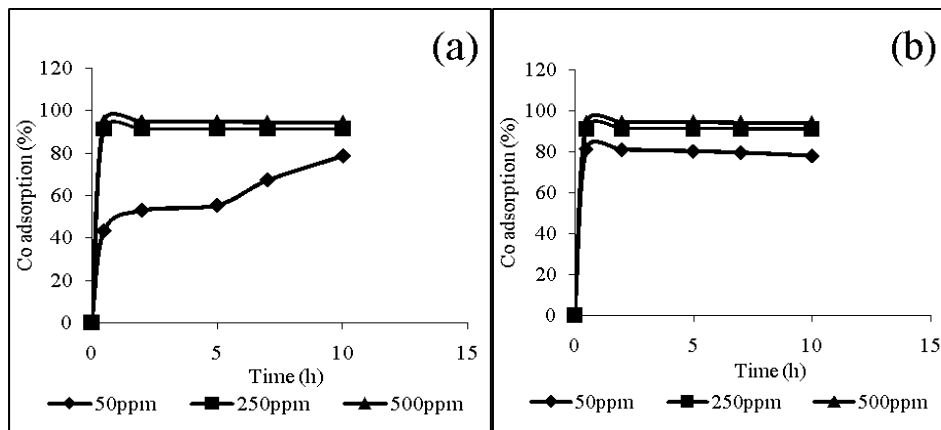


Fig. 6- Effect of equilibrium time on adsorption of Co(II) ion on (a) Tih, and (b) Tinh.

of affinity of these ions towards Tih and Tinh is related to the physicochemical characteristics of the heavy metal ions including ionic radius and hydration energy of the heavy metal ions assayed and effective interaction with the lattice oxygen.

4. Conclusions

In this paper, synthesis and characterization of

nanoporous TiO_2 materials and their properties as new adsorbents for removal of Pb(II), Ni(II) and Co(II) have been reported. The materials have high porosity and good surface areas that make them suitable for adsorption applications. Rate of removal for Pb(II), Ni(II) and Co(II) are about same 0.5h after shaking equilibrium is obtained. In batch systems the maximum uptake capacities

Table 1. Comparative data of the adsorption capacity of for both single and double surfactant system

adsorbent	qe (mg/g)			references
	Pb	Ni	Co	
Tih	222.92	231.30	237.66	This study
Tinh	221.88	230.10	236.01	This study
Ti2sh	239.52	226.79	238.36	[35]
Ti2snh	238.44	233.90	238.90	[35]

of Pb(II), Ni(II) and Co(II) on the Tih and Tinh nanoporous was Co(II) > Pb(II) > Ni(II) and Co(II) > Ni(II) > Pb(II), respectively. Comparison of adsorption efficiently for both single and double surfactant system table 1, Since adsorption capacity for the nanoporous TiO₂ materials at present study is not much lower than the nanoporous TiO₂ materials at previous study [35] and the adsorption results for single surfactant route approximately close to our previous paper reported values, we can use from single surfactant route because of the cost-effectiveness of this method.

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