Assessment of Adsorption Capacity of Thiol-functionalized Titanate Nanotubes for Removal of Cu(II) and Ni(II) from Aqueous Solution via Static Adsorption

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ABSTRACT

The significance of toxic metals pollution treatment has become incrementally manifested as an important environmental issue in the recent years due to the urgent need to access healthy water and increase of the anthropogenic activities in water contamination. For efficient treatment of water contaminants, the selective and novel materials are always welcomed. In this study, the hydrothermally synthesized titanate nanotubes (TNT) were modified by the mercaptosilane modifier for the removal of Cu(II) and Ni(II) toxic contaminants. The modified TNT adsorbant (TNT/Sil) was characterized in terms of the physicochemical aspects and then, the experiments for capturing metal cations were performed in batch mode. The modified adsorbent presented more affinity for the removal of Cu(II) than Ni(II). The results demonstrated that the experimental data were highly fitted to the Freundlich isotherm model and the maximum uptake capacities for Cu(II) and Ni(II) were found to be 53.77 and 45.29 mg g⁻¹, respectively. In addition, endothermic nature of the adsorption process was predicted by the thermodynamic study as well as the pseudo-second order model that was corresponded to the kinetic data. Considering these achievements and due to the surface hydroxyl and thiol functional groups, TNT/Sil adsorbant could be effective and promising material in the purification of wastewaters, contaminated with toxic metal cations.

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NOMENCLATURE

ΔG° Gibbs free energy change (kJ/mol) Kc Thermodynamic equilibrium constant (L/g)
ΔH° Standard enthalpy change (kJ/mol) qe Adsorption capacity at equilibrium point (mg/g)
ΔS° Standard entropy change (J/mol K) qt Adsorption capacity at time t (mg/g)
C0 Equilibrium concentration (mg/L) NPs Nanoparticles
C0 Initial metal ion concentration (mg/L) k1 Pseudo-first order model rate constants (min⁻¹)
kL Freundlich constant TNT Titanate nanotubes
kL Langmuir parameter (L mg⁻¹) TNT/Sil Thiol-functionalized titanate nanotubes

INTRODUCTION

In the last few decades, a leaping rise in the industrialization and urbanization of worldwide coupled with the population growth have led to increased discharge of wastewater to the water streams without adequate treatment. Because of daily and enormous application of the heavy metals (e.g. Cu(II), Ni(II), Pb(II), Zn(II), Cd(II), Hg(II) and etc.) in the industrial processes, threat of heavy metal ions in the industrial effluents is a consistent concern of the environmental activists. Heavy metals are highly toxic and possess carcinogenic effects even at trace levels, they resist to the biodegradation and have propensity to accumulate in the tissue of living...
organisms. These toxic metals disrupt physiological activities of human bodies in case of entering their food chain and followed serious vital problems [1].

According to the scientific reports, water scarcity will be a major challenge toward 2025 due to the limited available healthy water resources [2]. Significant anthropogenic sources such as electroplating, specialist alloys and steels, mining, batteries, etc. generate continuously copper and nickel containing effluents [3].

Wilson’s disease, acute hemolytic anemia, chronic renal disease, liver damage, etc. are some health risks which caused by Cu(II) and Ni(II) intake through the contaminated water and food. As the resources become limited more and more, treatment of these wastewaters is essential to protect the human and eco-system because of the daily utilization of these toxic metals in the industries [4, 5]. As reported by World Health Organization (WHO), the allowable limit for Cu(II) and Ni(II) contaminants in the potable water is 1.5 mg/L and less than 0.1 mg/L and in the industrial effluents is 0.05-1.5 mg/L and 2 mg/L, respectively [6]. In this matter, the removal and recovery of toxic metal ions from industrial effluents is essential; therefore various conventional and modern methods, including adsorption, precipitation, coagulation-flocculation, ion exchange, membrane filtration, electrochemical, etc. were implemented. However, all of these techniques own their remarkable excellence and drawbacks. High energy consumption, imperfect treatment, producing extra toxic wastes, low selectivity and high operating costs and low efficiency are the challenges which constrain their applicability [4].

Undoubtedly, there is a crucial need to search more cost-effective and efficient techniques to deal with the heavy metals health hazards.

Practically, a combination of the treatment methods should be applied to acquire the desired water quality owing to the complex nature of the metallic effluents. To date, adsorption is recognized as an alternative treatment method due to the high removal efficiency, flexibility in operation, convenient recovery of the adsorbent, low costs, suitable selectivity by particular functional groups, no need to the chemical reagents and production of high quality treated wastewater.

So far, a variety of inorganic and organic adsorbents such as carbonaceous nanomaterials, nanostructured mixed oxides or metal oxides, biosorbents, composite materials and polymeric sorbents have been proposed for the removal of metal impurities [4]. Nanosize metal oxides such as manganese oxides (MnO₂), silicon dioxide (SiO₂), zinc oxide (ZnO), iron oxide (Fe₂O₃), titanium oxide (TiO₂), aluminum oxide (Al₂O₃), etc. can provide high surface area and specific affinity toward the target compounds because of their different nanostructures and due to their low environmental effects and sludge production, many researches have been performed to develop adsorbents based on these materials [7]. Titanate nanostructures (e.g. nanotubes, nanosheets, nanowires, nanorods) are such hopeful metal oxide materials which have attracted tremendous attentions in the wastewater treatment; thanks to their high specific surface area, surface rich in -OH groups, ion-exchange capability, favorable structural stability and excellent physicochemical properties [8, 9]. Many research works were devoted to the potential of the titanate nanostructures as the promising candidate for the removal of Ni(II), Cd(II), Zn(II), Pb(II), Cr(III), Hg(II) and Cu(II). These studies have focused on the adsorption behavior of titanate adsorbents and found that they present excellent removal efficiency to the metal cations [9-13].

On the other hand, the metal oxide adsorbents have high tendency to aggregation which declined their adsorption capacity. Surface modification of the adsorbents with the specific coupling agents or ligands is one method to overcome this problem. Moreover, surface functionalization can improve the adsorbents selectivity toward special metal ions. Various organic or inorganic functional groups can be grafted to the surface of the metal oxides which can be categorized into different groups such as silanes, carboxylic acids, organophosphorus and polymer/copolymers [14].

Dobrzyńska et al. [15] modified mesoporous silica with the mercapto and amino silane agents and used them for the removal of Pd(II). They found that compared to the amino silane agent, the thiol-modified silica showed great uptake and affinity to the Pd(II) in the investigated range of initial concentration and pH [15].

Zhu et al. [16] investigated four types of silane coupling agents for the surface functionalization of halloysite nanotubes/Fe₃O₄ adsorbent and applied them for the removal of Sb(V) and Cr(VI). Achieved results indicated that the modified adsorbent had higher adsorption capacity in the both single and multicomponent solutions of the toxic metal ions [16]. In another researches, ligand based functional adsorbents were synthesized for the detection and removal of Ni(II), Pb(II) and Cu(II) from wastewater; which these adsorbents containing ‘S’, ‘O’ and ‘N’ donor atoms to form a stable complex with the metal cations and capture them [17-19].

This study was aimed to prepare the metal oxide nanostructure modified with organosilane agent for the removal of metal ions from wastewater. The titanate nanotubes (TNTs) were synthesized hydrothermally and successfully modified with mercapto silane agent. To the best of our knowledge, there are limited researches about the surface modification of TNTs; particularly the thiol-functionalization of their surface is not studied yet, neither in the environmental fields nor in others. This novel adsorbent was characterized by FTIR, SEM, EDS, XRD and TEM. A range of static adsorption experiments were carried out to evaluate the adsorption abilities of the mercapto-functionalized TNTs to Cu(II) and Ni(II) in the solutions. The modified TNTs have slightly more affinity to copper ions over nickel.
MATERIAL AND METHODS

NiCl₂·6H₂O and CuSO₄·5H₂O (from Aldrich) were used to prepare Ni(II) and Cu(II) stock solutions (1000 mg/L). To perform the batch adsorption experiments, working solutions were prepared by diluting the stock solutions. TiO₂ nanopowder (mixed of anatase and rutile crystalline phase, Evonik, Germany) and sodium hydroxide (NaOH 98 wt%, Merck) pellets were employed for the hydrothermally synthesis of TNTs. (3-mercaptopropyl) trimethoxysilane (MPTMS, HS(CH₂)₃Si(OCH₃)₃, 95 wt%, Sigma-Aldrich) was utilized as the coupling agent for the surface modification of TNTs. Deionized water (DI) was used for the preparation of all aqueous solutions. Acetone was supplied from Merck and used as the solvent.

Synthesis of titanate nanotubes

TNTs were prepared using the alkaline hydrothermal method according to the procedure of Kasuga et al. [20]. As a brief description of the synthesis method, 1 g TiO₂ nanopowder was added to the Teflon container with 50 mL of 10M NaOH solution and then, stirring and sonicating around 2 h; this milky suspension was transferred to the autoclave and heated at 160 °C for 72 hours. After the hydrothermal reaction, the resulted alkaline precipitates were filtered, washed several times with DI water until the pH value of the rinsing water reached near neutral and then, were dried at 80 °C for 12 h. The as-synthesized TNTs were milled, then sieved and kept in the desiccator until usage. During the hydrothermal reaction, some of the Ti-O-Ti bonds of TiO₂ powder are broken and the compounds (i.e. [Ti(OH)₆]²⁺) are formed and these compounds combined together to produce a nanosheet or layered structures. Finally, the nanosheets with some Na⁺ and H⁺ between their layers rolled into a cylindrical shape [21].

Surface modification of TNTs

Surface modification of TNTs was performed as follows: in two separate containers, 0.2 g as-prepared TNTs in 20 mL acetone in the first one and in the second container, mercaptosilane modifier (TNT/MPTMS = 3% w/w) in 20 mL DI water were stirred. TNTs mixture was added dropwise to the modifier solution and mixed around 2 h at ambient conditions. The obtained sample was centrifuged, filtered and washed firstly with acetone and then, thoroughly rinsed with DI water to remove excessive unattached silane agent and other impurities. Afterward, the modified sample with thiol groups was dried at 60 °C for 24 h and labeled as TNT/Sil adsorbent. In the functionalization process, some of silanol groups were hydrolyzed and then condensed. Finally, these groups interacted with the surface hydroxyl groups of TNT and attached to them. A schematic of thiol functional groups grafted on the hydroxyl groups of TNTs’ surface is presented in Figure 1.

**Figure 1.** Schematic for the surface modification of TNT

**Instruments and analyses**

The determination of metal cations concentration was executed by ICP-OES (Agilent 124 Technologies 5100) measurement. Transmission Electron Microscopy (TEM) image was obtained by Hitachi 7700 and Field Emission Scanning Electron Microscopy (FESEM) (Hitachi S-4800) supplied with energy-dispersive X-ray spectroscopy (EDS) were applied to study the morphology and elemental analysis of the as-synthesized adsorbents. For determination of NPs functional groups, the FT-IR spectra of the samples was obtained using the Vertex 70 by Bruker Optics (Germany). The crystalline pattern of the TNT/Sil adsorbent were studied by X-ray diffractometer (XRD, X' Pert PRO).

Static adsorption assay

The metal ions static adsorption was studied in batch mode. All the adsorption equilibrium tests at isothermal conditions and the kinetics studies were attained for 100 mL aliquot of the metal salts working solutions by mixing them with 0.125 g of the as-synthesized adsorbent in a flask on a shaker at 170 rpm for predetermined time periods. Syringe filter of cellulose acetate membrane was utilized for filtration of the solutions in all samplings. Subsequently, the concentration of the samples was analyzed by ICP-OES. Experiments on the adsorption isotherms were carried out at various temperatures in the range of 25-45 °C and with the initial metal cation concentrations in the range of 20-150 mg/L. Moreover, to avoid the precipitation of the ions, the pH of the copper and nickel solutions were adjusted around 5 and 6.5, respectively. The adsorption kinetic tests were lasted for 75 min and the samples were withdrawn at the determined time intervals. The achieved experimental data in batch mode were used to calculate the amount of adsorbed metal ions (qₑ) according to the Equation (1):

\[ q_e = \frac{C_0 - C_f}{m} V \]

where, \( q_e \) (mg g⁻¹) is the amount of adsorbed Cu(II) and Ni(II) per unit mass of TNT/Sil at the equilibrium, \( m \) (g) is the weight of TNT/Sil; \( V \) (L) is the volume of metal ion solution sample; \( C_0 \) and \( C_f \) are the initial and equilibrium copper and nickel concentration (mg L⁻¹), respectively.
RESULTS AND DISCUSSION

From the XRD pattern that is depicted in Figure 2, the peaks at $2\theta = 10^\circ$, $25^\circ$, $30^\circ$, $34^\circ$, $36^\circ$, $40^\circ$, $48^\circ$, $53^\circ$ and $61^\circ$ are attributed to the crystalline phase of the sodium titanate compounds that is consistent with the reported values in literature [22]. As can be observed from the crystal structure, a series of six-coordinate monomers (TiO$_6$ octahedra) were connected to form a layered structure where Na$^+$ and H$^+$ are situated between the layers [21].

The FT-IR spectra of TNT/Sil adsorbent is presented in Figure 3 as well as MPTMS spectra as the reference to validate the weak peak of thiol group [23, 24]. The wavenumbers of the characteristic peaks of the related functional groups were summarized in Table 1. As thiol group’s peak was naturally weak, this peak was not observed in TNT/Sil NPs spectra but the existence of Si-O-Ti and CH$_2$ groups confirmed the successful modification of the TNT sample [25, 26].

According to the morphological characterization test results as are illustrated in Figures 4(a, b), the hydrothermal and severe alkaline conditions changed the form of TiO$_2$ precursor to tubular/rod structure. This tubular structure of TNT/Sil with uniform diameter along

![Figure 2. XRD pattern of the functionalized TNT](image)

![Figure 3. FTIR spectra of TNT/Sil NPs and MPTMS modifier](image)

The length provide high surface area for uptake of the metal contaminants. The EDS analysis was carried out to certify the presence of S, C, Si, Ti, O and Na as major elements of TNT/Sil adsorbent [21, 27].

Uptake of copper and nickel ions on TNT/Sil adsorbent

**Isotherm study**

Adsorption isotherms provides data about the distribution of metal ions at adsorbent/adsorbate system at equilibrium point and the calculation of uptake capacity. Figures 5(a) and 5(b) represent nonlinear Freundlich and Langmuir adsorption isotherm models which were fitted to the experimental data of Cu(II) and Ni(II) uptake on TNT/Sil at different temperatures (298–318 K). Moreover, the Langmuir model describes monolayer adsorption on homogeneous surface of adsorbent while the Freundlich model is based on multi-layer adsorption on heterogeneous adsorbent and in spite of the Langmuir model, the energy level of the adsorption spots is not identical [28, 29]. The applied isotherm models’ parameters are summarized in Table 2. The correlation coefficient ($R^2$) suggested that the experimental data of the metal ions uptake can be properly fitted by the Freundlich model ($R^2 > 0.99$). According to Table 2, the values of $R_L$ for both metal ions at all operating temperatures lie at 0~$R_L$<1 which indicates favorable adsorption of metal ions on TNT/Sil. Furthermore, according to the Freundlich model the values of $n>1$ confirm favorable adsorption of studied metal ions. The maximum adsorption capacities of TNT/Sil for copper ions at $T = 298$, 308 and 318 K were 53.77, 54.02 and 56.34 mg g$^{-1}$, respectively which were more than the values for Ni(II) at the same conditions. The oxygen and

| Sample | Description of vibration | Wavenumber (Cm$^{-1}$) |
|--------|---------------------------|------------------------|
| TNT/Sil | -OH stretching vibration of silanol group | 3440-3740 |
| | -OH stretching vibration of water molecule | 1640-1690 |
| | aliphatic C-H stretching vibration | 2852-2922 |
| | Si-O-Ti and Si-O-Si stretching vibration | 900-1100 |
| | Thiol group | 2564 |
| | stretching vibration of C-H | 2839-2940 |
| | bending vibration of CH$_2$ | 1455 |
| | stretching vibration of Si-O-Si and Si-O | 800-1075 |
Table 2. Isotherm parameters for copper and nickel uptake on TNT/Sil adsorbent

| Isotherm model | Metal ion | Isotherm parameters | Temperature (K) |
|---------------|-----------|---------------------|-----------------|
|               |           |                     | 298             | 308            | 318            |
| Langmuir [29]: | Cu(II)    | $q_e = \frac{q_{\text{max}} k_L C_e}{1 + k_L C_e}$ | $q_{\text{max}}$ | 53.77          | 54.02          | 56.34          |
|               |           | $R_L$               | $k_L$ | 0.22          | 0.38          | 0.57          |
|               | Ni(II)    | $R_L$               | $R_L$ | 0.029         | 0.017         | 0.011         |
|               |           | $R^2$               | $R^2$ | 0.85          | 0.86          | 0.87          |
| Freundlich [28]: | Cu(II)    | $q_e = k_F C_e^n$ | $K_F$ | 29.07         | 30.67         | 35.53         |
|               |           | $R^2$               | $R^2$ | 0.99          | 0.98          | 0.97          |
|               | Ni(II)    | $K_F$               | $K_F$ | 9.45          | 10.89         | 13.76         |
|               |           | $R^2$               | $R^2$ | 0.99          | 0.99          | 0.99          |

$sulphur$ atoms in hydroxyl and thiol functional groups on the surface of TNT/Sil NPs are considered electron donor atoms and target metal cations are electron acceptor species which possess high selectivity to interact with these groups.

**Kinetic study**

The kinetic study assists to determine the rate limiting step of the adsorption process. The slow steps of adsorption process which involve film diffusion, pore diffusion and intraparticle diffusion are determinative for the prediction of predominant adsorption mechanism. Two conventional non-linear kinetic models including pseudo-first order and pseudo-second-order were applied to kinetic data which are expressed in Equations (2) and (3):

Pseudo-first order [30]: $q_t = q_e (1 - e^{-k_1 t})$ (2)

Pseudo-second-order [31]: $q_t = \frac{t q_e^2 k_2}{1 + t q_e k_2}$ (3)

where $q_t$ and $q_e$ (mg g$^{-1}$) refer to the uptake capacities at time $t$ and at equilibrium point, $k_1$ (min$^{-1}$) and $k_2$ (g mg$^{-1}$ min$^{-1}$) are the constants for first and second order kinetic models, respectively.

As is depicted in Figure 6, the kinetic data were fitted with these models at different metal ions concentrations (20-150 mg L$^{-1}$) and at $T = 298$ K. The TNT/Sil NPs become saturated by both metal cations after 15 min of
beginning the adsorption process (see Figure 6). According to $R^2$ values, the experimental data of both metal cations were fitted well to pseudo second order model and the predicted uptake capacities of this model are closer to the experimental kinetic data (see Table 3). It is predicted that the adsorption of metal cations on TNT/Sil NPs can be related to the ion-exchange with $H^+/Na^+$ cations situated between the layers of TNTs and/or the complex formation of surface thiol or hydroxyl groups with the metal ions as following:

**Ion exchange** [32]:

$$2(\text{TNT} - \text{OH}) + M^{2+} \rightarrow (\text{TNT} - \text{O})_2M + 2H^+ \quad (4)$$

$$2(\text{TNT} - \text{ONa}) + M^{2+} \rightarrow (\text{TNT} - \text{O})_2M + 2Na^+ \quad (5)$$

**Surface complexation** [33]:

$$\text{TNT} - \text{SH} + M^{2+} \rightarrow \text{TNT} - S - M^+ + H^+ \quad (6)$$

**Thermodynamic study**

The effect of temperature on the adsorption process and its spontaneity status can be evaluated by thermodynamic parameters including Gibbs free energy change ($\Delta G^0$), entropy change ($\Delta S^0$) and enthalpy change ($\Delta H^0$) according to the Equations (7) and (8) [34]:

$$\Delta G^0 = -RT \ln K_c \quad (7)$$

$$\ln K_c = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (8)$$

where $K_c$ and $R$ (8.314 J/mol K) correspond to the thermodynamic equilibrium constant and universal gas constant, respectively and $T$ is the metal cations solution temperature (K). As listed in Table 4, the positive values of enthalpy change indicated endothermic nature of the adsorption process and therefore, higher temperatures facilitate the adsorption of metal ions on TNT/Sil adsorbent [35, 36]. The negative values of Gibbs free energy change implied that the metal cations uptake performed spontaneously, moreover the quantity of $-\Delta G^0$ increased at higher temperature which demonstrate the degree of spontaneity of process enhances at higher temperatures. The positive values of $\Delta S^0$ further suggest increased randomness at the interface of TNT/Sil adsorbent and metal cation solution.
**Table 3.** Kinetic parameters for the uptake of copper and nickel on TNT/Sil adsorbent

| Metal ion | C₀ (mg L⁻¹) | qₑ,exp (mg g⁻¹) | Pseudo-first order model | Pseudo-second order model |
|-----------|-------------|-----------------|-------------------------|--------------------------|
|           |             |                 | k₁ (min⁻¹) | qₑ,calc (mg g⁻¹) | R² | k₂ (g mg⁻¹ min⁻¹) | qₑ,calc (mg g⁻¹) | R² |
| Cu(II)    | 20          | 16.79           | 1.5         | 14.5         | 0.99 | 0.54          | 14.70         | 0.99 |
|           | 60          | 38.08           | 1.14        | 32.25        | 0.99 | 0.099        | 33.17         | 0.99 |
|           | 100         | 46.24           | 1.09        | 42.93        | 0.99 | 0.063        | 44.42         | 0.99 |
|           | 150         | 52.32           | 1.31        | 50.74        | 0.99 | 0.088        | 51.86         | 0.99 |
| Ni(II)    | 20          | 12.16           | 0.49        | 10.69        | 0.95 | 0.066        | 11.52         | 0.98 |
|           | 60          | 29.44           | 0.88        | 21.97        | 0.97 | 0.072        | 23.18         | 0.98 |
|           | 100         | 36.56           | 1.08        | 29.96        | 0.99 | 0.087        | 31.05         | 0.99 |
|           | 150         | 41.92           | 1.14        | 37.27        | 0.99 | 0.078        | 38.52         | 0.99 |

**Table 4.** Thermodynamic parameters for Cu(II) and Ni(II) uptake onto the TNT adsorbent

| Metal ion | ΔG (kJ mol⁻¹) | ΔH (kJ mol⁻¹) | ΔS (J mol⁻¹ K⁻¹) |
|-----------|--------------|---------------|-----------------|
|           | 298 K | 308 K | 318 K |
| Cu²⁺      | 3.77  | 4.84  | 6.18  | 32.216 | 120.56 |
| Ni²⁺      | 0.938 | 1.282 | 1.769 | 11.42  | 41.39  |

**CONCLUSION**

In the present study, the organic moiety (i.e. thiol) of the mercaptosilane modifier were anchored to the surface of the hydrothermally synthesized TNT NPs and this material was assessed as the adsorbent for the removal of Cu and Ni from synthetic wastewater. The physicochemical properties of the modified TNT were investigated through some analyses such as FESEM, EDS, FTIR, XRD and TEM. The kinetic and isotherm results demonstrated that experimental data are highly corresponded to the pseudo-second order and Freundlich model, respectively. In addition, the thermodynamic study indicated endothermic nature of the adsorption process. The TNT/Sil adsorbent have high tendency for adsorption of copper ions than nickel and the maximum uptake for these two cations was 53.77 and 45.29 mg g⁻¹, respectively.

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چکیده
در سال‌های اخیر، اهمیت تصفیه آلودگی فلزات سنگین از جریان‌های آبی به دلیل نیاز به منابع آب سالم با توجه به محدودیت این منابع، پیامدهای زیست محیطی این آلایندها، افزایش‌فعالیت‌های صمتی بشر با توجه به استفاده روانته از این فلزات در فناوری‌های مدرن و اثرات سmmo و سرطان‌زا این آلودگی‌ها به شیوه‌ای بالا گزارش‌گری محیطی و تبدیل شده است. استفاده از مواد گزینش‌پذیر و کارآمد جهت تصفیه کامل و موثر این آلاینده‌ها با توجه به ترخیص آلاینده‌های فلزی مورد استقبال بسیاری محیط‌زیست بوده است. در این پژوهش، سطح بالاولویه‌های اکسید تیتانیوم که با روش هیدروترمال سنتر شدند، از پای سنتزی استفاده شد. تغییرات شیمیایی و شیمیربدی تیول‌دار ساخته شده توسط آنالیزهای مختلف ارزیابی و نتایج ذاتی نشان داد که جذب تهیه شده می‌تواند به‌طور معمول مقیاس‌های سنتزی استفاده شده با توجه به سنتزی هیدروترمال، همچنین داده‌های آزمایشگاهی تطابق پذیری بیشتری با طبیعت‌های سندرمی داشتند و عاملی می‌تواند مناسب و کارآمد جهت پالایش پساب های فلزات سنگین باشد.