Green Synthesis of Nano-V–biotite for Removal of Toxic Heavy Metals, Th (IV) and U (VI) from Aqueous Solutions

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ABSTRACT

Development of reliable and eco-friendly processes for synthesis of metallic nanoparticles is an important step in the field of application of nanotechnology. In this study, we report the synthesis of new free fluoride V-biotite having the optimized formula NaV$_2$$_3$(Al, Si)$_4$O$_{10}$(OH)$_2$ for the removal of several toxic metals in aqueous system. The synthetic clay was first characterized by different techniques including X-ray diffraction (XRD), infrared absorption spectra (IR), electron spin resonance (ESR), thermal analysis (TG/TDA), scanning electron microscopy (SEM) and DC- electrical conductivity was measured as a function of absolute temperature. Then, the possible use of studied clay as adsorbent for removal of Ag (I), Hg(II), As(V), Cr(III), and Pb(II) from aqueous solutions was evaluated. The removal efficiency varied between 40% and 98%. The same clay was applied to removal of Th (IV) and U(VI) showing higher results than the relevant previous studies. The results suggest that the studied biotite can be effectively used for the treatment of contaminated wastewater.

Key words: Biotite, heavy metals, uranium, thorium, removal, free-fluoride, Green synthesis.

1. INTRODUCTION

An increase demand for fresh water along with the larger amounts of waste water generation due to increase the world population and development of industrial application make the recycling of the waste waters an imperative issue. Removal of the heavy metal ions existed in water is always an issue because they cause a serious biological danger. An exclusion of the heavy metal ion is commonly carried out by an adsorption based on an ionic interaction between positively charged metal ions and negatively charged matrices. Based on this fundamental principle, various technique and materials have been developed for ion exchange, precipitation and cementation [1].

Industrial waste materials can be classified as toxic, ignitable, corrosive or reactive industrial waste and according to EPA classification, industrial wastes can be also classified into three main categories. First, is known as a source-specific waste that is mainly generated from specific industries such as wood preserving, lead smelting and petroleum refining.

Second, is termed as a generic waste such as waste from common manufacturing and industrial processes including degreasing operations, spent solvents, landfills and ink formulation waste. Third, is the commercial chemical products and this includes some pesticides, creosote and other commercial chemicals [2].

There is considerable interest in the behavior of actinides at trace levels in environmental and biological samples due to the increasing public attention to radioactive waste disposal and potential public health effects of releases of radioactive materials into the environment. Uranium is a toxic radioactivity element. It is usually found in the environment in the hexavalent form. Excessive amounts of uranium have entered into environment through the activities of nuclear industry [3]. Uranium disposed into the environment can eventually reach the top of the food chain and be ingested by humans, causing severe kidney or liver damage and even death [4].

Thorium has been extensively used in a variety of applications since the last century. These applications have produced various gaseous, liquid and solid wastes containing isotopes of uranium and thorium and their daughter products. Although direct toxicity of thorium is low due to its stability at ambient temperature [5], since the liquid wastes of these applications may leak to the surface and may mix with the underground waters, it becomes a concerning environmental issue. When thorium nitrate enters living organisms it is mainly localized in liver, spleen and marrow and it precipitates in a hydroxide form [6]. Thorium is only stable at its valence IV in solution and has been selected as a chemical analogue for other tetravalent actinides [7]. Thorium, uranium and other actinides are also potential environment pollutants [8]. One of the easiest ways to remove these elements from aqueous solutions is by
adsorption. The preconcentration/separation of Th(IV) ions through adsorption is important in nuclear/radiation chemistry and environmental and waste treatment chemistry[9]. Different types of materials have been used as adsorbents for thorium adsorption, such as activated carbons and [10], gibbsite [8], alumina, silica [11], ignited Sarcotagus muscarum [12], molecular sieve powder [9] and montmorillonite [13], but no data were available for its adsorption on biotite.

When toxic metals are present in the aquatic system, the abatement of the pollutant to an acceptable level is necessary. The toxic nature of these radionuclide’s, even at trace levels, has been a public health problem for many years, the exposure of these elements to plants and human being occurs through ingestion of foodstuffs and by drinking water. After accumulating, these toxic elements clearly interface in the physiological systems of living organisms [14].

Green chemistry is a design, development, implementation of chemical products and processes to reduce or eliminate the use and generation of substances hazardous to human health and environment, the essential goals of the present work is to: (1) synthesis the V-biotite adsorbent from environmentally friendly and low cost raw materials: - i- by attempt to synthesize the mica without using fluorine to prevent release of fluorides into the environment during synthesis process. ii- by using Na⁺ as interlayer ion to increase cation exchange of the mica for remediation; (2) characterize the adsorbent with a variety of techniques; and finally (3) evaluate the performance of V-biotite for effective Ag(I), Hg(II), As(V), Cr(III), Pb(II), Th (IV), U(VI), removal from aqueous solution.

2. EXPERIMENTAL

2.1 Materials

All reagents used were of analytical grade (each purity >99%) Aluminium silicate Al₂SiO₃ from BHD Laboratory reagent, sodium carbonate (anhydrous) Na₂CO₃ (GPR), and ammonium metavanadate NH₄VO₃ (A.R. grade for laboratory and research uses) were mixed in the chemical compositions corresponding to synthesizing {NaV₂.₅(Al, Si)O₁₀(OH)₂} which have chemical formula of V-biotite.

2.2 Adsorbent Preparation

V-biotite was prepared carefully by using solid-state reaction technique using nominal compositions of individual oxides in the main formula, aluminium silicate Al₂O₃ SiO₂ ≈ 10.7g, sodium carbonate (anhydrous) Na₂CO₃ = 0.8g, ammonium metavanadate NH₄VO₃ = 3.5g. The powder mixtures were mixed in an agate mortar for 1 h. The green compacted metals powder was subjected to firing in a controlled atmosphere furnace to a temperature below its melting point in sealed platinum container at 900-950°C for 9 h, followed by sintering step at 880 °C to allow packed metal powders to bond together and finally, the furnace was cooled slowly down to room temperature and the material was kept in vacuum desiccators over silica gel dryer.

2.3 Adsorbent Characterization Techniques

a. X-Ray Diffraction Investigation

XRD powder diffraction measurements were performed on an XPert SW. X-ray diffractor with filtered Cu Ka radiation (λ=1.54 Å), at 40 Kvs and 30mA with a scanning speed in the range of 20–5–70 (298 K). To determine the crystallite size, Scherer equation was used [15]:-

\[ D = \frac{0.9\lambda}{\beta \cos \theta} \] (1)

where \( \lambda \) is the wavelength, \( \beta \) is the FHWM (full half width maximum) of Bragg's peak corrected using the corresponding peak in micron-sized powder and \( \theta \) is the Bragg's angle.

b. Infrared Spectra Studies

The IR spectra of the clays were recorded between 4000 and 400 cm⁻¹ using a KBr method with a NICOLET 6700 FTIR thermo scientific spectrophotometer.

c. Scanning Electron-Microscope

Scanning electron microscope measurement was carried out using small pieces of the prepared sample by using a “Philips model XL 30 CP”. The sample was coated with gold. Scanning electron microscope (SEM) was used to take micrographs of the clays.

d. Electron Spin Resonance Spectra

The (ESR) spectra were taken using (Bruker Elexys.500) operated at X-band frequency for investigation with fixed parameters were microwave frequency: 9.71 GHz, receiver gain: 30, sweep width: 6000 center at 3480 Gs, and microwave power: 0.002026W.

e. Thermal Studies

Thermo gravimetry (TGA) and differential thermal analysis (DTA) were carried out on using a shimadzu DTA-50H thermal analyzer. The sample was placed in platinum crucible (0.1 cm³) the system were studied under nitrogen atmosphere with a heating rate 10 °C min⁻¹ and following rate at 20 ml min⁻¹ , constant weight of sample 4.7 mg was used.
f. Electrical Conductivity Studies

The DC-electrical conductivity of synthetic V-biotite was measured using two terminals DC-method. The pellets were inserted between spring loaded copper electrodes, a KEITHLEY 175 multi meter (ASA) was employed from 10-500 °C. The temperature was measured by a calibrated chromel-alumel thermocouple placed firmly at the sample. Measurements were conducted in such a way that at each temperature, sufficient time was allowed to attain thermal equilibrium. The number of conduction electron n is given by:

$$n = n_0 e^{-\frac{E_g}{kT}}$$  \hspace{1cm} (2)

where \( n_0 \) is the concentration of atoms at the lattice site, \( E_g \) is the band gap, and \( K \) is the Boltzmann constant (assuming \( E_g \approx KT \)), the conductivity relationship becomes

$$\sigma = (n_v e^{-\frac{E_g}{kT}})\mu$$  \hspace{1cm} (3)

$$\sigma = \frac{A e^{-\frac{E_g}{kT}}}{v}$$  \hspace{1cm} (4)

where \( A = n_0 \mu \)

$$\log \sigma = \log A - \frac{E_g}{2.303 K T}$$  \hspace{1cm} (5)

The plot of \( \log \sigma \) against \( 1/T \) should give a straight line with a slope of \( -E/2.303K \).

The measurements of \( \sigma \) as a function of temperature will permit calculation of the band gap energy \( E_g \) of materials behaviour (conductor, semiconductor and insulator).

2.4 Adsorption Studies

In each experiment, silver, mercury, arsenate, chromium, lead, thorium and uranium were sorbed from a “sorption solution” that contained equal mass concentrations of each metal (10mg/L of each). In each experiment, (2g) of sorbent material was suspended in 50 mL of sorption solution [16]. The PH was adjusted as previous studies, The specific adsorption of Pb\(^{2+}\) ion was examined at the PH app. 4 to avoid the occurrence of the hydrolysis, at higher PH values, and the dissolution of biotite, at lower PH values [17]. The optimum pH for adsorption silver ions from aqueous solution was found to be 4.0 [18], Arsenate sorption onto biotite shows a broader maximum in the pH range 4.6–5.6 [19], The optimum pH value appeared to be about 5.0 At lower pH (<5), Hg(II) was in the free ionic form of Hg\(^{2+}\) [20] and Cr(III) Sorption was found to be at pH5.0 [21]. The pH adjusted by additions of non-complexing substances such as HNO\(_3\) or NaOH, and did not observe desorption to the solution directly in contact with biotite, and after equilibration by shaking keep the solution for 24h at room temperature then filtered using what man filter paper 40 ashless/circles 125 mm Dia. Metal concentration in the solution was determined by atomic absorption spectroscopy (AAS), and the amount of each metal sorbed by sorbent was calculated by difference.

The adsorption removal efficiency of heavy metals from aqueous solution was calculated as follows:

$$\text{removal efficiency (}) = \frac{C_0-C_f}{C_0} X 100$$  \hspace{1cm} (6)

where \( C_0 \) and \( C_f \) are the liquid-phase concentrations of heavy metal before and after adsorption, respectively. Cation selectivity / exchange was determined and expressed as distribution ratio (Kd) was measured as follows:-

$$K_d = \frac{\text{amount of element in adsorbent}}{\text{amount of element in solution}} \times \frac{v}{m} (\text{mL/g})$$  \hspace{1cm} (7)

where \( v \) is the volume of the solution (mL) and \( m \) is the weight of adsorbent (g)

The uranyl nitrate UO\(_2\) (NO\(_3\))\(_2\) and thorium dioxide ThO\(_2\) solutions of given concentration, volume was added to a conical flask containing the synthetic V-biotite. The mixture was shaken and leave at room temperature and pH 4.0 for 24h. The uranium (VI) and thorium (IV) in solution was determined by using CARY 400 scan uv-visible spectrophotometer at 652 and 660nm respectively. The amount of adsorption at equilibrium time \( t,q_e \) (mg/g), was calculated by:

$$q_e = \frac{(C_0-C_e)W}{w}$$  \hspace{1cm} (8)

where \( C_0 \) and \( C_e \) are the liquid-phase concentrations of uranium (VI) and thorium (IV) at the initial and equilibrium time, respectively; \( v \) the volume of the solution (mL); \( W \) is the mass of dry adsorbent used (g). The adsorption removal efficiency of uranium (VI) and thorium (IV) from aqueous solution was calculated as described above.

3. RESULTS AND DISCUSSION

3.1 Synthetic V-Biotite Characterization

Figure(1): displays the X-ray powder diffraction pattern recorded for synthetic free fluoride biotite which has the formula NaV\(_{2.5}\)(Al,Si)\(_3\)O\(_{10}\) (OH)\(_2\).
the analysis of corresponding 2θ values and interplanar spacing d(Å) were carried out using computerized program. a change in the interlayer distance than the original phyllosilicates is observed because replacement of potassium ions with sodium ions and without using fluorine in the structure formation. The d(001)-spacing of natural micas with potassium ions in their interlayer is≈10 Å \[22\]. one indicate the monoclinic phase of mica-clay the dominating phase by ratio exceeds than 92% confirming that nano-oxide component are successfully reacted and formed monoclinic biotite phase with very good degree of crystalline\[23\].

**Figure 1:** XRD pattern of V-biotite

The FTIR spectra of V-biotite have shown in (Figure. 2) the bands in the 4000-2000 cm\(^{-1}\) rang corresponding to the vibrations of the V-OH group and coordinated water. Bands in the 1200-600 cm\(^{-1}\) rang characteristic of silicate; band centered at 1030 cm\(^{-1}\) was attributed to Si-O-Si asymmetric stretching mode. The peak at 621 cm\(^{-1}\) was assigned to O-Si-O asymmetric stretching as reported in silicate system [24].

**Figure 2:** FTIR spectra of V-biotite

Fig. 3 represents the (TGA–DTA) curves of V-biotite. From this figure it can be seen that: (i) The TGA-curve of this sample consisted of three weight loss processes in temperature ranged between (173)–(215) °C, (425-556) °C and (856)–(994.) °C. The first two steps represented the thermal decomposition of ammonium metavanadate into different types of vandal compounds species as, (NH\(_4\))\(_2\)V\(_6\)O\(_{16}\) and NH\(_4\)V\(_4\)O\(_{10}\) with a constant weight losses of 2.9% and 0.44%, before the formation of V\(_2\)O\(_5\) as a final product with a constant weight loss of 2.2% at 994 °C. (ii) The DTA-curve of this solid consisted of three endothermic peaks their minima located at 98, 190 and 400 °C. In addition, strong and broad exothermic peak; its maxima; located at 850 °C was detected without the observation of any weight change in the TG-curve. This peak might correspond to the formation of solid state reaction [25, 26]
Figure 3: Thermal analysis (a) TG (b) DTA of V-Biotite sample

Figure 4 shows ESR spectra of V-biotite. From this figure, we clearly shown decreasing with increasing calcinations temperature represented by a sharp isotropic signal centered at magnetic field 3600 Gs [27] only one signal appeared in V-biotite sample centered at $g=1.98$, it’s suggested that synthetic V-biotite have a paramagnetic property. Biotite is a common hydrated ferromagnesian silicate in most mafic, intermediate and felsic plutonic rocks which related to V metal species and confirmed by another g signal which appear at a lower magnetic field 3600 G. The observed g-value suggests that one ESR signals originates from V ion situated on an interstitial site.

Figure 4: ESR spectra of V-Biotite sample

Scanning electron micrographs (SEM) image indicates the morphology and size of the mica particles synthesized. The sample has a flake-like morphology, which is typical for this synthetic mica (Fig.5). However, the particles appear to have aggregated, which would influence the surface area [28]. The estimated average grain size was found in the range of 2-4 µm with a particle thickness 0.5µm, which influence the surface area. This type of morphology is typical for synthetic clays and supporting the data reported [29].

Figure 5: SEM photographs of V-Biotite sample
While the estimated crystallite size of detected phase was calculated using Scherrer's equation and found to be 55 nm. This indicates that, the actual grain size in the material bulk is smaller than that detected on the surface morphology of investigated clay. This trend of mismeasuring grain size was observed [30, 31].

The temperature dependence of the electrical conductivity of synthetic V-biotite shows in (Fig. 6). The electrical conductivity at a given temperature is significantly lower after heating than before heating. We conducted stepwise heating experiments of biotite. With increasing the temperature the conductivity decreases and gradually reaches a stationary value. Then the conductivity increase at a fixed temperature is not significant below 450 °C. Remarkable increase is observed at the temperature of 450-500 °C. The band gap energy result calculated from fig.6 was 359 JK\(^{-1}\) this mean that the synthetic V-biotite has insulator behavior. The result can be interpreted as the resistivity of a metal arises from the scattering of the conduction electron by static lattice defects such as vacancies and thermal scatters which are created by the thermal motion of atoms or electrons [32].

The synthetic biotite gave high removal efficiency (%E) and good distribution ratio (K\(_d\)) value for uptake of investigated heavy metals from 10 ml/g background solution. The sorption efficiency of V-biotite for selective heavy metals as following sequences:

Ag>Pb>Cr>As>Hg

The adsorption behavior of these metals onto synthetic biotite is likely due to difference in their physicochemical properties, such as electro negativity, ionic radius, and electronic charge.

For each sorbent element, Figs. (7-11) and Figs. (12-16) plots the XRD and FTIR respectively of each element sorbed retained on the sorbent in the sorption experiments against its initial concentration in the sorption solution (ICSS).

**Figure 6**: Temperature dependence of the electrical conductivity of V-Biotite

**Figure 7a-e**: XRD V-biotite after (a) Ag adsorption, (b) after Hg adsorption.

Diffraction grams of the samples and FTIR Figs. (7-11) and Figs. (12-16) respectively showed that structures after adsorption of heavy metals almost changed than the original before treatment, these mean the selectivity of V-biotite towards mono-, di-, penta- and tri- valent ions 40% to 98% were captured through cation exchange process in between silicate layers which confirm and reflect superior efficiency of V-biotite clay towards selected toxic metals. The peaks centered between 2930 cm\(^{-1}\) and 2360 cm\(^{-1}\) are
due to the presence of KBr disc used as a “matrix” and therefore are not diagnostic of any mineral [33].

(c) after As adsorption, (d) after Cr adsorption

**Figure 7c:** XRD V- biotite after Pb adsorption

**Figure 7e:** XRD V- biotite after Pb adsorption

**Figure 7f:** XRD V- biotite after Cr adsorption

**Elements**

<table>
<thead>
<tr>
<th>Elements</th>
<th>Removal efficiency %</th>
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<tbody>
<tr>
<td>Ag (I)</td>
<td>97.7</td>
</tr>
<tr>
<td>Pb (II)</td>
<td>96.7</td>
</tr>
<tr>
<td>Cr (III)</td>
<td>71</td>
</tr>
<tr>
<td>As (V)</td>
<td>61.5</td>
</tr>
<tr>
<td>Hg (II)</td>
<td>40.3</td>
</tr>
</tbody>
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**Figure 8a:** FTIR spectra for V- biotite after (a) Ag-adsorption, (b) after Hg-adsorption

**Figure 8b:** FTIR spectra for V- biotite after (a) Ag-adsorption, (b) after Hg-adsorption
4000 3500 3000 2500 2000 1500 1000 500
80
85
90
95
100

Wavenumber    (cm$^{-1}$)

FTIR-Pb-V-Biotite (e)

Figure 8c-e: (c) After As-ions adsorption, (d) After Cr-ions adsorption, (e) After Pb-ions adsorption

Figure 9a,b: X-ray diffraction patterns of V-biotite after; (a) Th-adsorption. (b) U-Adsorption

Figure 10a,b: Infrared absorption spectra recorded after U and Th capture on the V-biotite

Figure 11: Removal performance efficiency values of V-biotite towards uranium and thorium ions solutions.

The metal uptake is attributed to different mechanisms of ion-exchange and adsorption processes [34]. During the ion-exchange process, metal ions move
through the pores of the biotite and channels of the lattice, and they replace exchangeable cations (mainly sodium) and additionally exchange with protons of surface hydroxyl groups. In the case of exchange with sodium, Na(g) + M₂⁺(solution) → M₂⁺(biotite) + Na⁺(solution) reaction, in which sodium ions placed on the biotite surface exchange with the metal ions (M⁺) in the solution, occurs. When the exchange site is a hydroxyl group, biotite–OH⁻ + M⁺(solution) → biotite–O–M⁺ + H⁺(solution) exchange reaction occurs and in this case, metal ions (M⁺) exchange with the H⁺ ions. Diffusion was faster through the pores and retarded when the ions moved through the smaller diameter channels. The ion-exchange processes in biotite are affected by several factors such as concentration and nature of cations, pH, and crystal structure of the biotite. The effect of these parameters has been investigated in several studies due to the importance of biotite’s mineral stability in the applications of biotite as an ion exchanger [35, 36].

5. Synthetic V-Biotite for Removal of Thorium (IV) And Uranium (VI) From Aqueous Media

The clay sample has been used to evaluate the maximum adsorption capacity for up taking metal ions, such as Th⁴⁺ and UO₂²⁺, from aqueous solutions. In fact, these cations act as acidic Lewis centers that interact with the basic Lewis center attached to the pendant molecules covalently bonded to the modified clay surfaces [37, 38].

As clearly shown in Figs. 9a,b with the highest pronounced adsorption for thorium and uranium values were obtained after adsorption on synthetic V-biotite from aqueous solution. The maximum adsorption capacities for each metal on silicate matrices were found 95.6% and 53.2% for uranium and thorium respectively. This can be attributed to the higher mobility of uranyl ions (UO₂)²⁺ in the diluted solutions, the interaction of this ion with the adsorbent also increases. The results of removal uranium and thorium showing higher removal efficiency than previous studies that reported [39, 40].

The applicability of these kinds of porous materials depends on a series of properties, on the degree of molecules immobilized, mainly when the adsorption is considered. In addition, the variation in adsorption capacities of these metal ions probably arises due to differences in their sizes, degree of hydration and binding constants with the chelating matrix.

6. CONCLUSIONS

The conclusive remarks inside this work could be summarized as follows:
1- Green synthesis of free-fluoride V-biotite
2- SE-micrographs analysis confirmed that free fluoride NaV₂₄(Al₃Si)₄O₁₀(OH)₂ has meso-porous structure with grain size in the range between 2-4 µm and a particle thickness 0.5 µm, while found to be 55 nm confirming the actual grain size in the material bulk is smaller than that detected on the surface morphology of investigated clay.

3- Selectivity of V-biotite towards tested heavy metals ions up to 98% were captured through cation exchange process in between silicate layers which confirm and reflect superior efficiency of V-biotite clay towards selected toxic metals.
4- Uptaking metal ions, such as UO₂²⁺ from aqueous solutions reaches 95.6% showing higher removal efficiency than previous studied that reported

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