TI-MODIFIED CLAY COMPOSITE FOR REMOVAL OF HIGHLY TOXIC CHROMIUM COMPOUNDS FROM POLLUTED WATER BY THE MEANS OF ADSORPTION

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Abstract

In the current work, 12 different Ti-modified clay composites were synthesised. XRD analysis and surface area measurements have been used to investigate the samples. The influence of the synthesis approach and adsorption experiment parameters on the final adsorption values of dangerous carcinogen Cr (VI) were investigated in concentration range from 2 mg/L to 42 mg/L with pH 4 and 6. In the result of the work the efficiency of carcinogen hexavalent chromium removing can be up to 98,5 % depending on the conditions.

Introduction

The amount of highly concern reports regarding dangerous of hexavalent chromium is increasing. It has been already proven by the National Institute for Occupational Safety and Health (NIOSH) that all hexavalent chromium compounds are occupational carcinogens[1]. Moreover, accordingly to the list the top 275 most toxic substances the Agency for Toxic Substances and Disease Registry ranked Cr (VI) on the 16th position. The most dangerous way of chromium penetration to the human body is its inhale and Cr (VI) has been connected with sinus, nasal and lung cancer. It calls immunity disorders neuropsychiatric disorders, atherosclerosis, neurodegenerative disorders, congenital disorders, DNA damage, and disruption of bodily processes[2].

Chromate dusts and acids can permanently damage eyes if they come into direct contact, and other kinds of skin contact may lead to allergic dermatitis, corrosion, skin irritation, sensitization, and even ulcers[3].

Although chromium hexavalent is dangerous and toxic, it is useful in industrial applications. Workers involved in electroplating, photography, pyrotechnics, plastics, paints and primers, textiles, leather tanning, and wood preservation industries are at high risk of exposure[2,3].

One of the most important directions in the technology of removing pollutants from different kinds of polluted waters, is the use of ion-exchange materials in sorption processes, which were derived from cheap and available compounds. The using of clay minerals as a supply material or substrate is opening a big area for new generation sorbents obtaining with improved characteristics regarding adsorption and selectivity. Clay minerals are cheap and can be easily modified by positively-charged modifiers. Thus, recently, much attention is given to modified clay minerals[4,5].

In our current work, we tried to solve the hexavalent chromium problem by the mean of synthesising and testing of clay based composites, that are able to remove about 98,5 % of Cr (VI) from polluted waters depending on the conditions.

To do that, muscovite (MMT) has been used as an initial clay mineral due to its high specific area and strong surface negative-charge, and as a consequence, can be effectively modified by positively-charged compounds or neutral molecules with the ability to be polarized in the condition of their surroundings.

We chose to synthesise TiO^{2+} as a modifying agent because of its ability to form TiO_2 by the means of temperature treatment in aqueous solutions. The TiO_2 produced has high properties of adsorption[6,7], and can also act as a potent catalyst or photocatalyst.

Synthesis

The full synthesis scheme is represented on the Figure 1.

The initial clay mineral was ordered from Aldrich company. The XRD analysis was used to prove the presence of muscovite phase. This result is present on the Figure 2.

The synthesis of TiO^{2+} was performed in acid solution (pH 0.01) because titanium compounds are positively charged in low pH (Figure 3). To obtain TiO^{2+}, the necessary amount of initial $TiCl_4$ (Aldrich) was dissolved in water to get the final concentration of 1 µM.

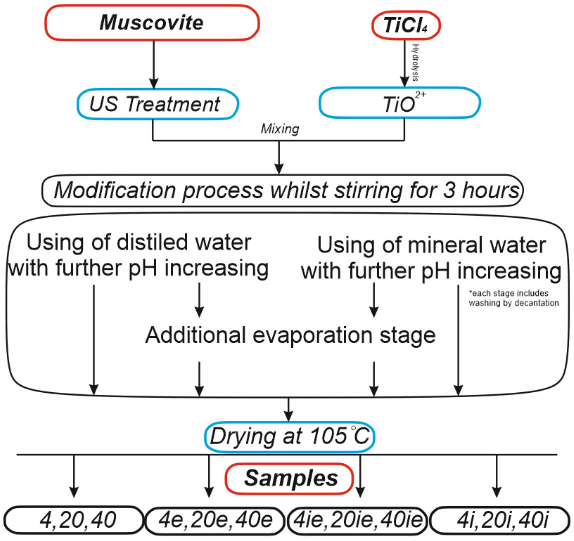

Figure 1. Synthesis scheme

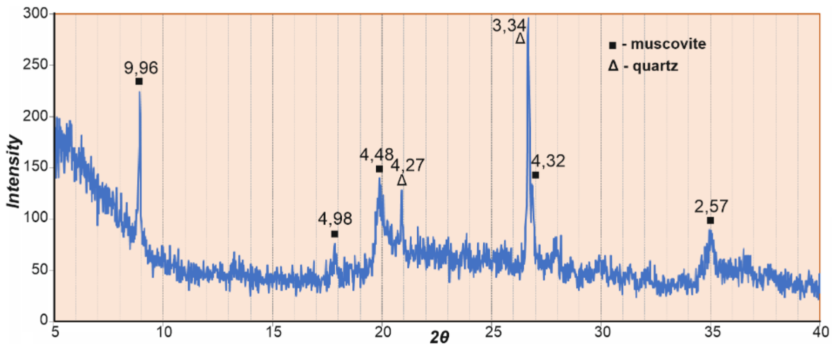

Figure 2. XRD analysis of the clay mineral

The modification processes: TiO^{2+} solution was added by drops to the muscovite suspension previously treated with ultrasounds, whilst stirring. The final ratios were 4, 20 and 40 mmol of Ti/1g of the clay mineral. Time of their contact was equal to 3 hours. Then, the suspension was separated on two parts. In order to increase pH of the solutions, mineral water was added to one of them, to the second one – distilled water was added.

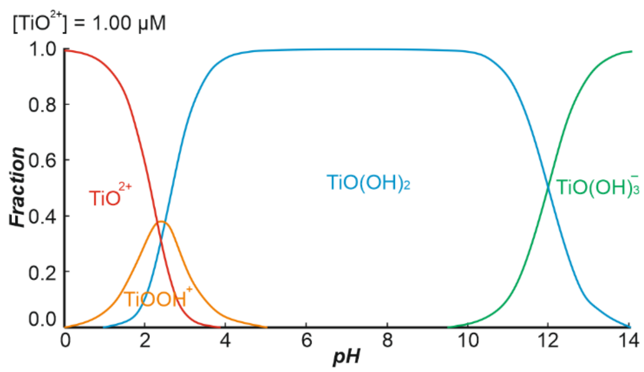

Figure 3. Ti^{4+} state diagram for concentration equal to 1 μM

Then, we used two different approaches to modify the muscovite:

Approach 1: both the suspensions were filtrated and washed to remove the remains of chlorides and TiO^{2+}. The temperature treatment was performing over 24 hours at 105 °C (samples are marked as *4i, 20i, 40i* and *4, 20, 40* with mineral water and with distilled water treatments, respectively).

Approach 2: both the suspensions were evaporated up to the viscous paste on heater at 200 °C, whilst stirring. To each sample the appropriate water was added again to remove the remains of chlorides and TiO^{2+}. Cleaned composite was decanted and evaporated up to the viscous paste on heater at 150 °C, whilst magnetic stirring. The obtained samples were treated over 24 hours at 105°C (samples are marked as *4ie, 20ie, 40ie* and *4e,20e,40e* with mineral water and with distilled water treatments, respectively).

Samples Analysis

The XRD analysis was performed to detect results of the modification (Figure 4a).

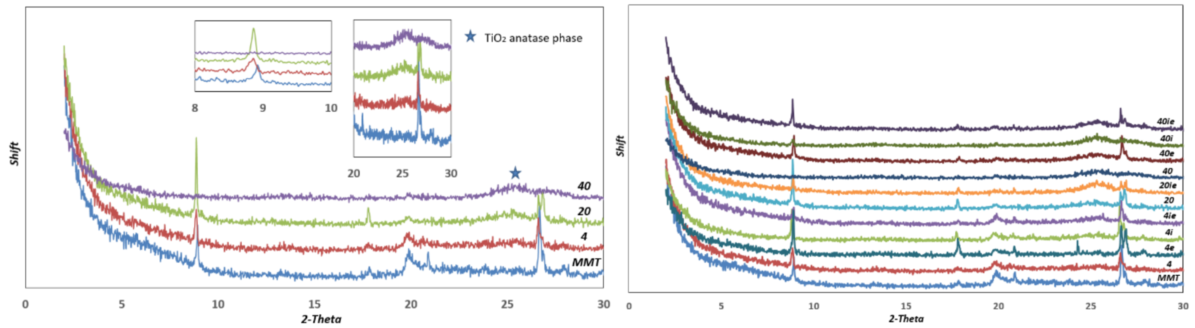

Figure 4. The XRD analysis

The shift of the basal peak d = 9,96 for the muscovite mineral was shifted into low angle direction in the case of *samples 4* and *20* due to partial TiO^{2+} particles intercalation into the interlammelar mineral space. For the *sample 40*, this peak was not grown due to total loss of regular sheet structure. The fact is supported by detected high amount of anatase particles within the composite. These particles were leading to loss of the regular sheet structure.

The XRD analysis was used for other samples as well (Figure 4b). For each sample set has been observed the same behaviour – increased amount of the modifier caused anatase phase appearing. Accordingly to the diffractograms this can be detected from *40e* and *40ie*, the additional evaporation stage helps to save the sheet structure because all signature clay mineral peaks were maintained. Significant shift of the basal reflex as such samples *4* and *20* has, was detected for *4i* and *40ie* samples.

The surface area and porosity measurements were carried out on several samples to detect differences induced by modification process (Figure 5).

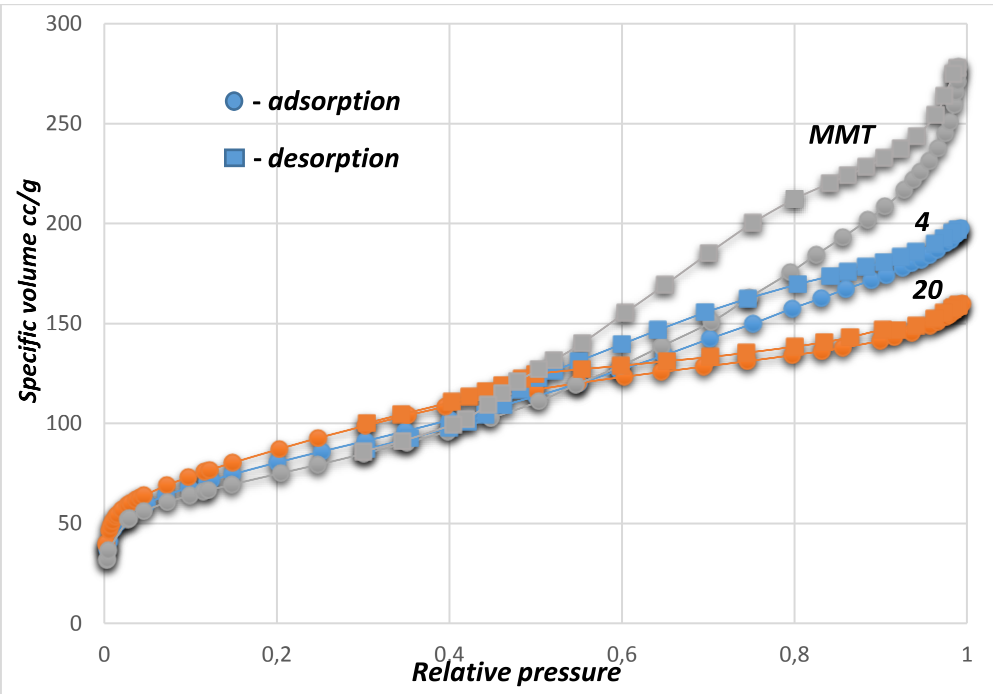

Figure 5. Surface area and porosity measurement for *MMT, 4* and *20*

The obtained results based on the BET theory calculation:
MMT – 263 m^2/g;
4 – 290 m^2/g;

$20 – 315\ m^2/g$.

Adsorption Expertise

Derived 12 samples were examined in adsorption experiment relative to removing of Cr (VI) compounds from aqueous solutions, that causes cancer diseases.

1 g of the sample was weighted accurately up to 4th number after point and added to Cr (VI) solution with fixed concentration and pH. The range of measured concentration was from 2 to 42 mmol/L; the chosen pH: 4 and 6. The contact time was 4 hours, whilst shaking. The residual concentration was measured by the means of atomic-adsorption analysis in air flame.

The results are demonstrated on the fig.6.

The efficiency of removal or Cr (VI) from aqueous solution was considerably improved for all samples in comparison with the initial clay and TiO_2. In the current conditions, the most effective sample is 40 pH = 4.

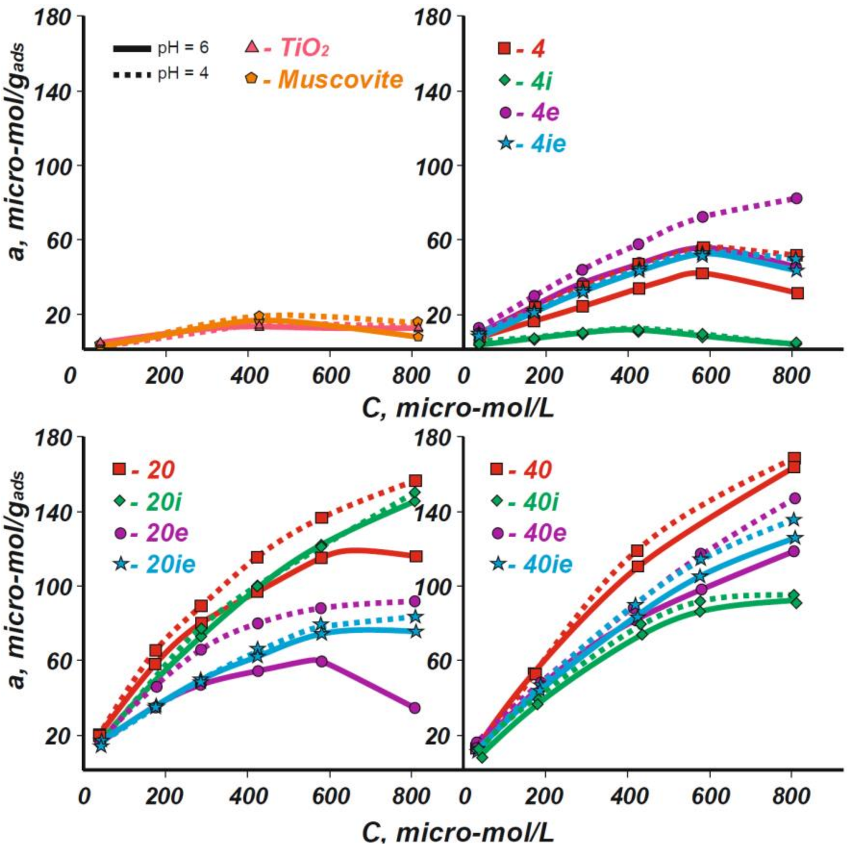

Figure 6. Adsorption experiment isotherms

Statistical Analysis

Multiple linear regression was used to create a model for predicting the amount of chromium removed by absorption clays from the amount of titanium, temperature, pH applied and the synthesis method used variables (Figure 7). Regression statistics and coefficients are shown on the Figure 8. Only titanium correlated significantly with the amount of chromium removed independently (cor = 0.82, p-value = 1.233×10^{-6}). In the multiple linear model however, both titanium and temperature had significant partial effects with p-values < 0.05. Overall, this linear model using the 4 predictor variables, accounted for 75% of the variance of chromium removal from the clay adsorption.

The importance of the 4 variables was assessed by removing one predictor variable at a time from the model and using Anova to compare the difference between the original model and the new one. Removing titanium gave significant Anova results with a p-value of 4.77×10^{-7} ***. The second most important variable was temperature, with an Anova p-value of 0.04 *, with synthesis method third and finally pH being the least important variable in determining the amount of chromium removed by the adsorbent clay.

The Figure 7 shows 3 different concentrations of Titanium added and the amount of chromium removed. A two sample t-test between titanium amounts is highly significant, showing the major impact titanium has on the amount of chromium removed.

The summary statistics of multiple regression model is represented on the Figure 8.

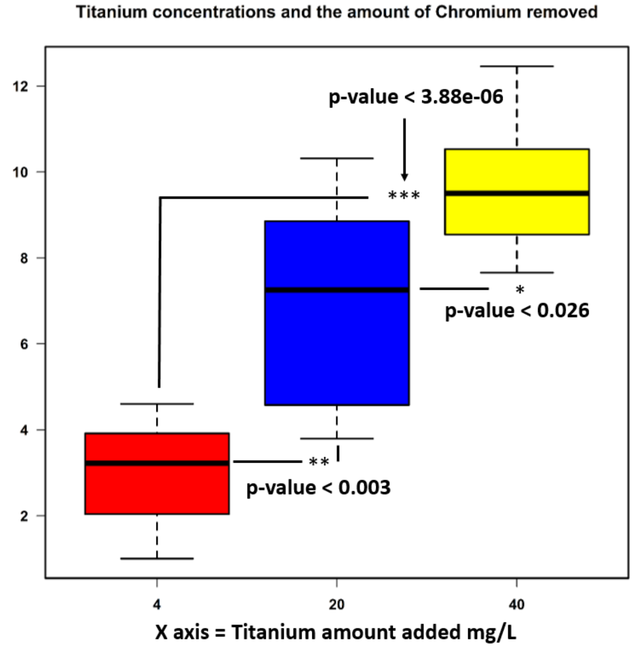

Figure 7. Box|Whisker Plot

```
lm(formula = CrRem ~ ., data = mat)

Residuals:
    Min      1Q  Median      3Q     Max
-2.6364 -0.9322  0.2355  0.7149  3.2026

Coefficients:
                Estimate Std. Error t value Pr(>|t|)
(Intercept)     5.256329   1.922019   2.735   0.0136 *
TitanConc       0.183714   0.024075   7.631 4.77e-07 ***
synthsynthesis  1.244401   0.698272   1.782   0.0916 .
Temp           -0.018974   0.008728  -2.174   0.0433 *
pH             -0.424201   0.349136  -1.215   0.2401
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Residual standard error: 1.666 on 18 degrees of freedom
Multiple R-squared:  0.7943,    Adjusted R-squared:  0.7485
F-statistic: 17.37 on 4 and 18 DF,  p-value: 5.38e-06
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Figure 8. Summary statistics of multiple regression model

Conclusions

In the current work, 12 different Ti-modified clay composites were synthesised. XRD analysis and surface area measurements have been used to investigate the samples. The influence of the synthesis approach and adsorption experiment parameters on the final adsorption values of dangerous carcinogen Cr (VI) were investigated. In the result of the work, we can conclude:

Pure TiO_2 and pure muscovite mineral have not good adsorption values (the highest is 5 % of removal);

Efficiency of adsorption was significantly improved by the means of muscovite mineral modification by Ti containing compounds;

Synthesis approach has a high influence to the final composite properties and pH influence of the adsorption values depends on the synthesis approach;

The adsorption is occurring mainly on the added Ti-modifier and its OH-groups because of adsorption efficiency dependents on the amount of Ti-modifier, that was proved by statistical analysis.

*Samples 4, 20, 4*0: synthesis with using distilled water without additional evaporation stage demonstrated high adsorption results in each Cr (VI) removing experiment caused by TiO^{2+} particles intercalation inside interlamellar muscovite space (proved by XRD) that partially re-charged clay mineral surface and created additional centres to adsorb Cr (VI) from aqueous solutions;

Samples 4e, 20e, 40e: in the case of adsorption experiment with amount of modifier equals to 4 mmol, the highest efficiency was demonstrated by *4e* sample possibly caused by well-structured frame because of additional evaporation stage and XRD shift in the low angles direction which proves partial mineral surface re-charge. However, *20e* and *40e* didn’t demonstrate extra good adsorption results because of increased amount of Ti modified prevents the structuring process;

Samples 4i, 20i, 40i: synthesis with using mineral water showed less removal ability of chromium ions in aqueous solution than samples obtained in distilled water due to possible reactions of Ti-compounds with free ions in the mineral water and as a consequence reduced amount of efficient active centres for pollutants removal.

Samples 4ie, 20ie, 40ie: in the case of these sample, there is two different effects affect the final result. From the one side, the mineral water was removing Ti-modifier partially with further reducing of adsorption value. However, the reduced amount of the modified could cause well-structured frame with consequently increased adsorption efficiency. Ergo, the capacity of these samples is extremely depending on the ratio between mentioned effects.

pH influence of the final adsorption values depends on the synthesis approach. For distilled water synthesis method, the lower pH is leading to increase the adsorption values. The mineral water synthesis approach does not reveal significant pH adsorption dependency. These effects can be explained by the means of different adsorption mechanism with mainly ion-exchange in the case of distilled water samples and partially complexation mechanism in the case of mineral water composites.

All in all, we are pleased to report, that high efficient composite adsorbent derived from over-cheap and available compounds were synthesised and tested. The removal efficiency gained values up to 98,5 % of Cr (VI) compounds depending on the synthesis condition.

Acknowledgements

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