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Highly-efficient removal of Pb(II), Cu(II) and Cd(II) from water by novel lithium, sodium and potassium titanate reusable microrods†

 Monika Motlochová,^a *^{ab} Václav Slovák,^c Eva Plízingrová,^a Sven Lidin^b and Jan Šubrt^a

In this work, we report on the efficient removal of heavy metal ions with nanostructured lithium, sodium and potassium titanates from simulated wastewater. The titanates were obtained *via* a fast, easy and cost effective process based on extraction of sulfate ions from the crystals of titanyl sulfate and their replacement with hydroxyl groups of NaOH, LiOH and KOH solutions leaving the Ti–O framework intact. The as-prepared titanates were carefully examined by scanning and transmission electron microscopy. Furthermore, the effect of contact time, pH, annealing temperature, together with adsorption in real conditions including competitive adsorption and reusability were studied. It was found that the maximum adsorption capacity, as calculated from the Langmuir adsorption model, is up to 3.8 mmol Pb(II) per g, 3.6 mmol Cu(II) per g and 2.3 mmol Cd(II) per g. Based on the characterization results, a possible mechanism for heavy metal removal was proposed. This work provides a very efficient, fast and convenient approach for exploring promising materials for water treatment.

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1. Introduction

All over the world, the pressure on industries for reduction of heavy metals in water is on the rise. Disposal of wastewater is one of the most pressing issues in the world, as such effluents usually contain considerable amounts of heavy metal ions such as Pb(II), Cd(II), Cr(VI), Hg(II), and Ni(II).^{1–8} One of the fields of interest in this area focuses on environmental clean-up,^{9–11} mainly the quality of public health and drinking water.

There are various methods of removing metals from water, including chemical precipitation, electrochemical or adsorption methods.¹² Nanoparticles could be another alternative option as a sorbent of metallic contaminants. Their larger surface area translates into larger sorption capacity, *i.e.* decrease in the required sorbent volume resulting in less waste in need of disposal. Furthermore, the smaller the particle size the larger the surface of an unsaturated system with more functional groups available, thus, leading to more reactivity and possibly a nanometric effect with particles smaller than 20 nm.¹² Therefore, it has been proposed that they have high adsorption capacity.¹³

Titanium dioxide and different titanates are among the materials that are often mentioned in this context due to their outstanding properties.^{4,12,14–23} Recently, mesoporous TiO₂ has attracted great attention due to its large surface area, which significantly increases its adsorption capacity potential. Its solubility is negligible and the zero charge point at neutral pH allows the adsorption of metal ions to TiO₂ over a wide range of pH and ionic strengths.²⁴ The titanium dioxide nanoparticles have shown to be effective as sorption agents,¹⁵ nevertheless, with the drawback of forming stable dispersion in the aqueous medium resulting in a very difficult, almost impossible separation from an aqueous medium.²⁵ Layered titanate nanotubes prepared by the hydrothermal method possess flexible inter-layer distances, high cation exchange capacity, high surface area and high density of functional hydroxyl group on the surface.^{4,20,21,23,26} The basic mechanism is expected to be the ion exchange^{3,4,6} even though other mechanisms are also possible (*e.g.* complexation).

Conventionally, anatase nanoparticles and their aggregates are prepared by sol–gel methods²⁷ or by precipitation from an aqueous medium.^{25,27,28} Despite the clear benefits of these methods to the preparation of titanium dioxide nanoparticles with controlled properties, they also present a drawback in the form of high input requirements, therefore, rendering it expensive for large scale use and with product properties being often sub-optimal. Among other general limitations in use of nanoparticles, we can state *e.g.* longevity, stability, toxicity or recovery.

Hydrous titanium oxide usually prepared by mixing titanyl oxalate or TiCl₄ solutions with sodium hydroxide was suggested

^aInstitute of Inorganic Chemistry of the Czech Academy of Sciences, Husinec-Řež 1001, CZ-250 68 Řež, Czech Republic. E-mail: motlochova@iic.cas.cz

^bCentre for Analysis and Synthesis, Lunds Universitet, Naturvetarvägen 14, Lund 222-61, Sweden

^cFaculty of Science, University of Ostrava, 30. dubna 22, Ostrava, CZ-701 30, Czech Republic

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as effective sorbent for heavy metals or radionuclides many years ago.²⁹ Inorganic ion-exchange materials, particularly, titanium(IV) hydroxides have been widely studied for purification of liquid radioactive waste and outflows, which contain heavy nonferrous metals.³⁰ Ion-exchange properties of these materials depend on their morphology and surface properties. The analysis of literature sources concerning the inorganic titanium ion exchanger showed that many of the synthetic ways are based on deposition of amorphous precipitates using the sol-gel method. The synthetic process includes several stages like formation of titanium(IV) hydro(oxo) complexes, the formation of multinuclear complexes, the growth of polymeric particles with the sol formation, and coagulation of initial colloid particles with gel formation. In such unstable systems it is complicated to control the system and to maintain stable properties of products. An uncontrolled synthesis, proceeding without the supervision of the solid phase formation rate, leads to the irregularity of phase and dispersive composition and has a negative influence on the characteristics of the final products. The regulation of the titanium containing ion exchanger synthesis is even more difficult when concentrated acidic titanium solutions, particularly, the solutions of titanium(IV) sulphates, are used. In addition, it is known that the titanium oxide compounds form stable, practically unfilterable colloids in the aqueous medium that are difficult to separate.³¹ This also complicates the use of titanium oxides as sorbents for both radionuclides and heavy metals. Thus, the development of an inexpensive titanium hydroxide-based sorbent, characterized by high sorption capacity, aqueous stability and easy separation from the aqueous environment, is still a significant problem.

Our group has previously prepared rod-shaped titania material precipitated by aqueous ammonia and tested it as an adsorbent for radionuclides.³² Following the general demand for preparation of heavy metal adsorbents, the group efforts focused on tailoring suitable modifications of this material.

In the present work, various titanate nanostructures with different precipitation agents were synthesized in a low-cost and input efficient manner and their application as adsorbents for the removal of heavy metal ions was studied.

2. Materials and methods

2.1. Synthesis of metatitanates

Based on alkaline controlled hydrolysis, three types of titanium dioxide materials with different ratio of Li : Ti, Na : Ti and K : Ti were prepared according to the following procedure:^{32,33} 100 mL of cooled distilled water was mixed with 50 g of ice and appropriate amounts of hydroxides (see Table 1; Penta Czech Republic), afterwards 4.80 g of titanyl sulfate dihydrate (Sigma Aldrich) was added to the cold alkaline solution. The resulting suspension was stirred for 120 min. Then, the suspension was decanted twice and filtered off. Finally, the solid product was dried at room temperature (RT).

2.2. Characterization of the products

The following methods were used for morphological, structural, and chemical characterization of the product: scanning electron microscopy (SEM/EDS), transmission electron microscopy (TEM/EDS), X-ray diffraction (XRD) and atomic absorption spectroscopy (AAS). Details including experimental conditions are described in ESI† – Characterization methods.

2.3. Adsorption experiments

To investigate the removal capacity of the metatitanates, toxic metal ions such as Pb(II), Cu(II) and Cd(II) ions in water solution were used. A series of systematic experiments has been performed to examine the removal of heavy metals.

For kinetic measurements, approximately 0.1 g of sample was mixed with 50 mL of 10 mmol L⁻¹ solution of Pb(NO₃)₂, Cu(NO₃)₂ or Cd(NO₃)₂ and put on a shaker at RT while the time was measured. Nine samples (0.5 mL) were taken from each mixture during the experiment (10–1440 min) and the concentration of heavy metal was determined by AAS.

Equilibrium experiments for the determination of the heavy metal ions adsorption and alkali metal ions desorption isotherms were performed by adding 0.1 g of the adsorbent into 50 mL of Pb(NO₃)₂, Cu(NO₃)₂ or Cd(NO₃)₂ aqueous solutions with concentration range of 0.5–10 mmol L⁻¹ and shaken for 24 hours. The solid residue was filtered off and the concentration of metal ions (heavy metal and appropriate alkali metal) in solution was determined by AAS.

The pH values of solutions after adsorption were determined between 6.3–7.1 in case of Pb(II), 7.1–7.9 in case of Cu(II) and 6.9–7.6 in case of Cd(II).

The adsorbed amount of heavy metals was calculated by using the following equation:

$$a = \frac{(c_0 - c_e) \times V}{m}$$

where a is the adsorbed amount (mmol g⁻¹), c_0 is the initial concentration of used solution of heavy metal cations (mmol L⁻¹), c_e is the equilibrium concentration (mmol L⁻¹), V is the volume of a solution (L) and m is the weight of a used adsorbent (g).

The equivalent desorbed amount of alkali metals ions was calculated by using:

$$d = \frac{c_e \times V}{m}$$

where d is the desorbed amount (mmol g⁻¹), c_e is the equilibrium concentration of alkali metal cations (mmol L⁻¹), V is the volume of a solution (L) and m is the weight of a used adsorbent (g).

The equilibrium adsorption isotherms were analysed by using the Langmuir model:

$$a = \frac{c_e \times a_m \times K_L}{1 + c_e \times K_L}$$

where a_m (mmol g⁻¹) is the adsorption capacity, a (mmol g⁻¹) is the amount of adsorbed metal at the equilibrium concentration c_e (mmol L⁻¹) and K_L is the Langmuir constant.



Table 1 Sample preparation's information

Alkaline	Amount of alkaline (mol)	pH of resulting suspensions	Sample name
LiOH	0.07	8	TIG-5 mL-LiOH
	0.21	10	TIG-15 mL-LiOH
NaOH	0.07	9	TIG-5 mL-NaOH
	0.21	11	TIG-15 mL-NaOH
KOH	0.07	9	TIG-5 mL-KOH
	0.21	12	TIG-15 mL-KOH

The influence of pH on sorption was studied by preparing solutions of metal ions at 10 mM wherein the pH levels were adjusted to fixed values with 5% HNO₃ and 5% NaOH. 0.1 g of adsorbent was added into the individual solutions and equilibrated for 24 h before analysis of adsorbed amounts in aqueous phase. Afterwards, the pH was measured and, if necessary, adjusted again to the fixed value and the procedure was repeated.

In order to determine the influence of annealing temperature on the prepared samples and the resulting sorption capacity of heavy metal ions, appropriate portions of each sample were annealed at 300 °C, 450 °C, 600 °C and 1000 °C, in argon, heating rate 10 °C min⁻¹.

A batch of experiments to determine the effect of real sample conditions was performed to compare the adsorption behaviour in distilled and tap water. Approximately 0.1 g of the sample was mixed with 50 mL of 10 mmol L⁻¹ solutions of Pb(NO₃)₂, Cu(NO₃)₂ or Cd(NO₃)₂ in distilled, resp. tap water and put on a shaker at RT, equilibrated for 24 h and adsorbed amounts were determined by AAS.

Measurement of competitive adsorption was performed in solution containing Pb(NO₃)₂, Cu(NO₃)₂ and Cd(NO₃)₂ in 1 : 1 : 1 ratio with total concentration 10 mmol L⁻¹. Approximately 0.1 g of the sample was mixed with 50 mL of this solution, put on a shaker at RT, equilibrated for 24 h and adsorbed amounts were determined by AAS.

The reusability of materials was tested by washing the already used in adsorption material in solution of NaOH for 2 hours and then, the adsorption experiment was performed again. Approximately 0.1 g of the sample was mixed with 50 mL of 10 mmol L⁻¹ solutions of Cu(NO₃)₂ in distilled water and put on a shaker at RT, equilibrated for 24 h and adsorbed amounts were determined by AAS.

All the adsorption experiments were repeated twice and the average values are presented.

3. Results and discussion

3.1. Characterization of the rod-shaped nanostructures

A typical morphology as obtained by SEM is shown in Fig. 1. The starting material is composed of rod-shaped crystals with a length of about 10–15 μm and diameter of 2 μm. The basic shape of the particles of titanyl sulfate remained unchanged throughout the controlled hydrolysis process which is in good agreement with the data for rods immersed into ice-cold

concentrated aqueous ammonia published earlier.^{32,33} The XRD patterns of the metatitanates (not shown) were identical to those reported in previous literature,³⁴ the diffraction patterns obtained in this study did not exhibit any peaks assignable to impurity phases and showed that the prepared materials are amorphous (Fig. S1†) as described in detail in the thermoanalytical study.³⁴

The total content of alkali metals in prepared materials was determined by dissolving 0.1 g of samples in 50 mL of concentrated HNO₃ under heating and analysing the obtained solution by AAS. The results are summarized in Table 2 and show that the higher the amount of hydroxide used for the synthesis, the higher amount of alkali metal in the prepared sample.

TEM investigation (Fig. 2) of materials used for the adsorption revealed that the morphology of titanyl sulfate rods used in the syntheses is well preserved in the transformed amorphous samples including, *e.g.* laminar structure and other details.³² The amorphous character of the material is demonstrated by the corresponding electron diffraction pattern with only very broad diffraction rings. The TEM/EDS spectra (20 measurements were taken for each material) of materials before sorption experiments show that Na and K (Li can't be detected by EDS) are homogeneously distributed in samples and the amounts are in good agreement with the results determined by the extraction in nitric acid (Table 2).

Decreasing trend of alkali metal content (in mmol g⁻¹) in series Li > Na > K is in agreement with increasing ionic radii. Small Li⁺ cation can be more easily accommodated in the cavities of titanate structure and its amount corresponds to stoichiometry Li_{1.25}TiO_{2.625}. On the contrary, the molar portion of heavier alkali metals is much smaller corresponding to Na_{0.47}TiO_{2.235} and K_{0.26}TiO_{2.13}, respectively. Thus, the increasing mass and size of alkali metal ion used for preparation shifts the composition of final material closer to pure TiO₂ while the use of LiOH lead to almost stoichiometric lithium titanate.

3.2. Adsorption experiments

3.2.1. Effect of contact time. Firstly, the sorption of Pb²⁺, Cu²⁺, and Cd²⁺ on the amorphous metatitanates was investigated by determining the effect of contact time. It is well known that two mechanisms are responsible for metal sorption on titanates: ion-exchange and surface complexations.^{35,36} It is also believed that the rate constant of adsorption is of great



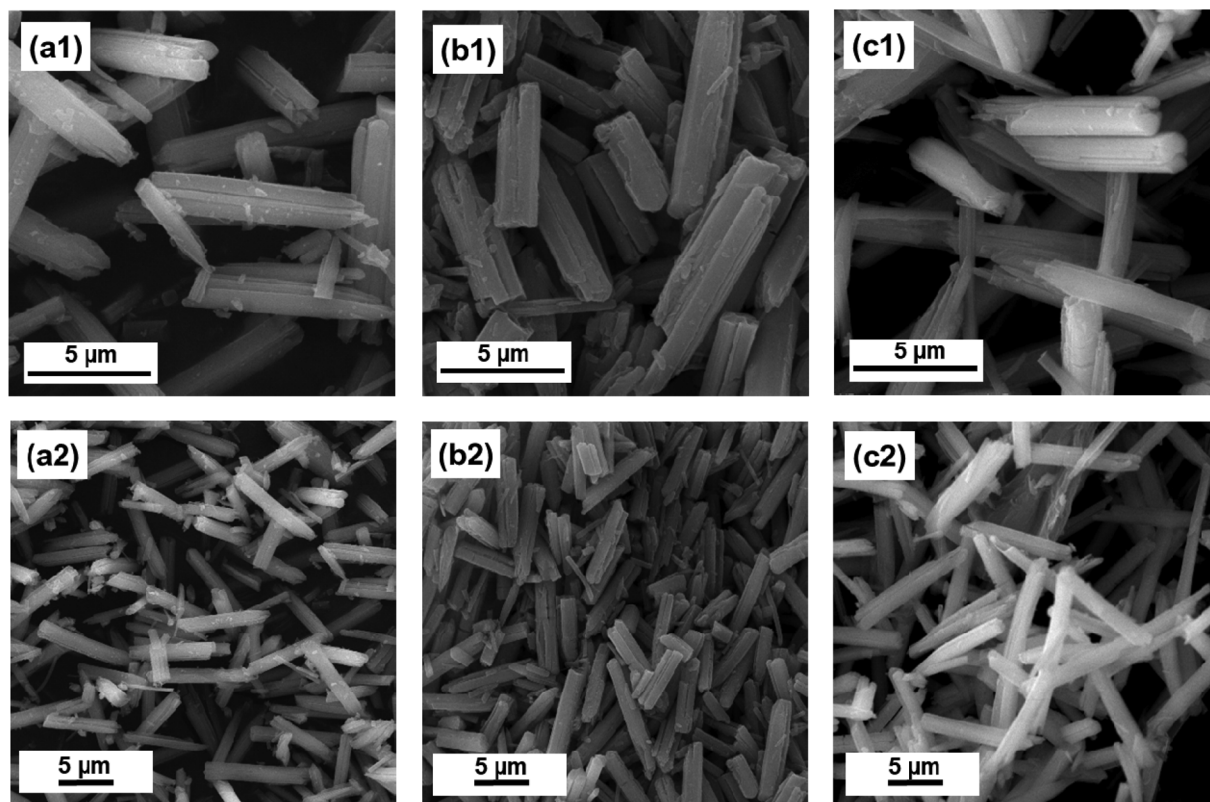


Fig. 1 SEM micrographs of adsorbents obtained by the controlled hydrolysis, TIG-5 mL-LiOH (a1), TIG-5 mL-NaOH (b1), TIG-5 mL-KOH (c1), TIG-15 mL-LiOH (a2), TIG-15 mL-NaOH (b2), TIG-15 mL-KOH (c2).

Table 2 Properties of tested materials

Sample	Alkali metal	Content of alkali metal	
		mg g ⁻¹	mmol g ⁻¹
TIG-5 mL-LiOH	Li	58.2	8.36
TIG-15 mL-NaOH		127.5	18.35
TIG-5 mL-NaOH	Na	134.1	5.61
TIG-15 mL-NaOH		179.3	7.54
TIG-5 mL-KOH	K	136.6	3.42
TIG-15 mL-KOH		151.8	3.89

importance in the waste water treatment by adsorption as the contact time between the adsorbate and the adsorbent directly affects the operation cost (faster adsorption enables lower cost of use in real-world environment).³⁶

The dynamics of adsorption process is shown in Fig. 3. Results show that the adsorption rate of materials towards all the tested heavy metals is comparable. The time necessary to reach the equilibrium is in range of 6–8 hours from the initial contact of adsorbents with the solution containing heavy metal ions which is faster than for titania nanoflowers,⁴ zeolite iron composites³⁷ or zeolites^{38,39} but also much slower than for titania nanotubes⁴⁰ where only 120 min were necessary to reach the equilibrium. Based on the kinetic experiments the contact time of 24 h was used for further equilibrium adsorption tests.

3.2.2. Adsorption isotherms of heavy metals and desorption isotherms of alkali metal cations. The adsorption isotherms of heavy metal ions on prepared materials are presented together with desorption isotherms of alkali metals. Equilibrium data for metal adsorption are shown in Fig. 4.

Materials precipitated with LiOH (Fig. 4(a1)) and NaOH (Fig. 4(b1)) present themselves as ion exchangers, *i.e.* the amount of adsorbed Pb(II) is nearly equivalent to the amount of desorbed alkali metal. This exchange is characterized by the fact that only a portion of the alkali metal is utilized while the remainder of the alkali metal is firmly incorporated into the titanate structure and the exchange capacity has, therefore, significant limitations due to this characteristic. The results achieved with the TIG-KOH (Fig. 4(c1)) show a behaviour quite different to the previously mentioned sorbents. Unlike the aforementioned partial alkali metal exchange, the TIG-KOH material desorbed and substituted almost all of the present K(I) ions by their Pb(II) equivalent during the adsorption process (compared with Table 2). In addition, compared to a standard ion exchange, the TIG-KOH material adsorbs more Pb(II) ions, therefore, a different way of binding has to be considered, *e.g.* complexation. Niu *et al.* have attributed this behaviour to the formation of anionic negatively charged surface complexes.²²

Comparison of the experimental data with the theoretical Langmuir isotherm enables a determination of adsorption capacities of tested materials for Pb(II) and maximal desorbed amount for alkali metals (Fig. 5(a)). The Langmuir adsorption



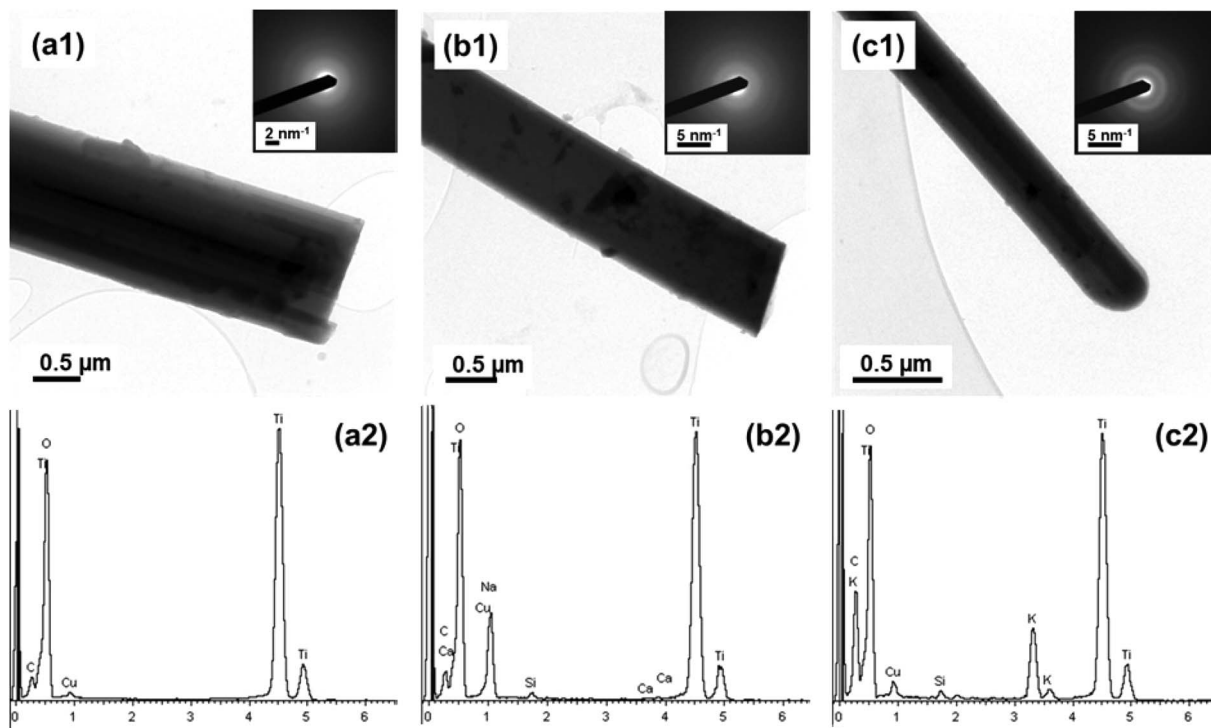


Fig. 2 TEM/ED/EDS observations of TIG-5 mL-LiOH (a1 and a2), TIG-5 mL-NaOH (b1 and b2) and TIG-5 mL-KOH (c1 and c2) before adsorption tests of lead.

capacities of prepared materials have increased in series TIG-NaOH < TIG-KOH < TIG-LiOH. The maximum adsorbed amounts for Pb(II) as calculated from the Langmuir adsorption

model are 3.8 mmol g^{-1} , 2.8 mmol g^{-1} , and 3.1 mmol g^{-1} , respectively. It is apparent that the adsorption capacities are larger than those of titanate nanoflowers (1.47 , 0.71 and

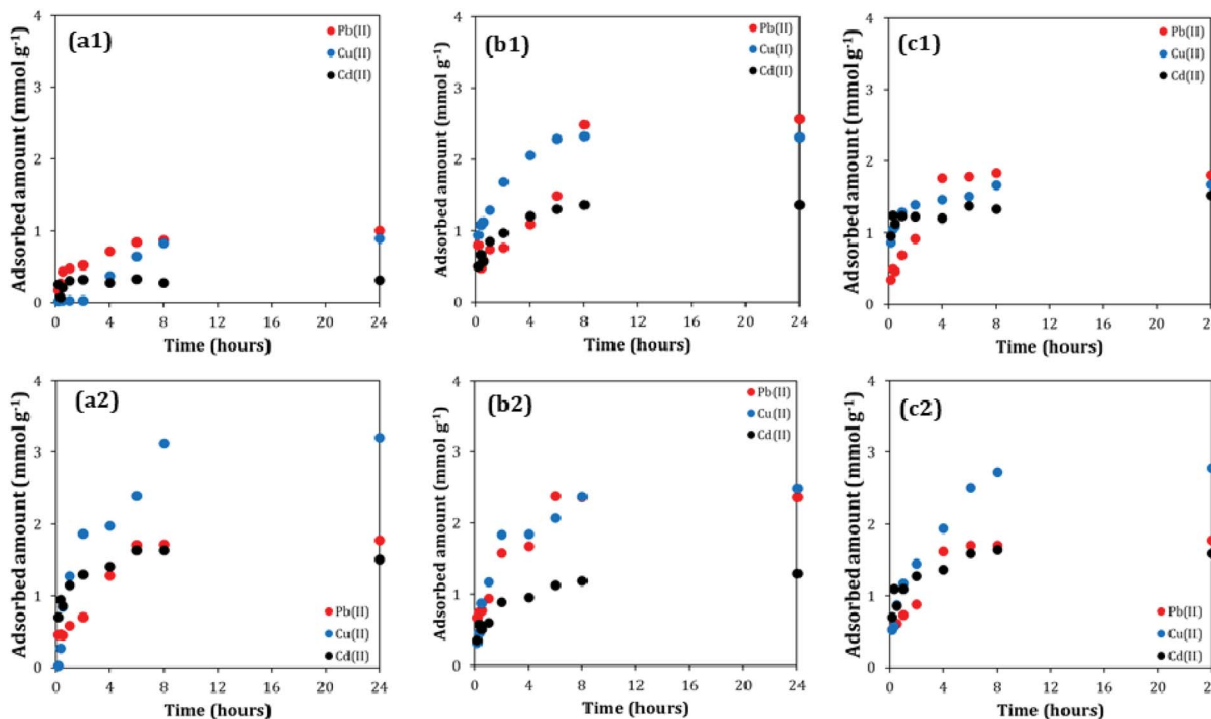


Fig. 3 The effect of contact time on adsorption of lead, copper and cadmium on TIG-5 mL-LiOH (a1), TIG-5 mL-NaOH (b1), TIG-5 mL-KOH (c1), TIG-15 mL-LiOH (a2), TIG-15 mL-NaOH (b2), TIG-15 mL-KOH (c2).



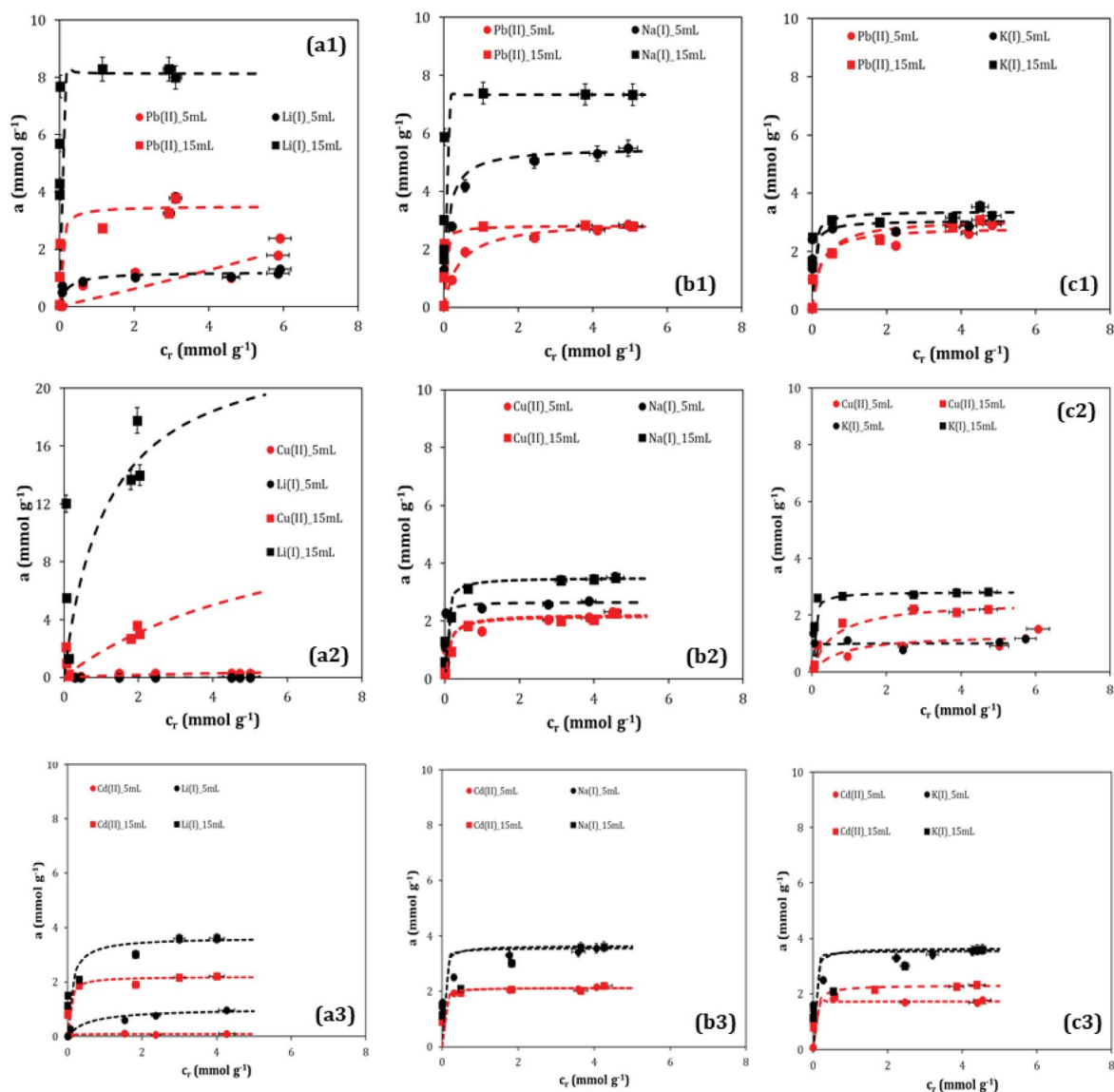


Fig. 4 Adsorption isotherms of lead (a1, b1 and c1), copper (a2, b2 and c2), cadmium (a3, b3 and c3) and desorption isotherms of lithium (a1–a3), sodium (b1–b3) and potassium (c1–c3) cations; dashed lines represents appropriate Langmuir fit; the error bars represent standard deviations.

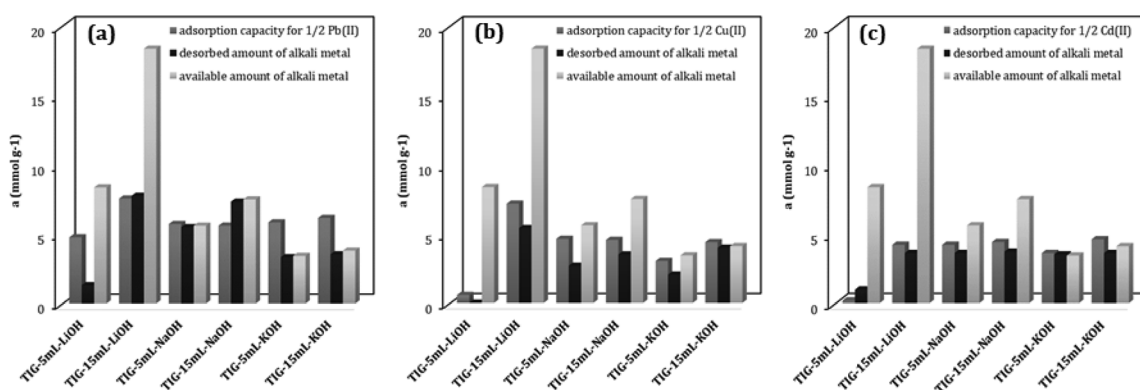


Fig. 5 Comparison of adsorption capacity for Pb(II) (a), Cu(II) (b) and Cd(II) (c), (expressed in equivalents $\frac{1}{2}$) with desorbed and total amount of alkali metals for all prepared metatitanates.



0.51 mmol g⁻¹),⁴ amorphous titanate (0.71, 0.51 and 0.54 mmol g⁻¹)²⁰ or zeolites (0.08 and 1.6 mmol g⁻¹).^{19,38}

By the experiments with copper and cadmium, it was proved that all three types of materials behaved as ion-exchangers, the amount of adsorbed copper (Fig. 4(a2, b2 and c2)) and cadmium (Fig. 4(a3, b3 and c3)) corresponded or was little higher than the amount of desorbed alkali metal. When comparing the influence of concentrations of alkali hydroxide during the synthesis, resp. the amount of alkali metals incorporated in the material, with the adsorbed amount of heavy metal, it seems that the amount of available alkali metal does not have a significant influence on the amount of adsorbed copper or cadmium with the exception of the TIG-5 mL-LiOH which is an unsuitable sorbent, the adsorbed amount is negligible.

The maximum adsorbed amounts for Cu(II) as calculated have increased in series TIG-NaOH < TIG-KOH < TIG-LiOH, in good agreement with data observed in adsorption experiments with lead. The maximum adsorbed amounts are 3.6 mmol g⁻¹, 2.3 mmol g⁻¹ and 2.7 mmol g⁻¹ for materials precipitated with LiOH, NaOH and KOH, respectively. It is apparent that the adsorption capacities are larger than those of titanate

Table 3 Comparison of adsorbed amounts of heavy metals (in mmol g⁻¹) performed in distilled and tap water

Sample	Adsorbed amount of Pb(II) in water		Adsorbed amount of Cu(II) in water		Adsorbed amount of Cd(II) in water	
	Distilled	Tap	Distilled	Tap	Distilled	Tap
TIG-5 mL-LiOH	2.4	2.2	0.3	0.2	0.1	0.0
TIG-15 mL-NaOH	3.8	3.7	3.6	3.1	2.1	1.8
TIG-5 mL-NaOH	2.9	2.8	2.3	1.8	2.1	1.9
TIG-15 mL-NaOH	2.8	2.7	2.3	1.9	2.2	2.1
TIG-5 mL-KOH	2.9	2.9	1.5	1.3	1.8	1.4
TIG-15 mL-KOH	3.1	3.0	2.2	2.0	2.3	2.1

nanotubes (2.0 mmol g⁻¹ (ref. 23)) or hydroxotitanate (0.9 mmol g⁻¹ (ref. 36)). These results indicate that prepared adsorbents can be considered as promising adsorbents for removal of copper from water.

The maximum adsorbed amounts for Cd(II) as calculated from the Langmuir adsorption model are 2.2 mmol g⁻¹,

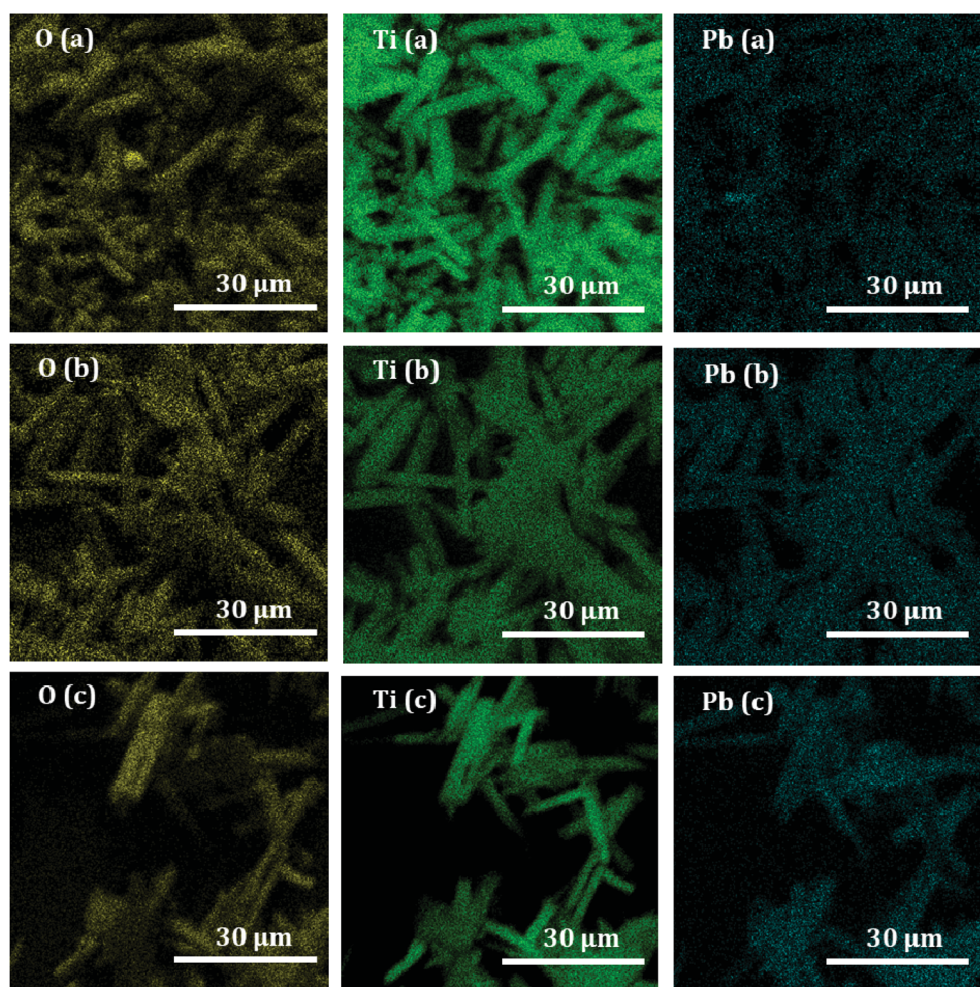


Fig. 6 SEM/EDS mapping of oxygen, titanium and lead in TIG-5 mL-LiOH (a), TIG-5 mL-NaOH (b) and TIG-5 mL-KOH (c) after adsorption tests of lead.



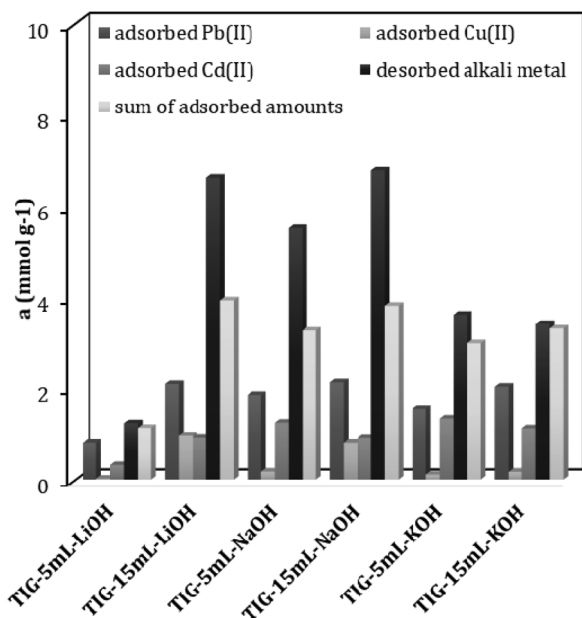


Fig. 7 Comparison of competitive behaviour of TIG-LiOH, TIG-NaOH and TIG-KOH towards solution containing Pb(II), Cu(II) and Cd(II) in ratio 1 : 1 : 1.

2.2 mmol g⁻¹ and 2.3 mmol g⁻¹ (NaOH < TIG-KOH < TIG-LiOH). It is apparent that the adsorption capacities are larger than those of titanate nanotubes (2.1 mmol g⁻¹ (ref. 40)). These results indicate that prepared adsorbents can be considered as promising adsorbents for removal of cadmium from water.

The adsorption capacity for heavy metals was compared to desorbed amount of alkali metal and the total amount of alkali metal available (Fig. 5). Based on the results it can be concluded that the mechanism of sorption is ion-exchange. These promising results are an opening to possible applications of these sorbents compounds into remove heavy metals from contaminated water.

In real-life applications, the reusability of prepared samples is crucial. Therefore, the wash-out of copper adsorbed in the materials was repeatedly tested (by cycling). It was concluded that the materials are recyclable, the copper adsorbed in the sample can be easily removed from the material by washing out in sodium hydroxide with a slight decrease (up to 5%) in uptake in the consequent cycles.

By mapping of samples by SEM/EDS analysis after adsorption tests it was proved that the heavy metals are homogeneously distributed in the sample in all rods as can be seen in Fig. 6 for

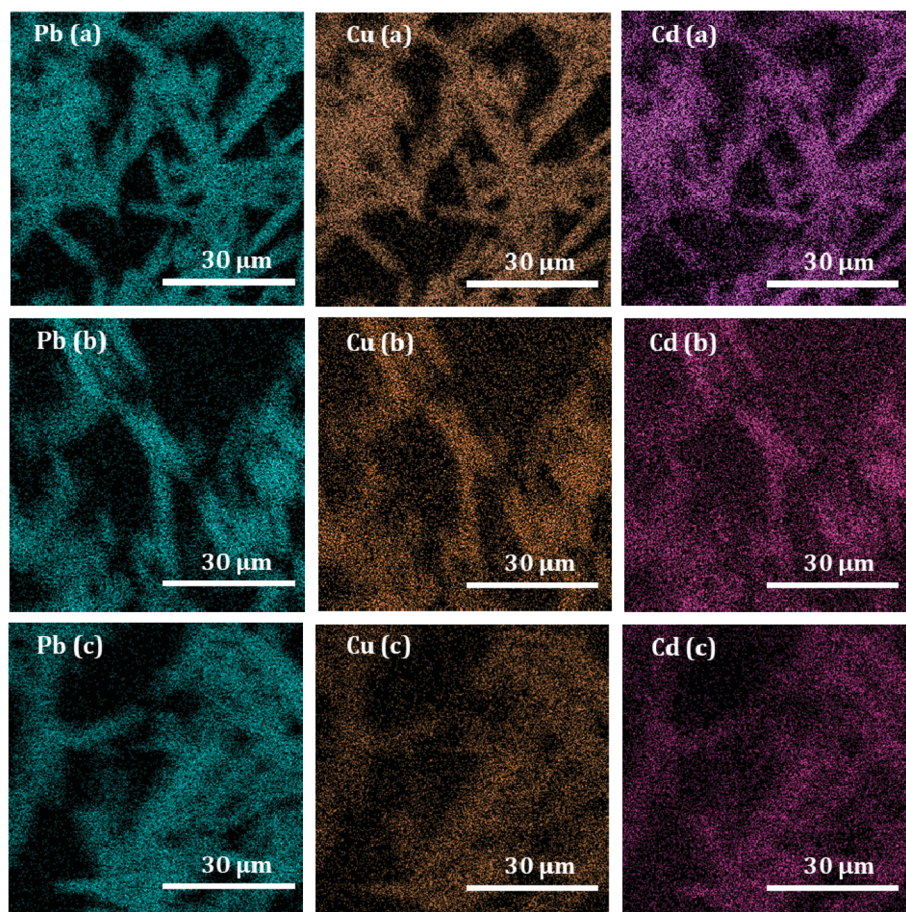


Fig. 8 SEM/EDS mapping of lead (cyan dots), copper (orange dots) and cadmium (magenta dots) of rods after competitive experiments in TIG-5 mL-LiOH (a), TIG-5 mL-NaOH (b) and TIG-5 mL-KOH (c).



lead sorption experiment for TIG-5 mL-LiOH, TIG-5 mL-NaOH and TIG-5 mL-KOH (other materials – see ESI, Fig. S2 and S3†).

The influence of the equilibrium pH on the uptake of heavy metals was studied in range between 2–8 as described in detail in ESI.† As shown in Fig. S4,† the sorption capacity increased with increasing pH.

The thermal decomposition of prepared materials has been already described.⁴¹ It was discovered that the materials are amorphous up to crystallization into mixtures of anatase and titanates. The influence on annealing temperature on sorption of radionuclides on titania materials showed that the higher the annealing temperature the lower the adsorbed amount.⁴²

In this study, the observation revealed very similar results as can be seen in ESI.† An increase in the annealing temperature led to a decrease in the adsorbed amount of heavy metal ions (Fig. S5†), therefore, the materials are not suitable for adsorption experiments when crystalline.

Real samples have an inherent presence of several inorganic ions which can interfere with heavy metal ion adsorption. For this reason, the influence of common cations and anions present in tap water (for composition see ESI, Table S1†) on heavy metal uptake was investigated and summarized in Table 3. The decrease of adsorption capacity of all three samples towards Pb(II), Cu(II) and Cd(II) ions was observed.

Based on the presented results, it can be concluded that the effect of interfering ions on the heavy metal uptake is not very significant, therefore, the prepared samples are meant to be suitable sorbents for sorption of Pb(II), Cu(II) and Cd(II) from drinking water.

The measurement of competitive adsorption showed that the lead ions are adsorbed preferably in all tested sorbents. The amount of adsorbed amounts decreases in series Pb(II) > Cd(II) > Cu(II) as can be seen in Fig. 7. The competitive behaviour can be explained by decreasing hydrated ion radii⁴³ which decreases in the same series 1.20 > 0.96 > 0.62 Å. To confirm these results mapping of samples was conducted after the aforementioned procedures. Results confirmed that the adsorbed amount of heavy metals towards prepared rods decreases in series Pb(II) > Cd(II) > Cu(II), while being homogeneously distributed among rods (Fig. 8).

4. Conclusions

Amorphous lithium, sodium and potassium metatitanates were successfully synthesized, characterized and used as adsorbents for the removal of heavy metals from natural water.

The adsorption rate of each heavy metal ion was quite low, the equilibrium was reached in about 8 hours. The maximum amounts of Pb(II), Cu(II) and Cd(II) were detected in pH range of 5–8. The study on equilibrium showed that the Langmuir model was the most appropriate and the adsorption capacities were in range of 2.4–3.8 mmol Pb(II) per g, 0.3–3.6 mmol Cu(II) per g and 0.1–2.3 mmol Cd(II) per g. It was discussed that the interfering ions from drinking water do not have any significant impact on the adsorbed amount and the competitive behaviour was also described. The influence of annealing temperature of prepared

materials on Pb(II), Cu(II) and Cd(II) showed that the higher the annealing temperature the lower the adsorbed amount.

Conflicts of interest

There are no conflicts to declare.

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References

- 1 J. S. Hu, L. S. Zhong, W. G. Song and L. J. Wan, Synthesis of hierarchically structured metal oxides and their application in heavy metal ion removal, *Adv. Mater.*, 2008, **20**, 2977–2982.
- 2 A. Dabrowski, Z. Hubicki, P. Podkoscielny and E. Robens, Selective removal of the heavy metal ions from waters and industrial wastewaters by ion-exchange method, *Chemosphere*, 2004, **56**, 91–106.
- 3 M. N. Akieh, M. Lahtinen, A. Vaisanen and M. Sillanpaa, Preparation and characterization of sodium iron titanate ion exchanger and its application in heavy metal removal from waste waters, *J. Hazard. Mater.*, 2008, **152**, 640–647.
- 4 J. Huang, Y. Cao, Z. Liu, Z. Deng, F. Tang and W. Wang, Efficient removal of heavy metal ions from water system by titanate nanoflowers, *Chem. Eng. J.*, 2012, **180**, 75–80.
- 5 H. Leinonen, J. Lehto and A. Makela, Purification of nickel and zinc from waste-waters of metal-plating plants by ion-exchange, *React. Polym.*, 1994, **23**, 221–228.
- 6 L. di Bitonto, A. Volpe, M. Pagano, G. Bagnuolo, G. Mascolo, V. La Parola, P. Di Leo and C. Pastore, Amorphous boron-doped sodium titanates hydrates: efficient and reusable adsorbents for the removal of Pb²⁺ from water, *J. Hazard. Mater.*, 2017, **324**, 168–177.
- 7 W. Liu, T. Wang, A. G. L. Borthwick, Y. Q. Wang, X. C. Yin, X. Z. Li and J. R. Ni, Adsorption of Pb²⁺, Cd²⁺, Cu²⁺ and Cr³⁺ onto titanate nanotubes: competition and effect of inorganic ions, *Sci. Total Environ.*, 2013, **456**, 171–180.
- 8 T. Wang, W. Liu, L. Xiong, N. Xu and J. R. Ni, Influence of pH, ionic strength and humic acid on competitive adsorption of Pb(II), Cd(II) and Cr(III) onto titanate nanotubes, *Chem. Eng. J.*, 2013, **215**, 366–374.
- 9 W. T. Liu, Nanoparticles and their biological and environmental applications, *J. Biosci. Bioeng.*, 2006, **102**, 1–7.
- 10 H. J. Shipley, S. Yean, A. T. Kan and M. B. Tomson, Adsorption of arsenic to magnetite nanoparticles: effect of particle concentration, pH, ionic strength, and temperature, *Environ. Toxicol. Chem.*, 2009, **28**, 509–515.
- 11 P. G. Tratnyek and R. L. Johnson, Nanotechnologies for environmental cleanup, *Nano Today*, 2006, **1**, 44–48.



- 12 K. E. Engates and H. J. Shipley, Adsorption of Pb, Cd, Cu, Zn, and Ni to titanium dioxide nanoparticles: effect of particle size, solid concentration, and exhaustion, *Environ. Sci. Pollut. Res.*, 2011, **18**, 386–395.
- 13 P. Liang, T. Q. Shi and J. Li, Nanometer-size titanium dioxide separation/preconcentration and FAAS determination of trace Zn and Cd in water sample, *Int. J. Environ. Anal. Chem.*, 2004, **84**, 315–321.
- 14 T. Ohnuki and N. Kozai, Adsorption behavior of radioactive cesium by non-mica minerals, *J. Nucl. Sci. Technol.*, 2013, **50**, 369–375.
- 15 R. Chakravarty and A. Dash, Role of Nanoporous Materials in Radiochemical Separations for Biomedical Applications, *J. Nanosci. Nanotechnol.*, 2013, **13**, 2431–2450.
- 16 B. K. Singh, R. Tomar, S. Kumar, A. S. Kar, B. S. Tomar, S. Ramanathan and V. K. Manchanda, Role of the humic acid for sorption of radionuclides by synthesized titania, *Radiochim. Acta*, 2014, **102**, 255–261.
- 17 W. F. Yang, L. D. Guo, C. Y. Chuang, P. H. Santschi, D. Schumann and M. Ayrano, Influence of organic matter on the adsorption of Pb-210, Po-210, Be-7 and their fractionation on nanoparticles in seawater, *Earth Planet. Sci. Lett.*, 2015, **423**, 193–201.
- 18 C. Santhosh, V. Velmurugan, G. Jacob, S. K. Jeong, A. N. Grace and A. Bhatnagar, Role of nanomaterials in water treatment applications: a review, *Chem. Eng. J.*, 2016, **306**, 1116–1137.
- 19 D. J. Yang, Z. F. Zheng, H. W. Liu, H. Y. Zhu, X. B. Ke, Y. Xu, D. Wu and Y. Sun, Layered Titanate Nanofibers as Efficient Adsorbents for Removal of Toxic Radioactive and Heavy Metal Ions from Water, *J. Phys. Chem. C*, 2008, **112**, 16275–16280.
- 20 J. Huang, Y. Cao, Z. Deng and H. Tong, Formation of titanate nanostructures under different NaOH concentration and their application in wastewater treatment, *J. Solid State Chem.*, 2011, **184**, 712–719.
- 21 H. Kochkar, A. Turki, L. Bergaoui, G. Berhault and A. Ghorbel, Study of Pd(II) adsorption over titanate nanotubes of different diameters, *J. Colloid Interface Sci.*, 2009, **331**, 27–31.
- 22 H. Y. Niu, J. M. Wang, Y. L. Shi, Y. Q. Cai and F. S. Wei, Adsorption behavior of arsenic onto protonated titanate nanotubes prepared via hydrothermal method, *Microporous Mesoporous Mater.*, 2009, **122**, 28–35.
- 23 S. S. Liu, C. K. Lee, H. C. Chen, C. C. Wang and L. C. Juang, Application of titanate nanotubes for Cu(II) ions adsorptive removal from aqueous solution, *Chem. Eng. J.*, 2009, **147**, 188–193.
- 24 S. Wang, L. Q. Tan, J. L. Jiang, J. Chen and L. D. Feng, Preparation and characterization of nanosized TiO₂ powder as an inorganic adsorbent for aqueous radionuclide Co(II) ions, *J. Radioanal. Nucl. Chem.*, 2013, **295**, 1305–1312.
- 25 M. Kolar, H. Mest'ankova, J. Jirkovsky, M. Heyrovsky and J. Subrt, Some aspects of physico-chemical properties of TiO₂ nanocolloids with respect to their age, size, and structure, *Langmuir*, 2006, **22**, 598–604.
- 26 R. Z. Ma, T. Sasaki and Y. Bando, Alkali metal cation intercalation properties of titanate nanotubes, *Chem. Commun.*, 2005, 948–950.
- 27 D. H. Chen and R. A. Caruso, Recent Progress in the Synthesis of Spherical Titania Nanostructures and Their Applications, *Adv. Funct. Mater.*, 2013, **23**, 1356–1374.
- 28 V. Privman, D. V. Goia, J. Park and E. Matijevic, Mechanism of formation of monodispersed colloids by aggregation of nanosize precursors, *J. Colloid Interface Sci.*, 1999, **213**, 36–45.
- 29 V. Vesely and V. Pekarek, Synthetic Inorganic Ion-Exchangers. 1. Hydrous Oxides and Acidic Salts of Multivalent Metals, *Talanta*, 1972, **19**, 219–262.
- 30 L. G. Gerasimova, M. V. Maslova and A. I. Nikolaev, Application of Colloid Titanium-Containing Precursors in the Inorganic Ion-Exchange Technology, *Glass Phys. Chem.*, 2011, **37**, 401–405.
- 31 P. Fernandez-Ibanez, J. Blanco, S. Malato and F. J. de las Nieves, Application of the colloidal stability of TiO₂ particles for recovery and reuse in solar photocatalysis, *Water Res.*, 2003, **37**, 3180–3188.
- 32 M. Klementová, M. Motlochová, J. Boháček, J. Kupčík, L. Palatinus, E. Plížingrová, L. Szatmáry and J. Šubrt, Metatitanic acid pseudomorphs after titanyl sulfates: nanostructured sorbents and precursors for crystalline titania with desired particle size and shape, *Cryst. Growth Des.*, 2017, **17**, 6762–6769.
- 33 M. Palkovska, V. Slovak, J. Subrt, J. Bohacek, Z. Barbierikova, V. Brezova and R. Fajgar, Investigation of the thermal decomposition of a new titanium dioxide material, *J. Therm. Anal. Calorim.*, 2016, **125**, 1071–1078.
- 34 M. Motlochová, V. Slovák, E. Plížingrová, M. Klementová, P. Bezdička and J. Šubrt, Thermal Decomposition Study of Nanostructured Amorphous Lithium, Sodium and Potassium Metatitanates, *Thermochim. Acta*, 2018, **670**, 148–154.
- 35 W. Liu, H. Chen, A. G. L. Borthwick, Y. F. Han and J. R. Ni, Mutual promotion mechanism for adsorption of coexisting Cr(III) and Cr(VI) onto titanate nanotubes, *Chem. Eng. J.*, 2013, **232**, 228–236.
- 36 A. Volpe, M. Pagano, C. Pastore, C. Cuocci and A. Milella, Sorption properties of an amorphous hydroxo titanate towards Pb²⁺, Ni²⁺, and Cu²⁺ ions in aqueous solution, *J. Environ. Sci. Health, Part A: Toxic/Hazard. Subst. Environ. Eng.*, 2016, **51**, 1121–1130.
- 37 S. A. Kim, S. Kamala-Kannan, K. J. Lee, Y. J. Park, P. J. Shea, W. H. Lee, H. M. Kim and B. T. Oh, Removal of Pb(II) from aqueous solution by a zeolite-nanoscale zero-valent iron composite, *Chem. Eng. J.*, 2013, **217**, 54–60.
- 38 S. Wang and E. Ariyanto, Competitive adsorption of malachite green and Pb ions on natural zeolite, *J. Colloid Interface Sci.*, 2007, **314**, 25–31.
- 39 X. Y. Wang, J. H. Cai, Y. J. Zhang, L. H. Li, L. Jiang and C. R. Wang, Heavy metal sorption properties of magnesium titanate mesoporous nanorods, *J. Mater. Chem. A*, 2015, **3**, 11796–11800.



- 40 L. Xiong, C. Chen, Q. Chen and J. R. Ni, Adsorption of Pb(II) and Cd(II) from aqueous solutions using titanate nanotubes prepared via hydrothermal method, *J. Hazard. Mater.*, 2011, **189**, 741–748.
- 41 M. Motlochova, V. Slovak, E. Plizingrova, M. Klementova, P. Bezdicka and J. Subrt, Thermal decomposition study of nanostructured amorphous lithium, sodium and potassium metatitanates, *Thermochim. Acta*, 2018, **670**, 148–154.
- 42 M. Motlochova, V. Slovak, E. Plizingrova, L. Szatmary, P. Bezdicka and J. Subrt, The influence of annealing temperature on properties of TiO₂ based materials as adsorbents of radionuclides, *Thermochim. Acta*, 2019, **673**, 34–39.
- 43 I. Persson, Hydrated metal ions in aqueous solution: how regular are their structures?, *Pure Appl. Chem.*, 2010, **82**, 1901–1917.

