Electronic Supplementary Material (ESI) for RSC Advances.

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

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Characterization Methods

Structural and morphology characterization of the samples were observed by scanning electron microscopy (SEM). A Philips XL 30 CP microscope (W-cathode, 20 nm resolution at 1 kV) was used for initial observation.

Detailed phase analysis including imaging and electron diffraction were carried out on a transmission electron microscope (TEM) JEOL JEM 3010 operated at 300 kV (LaB6, cathode, point resolution 1.7 Å). Images were recorded on a Gatan CCD camera with resolution of 1024 × 1024 pixels using the Digital Micrograph software package. The powder samples were dispersed in ethanol and the suspension was treated in ultrasound for 2 min. A drop of very dilute suspension was placed on a holey-carbon coated Cu-grid and allowed to dry by evaporation at ambient temperature.

In situ high temperature X-Ray powder diffraction (HT XRD) patterns were collected with a PANalytical X'Pert PRO diffractometer equipped with a conventional X-ray tube (CoKα radiation, 40 kV, 30 mA, line focus) and a multichannel detector X'Celerator with an anti-scatter shield. For experiments at elevated temperature the high temperature chamber (HTK 16, Anton Paar, Graz, Austria) was used. X-ray patterns were measured from room temperature to 1200 °C with a step of 25 °C in the range of 19 to 93° 2 θ (step of 0.0334° and 40 s counting per step yielding a scan of ca 12 min). In this case we used conventional Bragg–Brentano geometry with 0.04 rad Soller slit, 1° divergence slit, 2° anti-scatter slit, and 10 mm mask in the incident beam, 6.6 mm anti-scatter slit, 0.04 rad Soller slit and Fe beta-filter in the diffracted beam. Samples were ground in an agate mortar in a suspension with cyclohexane. The suspension was then placed on top of the Platinum heating element. After evaporation of solvent, thin layer of non-annealed sample was ready for analysis.

Qualitative analysis was performed with the HighScore software package (PANalytical, The Netherlands, version 4.5.0), and JCPDS PDF-4 database [17], DiffracPlus software package (Bruker AXS, Germany, version 8.0) and JCPDS PDF-4 database [17]. For quantitative phase analysis DiffracPlus Topas (Bruker AXS, Germany, version 4.2) with structural models based on ICSD database was used. This program permits to estimate the weight fractions of crystalline phases by means of Rietveld refinement procedure. The estimation of the size of crystallites was performed on the basis of Scherrer formula as implemented within the DiffracPlus Topas software.

The solutions were analysed by atomic absorption spectroscopy (AAS, Varian 240FS).

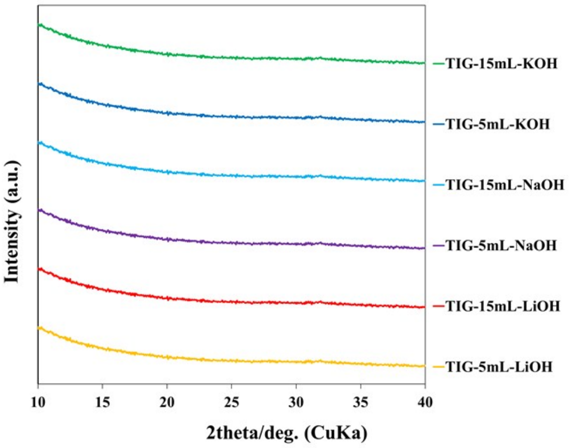

Figure S1. XRD patterns of prepared samples.

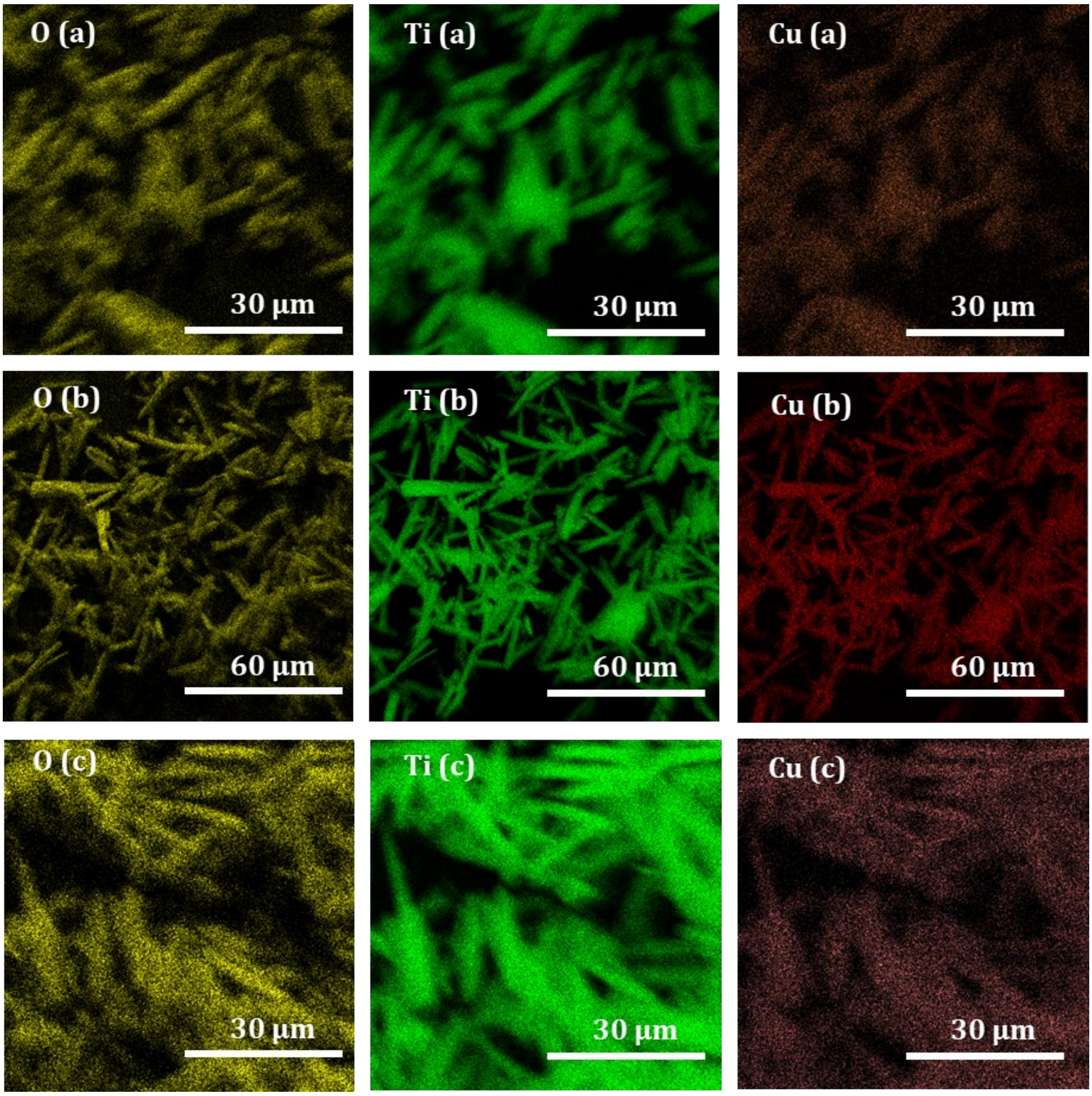

Figure S2. SEM/EDS mapping of oxygen, titanium and lead in TIG-5mL-LiOH (a), TIG-5mL-NaOH (b) and TIG-5mL-KOH (c) after adsorption tests of copper.

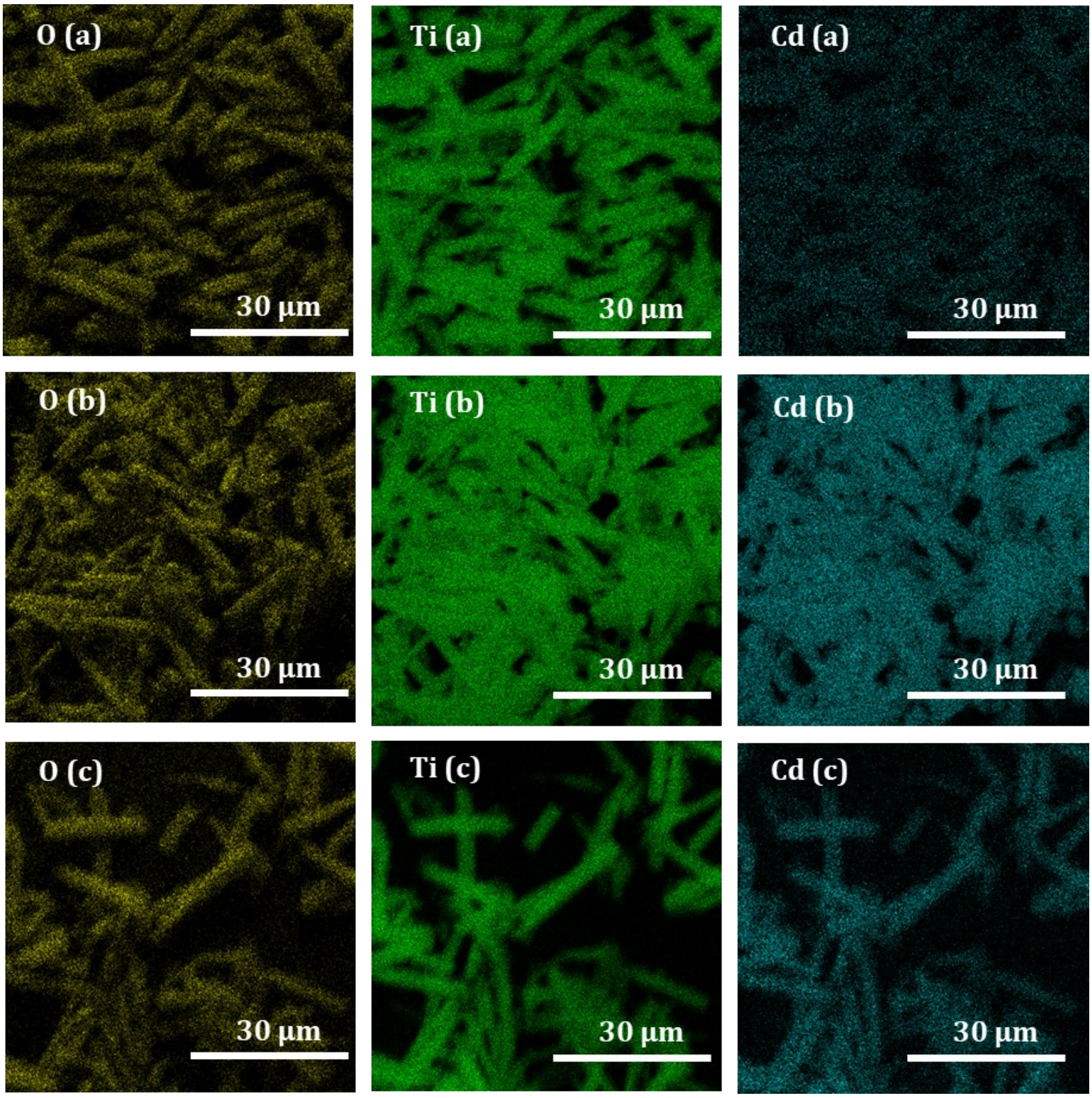

Figure S3. SEM/EDS mapping of oxygen, titanium and lead in TIG-5mL-LiOH (a), TIG-5mL-NaOH (b) and TIG-5mL-KOH (c) after adsorption tests of cadmium.

Table S1. Composition of water used for tap water sorption experiments.

Parameter	**Amount (mg L^{-1})**
HCO_3^-	146.1
Na^+	15.2
Ca^{2+}	56.0
Mg^{2+}	9.4
Cl^-	16.1

Influence of pH on sorption of heavy metals

The influence of the equilibrium pH on the uptake of heavy metals was studied in range between 2-8. As shown in Figure 11, the sorption capacity increased with increasing pH. At low pH values of 2 and 3, the equilibrium uptake was lowered due to the electrostatic repulsion between the positively charged surface of prepared metatitanates and Pb(II), Cu(II) and Cd(II) [1]. In addition, the H^+ ions compete with heavy metal ions for adsorption sites under strongly acidic conditions [2] and also the material is not suitable for sorption at low pH as it dissolves itself. At pH=4, the surface potential of prepared metatitanates turned negative, resulting in sufficient uptakes. At pH=5, nearly complete removal of heavy metals was achieved, indicating the high adsorption capacity over broad pH range. Over pH 7.5, the precipitation of Pb(II) can be observed, over pH 6 in case of Cu(II) and over pH 8 in case of Cd(II). The formation (and precipitation) of Pb-, Cu- and Cd- hydroxide species could strongly influence the adsorption data, therefore the experiments are recommended to run under these pH values [3].

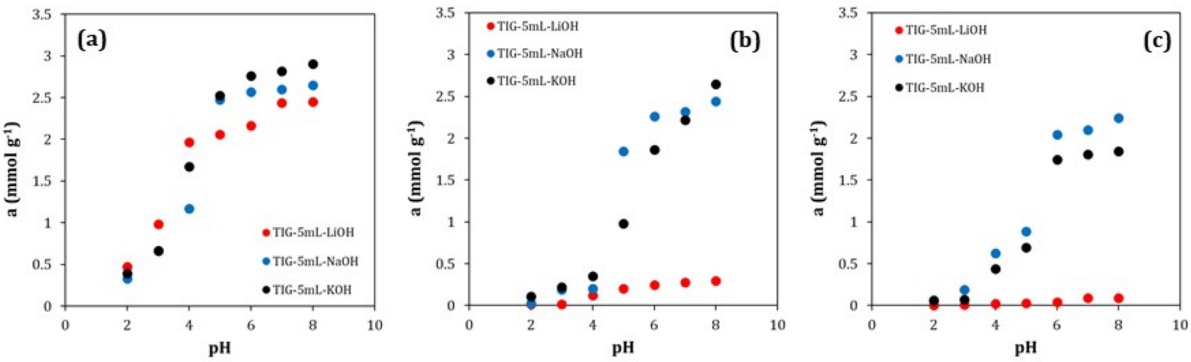

Figure S4. Dependence of pH on adsorbed amount of Pb(II) (a), Cu(II) (b) and Cd(II) (c) on of TIG-5mL-LiOH, TIG-5mL-NaOH and TIG-5mL-KOH.

Influence of annealing temperature on adsorption of heavy metals

The thermal decomposition of prepared materials was already described [4]. It was found out 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 revealed that the higher the annealing temperature the lower adsorbed amount [5].

In this study, the observation revealed very similar results as can be seen in Figure 10, with the increasing annealing temperature decrease the adsorbed amount of heavy metal ions, therefore the materials are not suitable for adsorption experiments when crystalline.

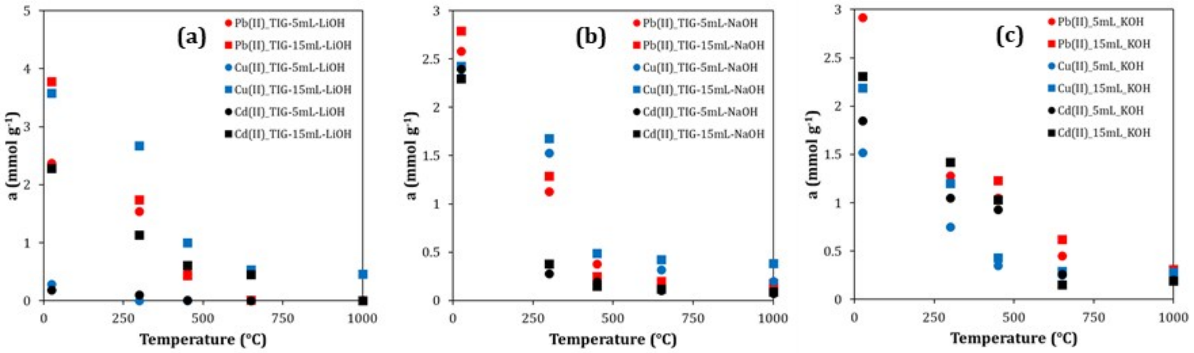

Figure S5. Dependence of adsorbed amount of Pb(II), Cu(II) and Cd(II) on annealing temperature of TIG-LiOH (a), TIG-NaOH (b) and TIG-KOH (c).