Synthesis of sorbents from industrial solid wastes by modification with atomic layer deposition (ALD) for mine water treatment

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Abstract Novel sorbents for acid mine water treatment were developed from industrial solid waste, such as iron sand. The surface of raw materials was modified by atomic layer deposition (ALD) of TiO2 and Al2O3 at the growth rates of approximately 1 Å for each metal oxide. Adsorption properties of synthetic sorbents were studied for the removal of nickel, copper, zinc, iron and sulphate from the synthetic and real acid mine water. It was proved that the deposition of the thin films of metal oxides on the sorbent surfaces increased the removal of ion pollutants compared to original materials. The sorption capacity follows the order of Fe>Cu>SO4>Zn>Ni for unmodified and both modified sorbents. The maximum adsorption capacities of the modified adsorbents were founded at approximately 650, 220, 200, 150 and 100 mmol g-1 for sulphate, iron, copper, zinc and nickel ions, respectively. In addition, the produced sorbents can be successfully used for the real AMD treatment, achieving removal efficiency of metal ions to 80%.

Keywords Adsorption; metal ions removal; sulphate ions removal; metal oxides coating.

Introduction

Minimisation of water consumption and search for new solutions for effective and low-cost water treatments are challenges for industries and environmental science (Cousin & Taugourdeau, 2016). Mining is one of the largest water consumers for the exploration, extraction and ore processing (Lei et al. 2016; Mudd, 2008) and produces various waste-waters. One of them is acid mine drainage (AMD). Most part of AMD pollutants are iron, copper, zinc and nickel in the sulphates forms (Lei et al. 2016).

Removal of both metal and sulphate ions is the main task for efficient AMD treatment. Such treatment can be active and passive methods (Wolkersdorfer, 2008). Compared to other methods of acid mine drainage treatment, adsorption is one of the cheapest and widely applied for removal of various pollutant compounds (DiLoreto et al. 2016). The choice of sorbents for removing metal ions and sulphates is one of the challenges for purification of AMD. Many methods are based on preliminary neutralization of acid mine water followed by removing of contaminating ions. However, AMD neutralization can lead to precipitation of metals as insoluble salts that increase the amount of solid wastes. A sorbent that will be able to remove a large amount of ions from wastewater with complex composition without precipitation would be a good solution for this problem.

Modified sorbents based on iron compounds from solid industrial wastes have a good capacity for removal of metal ions and some cations from acid solutions without precipitation (Reddy & Yun, 2016; Theiss et al. 2016; Flores et al. 2012; Iakovleva et al. 2016).
In this study, we employed atomic layer deposition (ALD) to deposit metal oxides on the surface of granulated adsorbents, as modification method of sorbent surfaces. ALD is based on chemical interaction between gaseous reactants and active sites on the substrate surface. The method features a fine control on the film thickness and coating uniformity for the flat surfaces (George, 2010; Puttaswamy et al. 2016), making it ideal for coating complex shape substrate including powders (Iakovleva et al. 2016; Kilbury et al. 2012; Kukli et al. 2016; Tiznado et al. 2014). In this study, deposition of aluminum oxide and titanium dioxides, such as more reactive oxides (Borai et al. 2015), on iron content sorbent surfaces were applied for increasing strenght of granules and sorption capacity. The modified sorbents with ALD will be checked for effective capture of ions (Cu, Zn, Fe, Ni and sulphate) from synthetic and real AMDs.

Materials and methods

Solid waste iron sand, named RH, was obtained from Finnish company Ekokem Ltd. The chemical composition and physical properties of raw and modified material are presented in Table 1.

***Table 1**. Chemical composition of raw and modified RH.*

Chemical composition, w%	**RH**	**RH_Al_2O_3**	**RH_TiO_2**
Si	5.0	5.0	5.0
S	17.6	17.6	17.6
K	0.3	0.3	0.3
Ca	14.4	14.4	14.4
Fe	7.2	7.2	7.2
Al	-	1.5	-
Ti	-	-	2.8

Synthetic AMD solutions of SO_4^{2-}, Fe^{3+}, Cu^{2+}, Zn^{2+} and Ni^{2+}, were prepared from analytical grade $Fe_2(SO_4)_3{\cdot}5H2O$, $CuSO_4{\cdot}5H_2O$, $ZnSO_4{\cdot}H_2O$, and $NiSO_4{\cdot}6H_2O$, respectively (obtained from Merck). The concentration of metal ions in stock solutions were 1000 mg L^{-1} with pH 1.5. All solution were prepared with ultrapure water.

Real mine water were obtained from a sulphide mine in Finland from 700 m depths.
The chemical composition of real and synthetic AMD before and after adsorption tests was determined by inductively coupled plasma atomic emission spectroscopy (ICP-OES) and

high-performance liquid chromatography (HPLC) for metal and sulphate ions, respectively. The elemental composition of real mine water is shown in Table 2.

Table 2. *Chemical composition of real AMD.*

Level m	Cu mg L^{-1}	Zn mg L^{-1}	Fe mg L^{-1}	Ni mg L^{-1}	Sulfate mg L^{-1}	Redox E	pH	Cond. ms m^{-1}
720	4.41	242	52.6	8.1	3470	422	3.2	481

Raw and modified sorbents were characterized with nitrogen sorption at 196 °C using TriStar 3000 (Micromeritics Inc., USA); ZetaSizer Nano ZS, Malvern, UK; XRD, PANanalytical Empyrean powder diffractometer, UK; FTIR, Bruker Vertex 70v spectrometer; SEM, Nova Nano SEM 200, FEI Ltd.

Batch adsorption tests were conducted by mixing RH and modified forms with 45 mL of synthetic and real AMD solutions with known concentrations in a range of 10-300 mg L^{-1} for all metal ions, according to experiments. All batch experiments was carried out in triplicate. The systematic error of results did not exceed 3%. The mixture was shaken in a mechanical shaker ST5 (CAT M.Zipper GmbH, Staufen, Germany) from 30 min to 72 h, and 10 mL of the solution were taken from the flasks at certain time intervals and then filtered, using 0.20 μm polypropylene syringe filter. The temporal evolution of the solution pH was monitored.

The percentage adsorption (%) was calculated as

$$\%\text{Adsorption} = (C_i - C_t) \times 100/ \text{Ci}, \quad (1)$$

where, C_i and C_t are the concentrations of the metal ions in the initial and after treatment solutions, respectively.

Sorbents modification

Raw material was granulated befor modification by wet-granulation with polyvinyl acetate (PVAc) as a binder. To improve the strength of the granules and their adsorption capacities, modification of their surface with ALD was used. TiO2 and Al2O3 thin films were deposited on the surface of the granules using a TFS500 ALD reactor (Beneq Oy, Finland). For the TiO2 ALD process, the adsorbent surface was exposed to TiCl4 and H2O vapors intermittent with inert gas (N2) pulses in order to purge the reactor. The pulse time of TiCl4 and H2O was 0.6 and 0.25 seconds respectively. In turn, Al2O3 film was synthesized by sequential pulses of trimethylaluminium (TMA) and H2O into the reactor with a pulse time of 1 and 2 seconds respectively. The ALD process was carried out at 350 °C for TiO_2 and 200 oC for Al_2O_3 under pressure of 1 mbar. 300 ALD cycles were used for this material. The silicon substrates <100> (Si-Mat, Germany) were used to control the film thickness of both metal oxides.

Results and discussion

Characterisation of raw and modified adsorbent materials

The adsorbent chemical compositions were obtained with XRD and ED-XRF analyses. The raw RH material contains around 14% of Ca, 7% of Fe and 17% of S. A large amount of sulphur may cause secondary pollution due to desorption during water treatment. However, previous studies have shown (Iakovleva et al. 2016; Iakovleva et al. 2015a), the presence of sulfur is not observed on the surface of the sorbents after modification. FTIR results also confirm the absence of sulphur compounds on the surface of modified sorbents (Table 3). The new bending vibrations corresponding to aluminum oxide at the peak between 980 – 1000 and 610 – 611 cm^{-1}, and titanium oxides with the peak between 450 – 800 cm^{-1} were observed after modification of original RH with TMA and TiCl4, respectively. The peak from sulphur compounds (1120 – 1160 cm^{-1}) was observed only from raw RH (Table 3).

Table 3. *Band assignment of the FTIR spectra of raw and modified materials.*

Adsorbent	**Wave number, cm^{-1}**						
	O-S-O 1120-1160	**Si-O-Si 600-661**	**O-Si-O 466-473**	**H-O-H 1620-1690**	**O-Ti-O 450-800**	**Al-O 980-1000**	**O-Al-O 610-611**
RH	+	+	+	+			
RH_TiO_2		+	+	+	+		
RH_Al_2O_3		+	+	+		+	+

The average pore size and specific surface area of unmodified and modified sorbents are presented in Table 4. The pore size of modified sorbents is decrised, hovever, specific surface area incrises about twice compared with unmodified one (Table 4).

Table 4*. The pore size and specific surface area of unmodified and modified sorbents from this and previous experiments (Iakovleva et al. 2016).*

Sorbent	**Specific surface area, $m^2\ g^{-1}$**	**Pore size, nm**	**pH**
RH	62	180	2.5
RH_TiO_2	125	3	3
RH_Al_2O_3	115	20	2.8

SEM images showed changes in the surface structure of both modified sorbents (Figure 1b and 1c) compared to raw RH (Figure 1a). The distinctive fine-pored layers of TiO_2 and Al_2O_3 on the surface of RH can be observed (Figures 1b and 1c). Film thickness measurements on reference Si substrate showed that the growth rates were 1.10 Å/cycle and 0.63 Å for Al2O3 and TiO2, respectively, and correlated with previous publication (George, 2010).

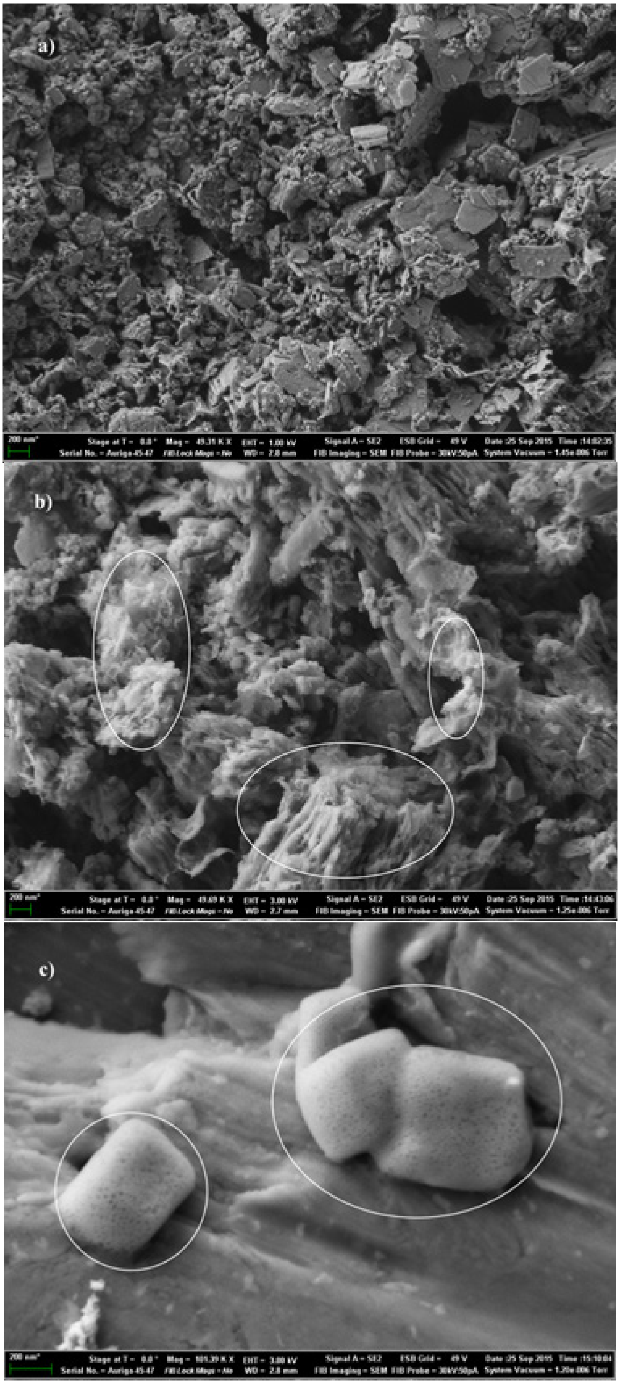

Figure 1. *SEM images of a) unmodified RH, b) modified RH with TiO2, c) modified RH with Al2O3.*

The presence of metal oxides on the surface of the modified sorbents was also confirmed by XRD as well (Figure 2). The peaks (011), (013) and (122) indicate the orthorhombic kappa-Al_2O_3, while the peaks of (011) and (020) correspond to anatase-TiO_2 (Figure 2).

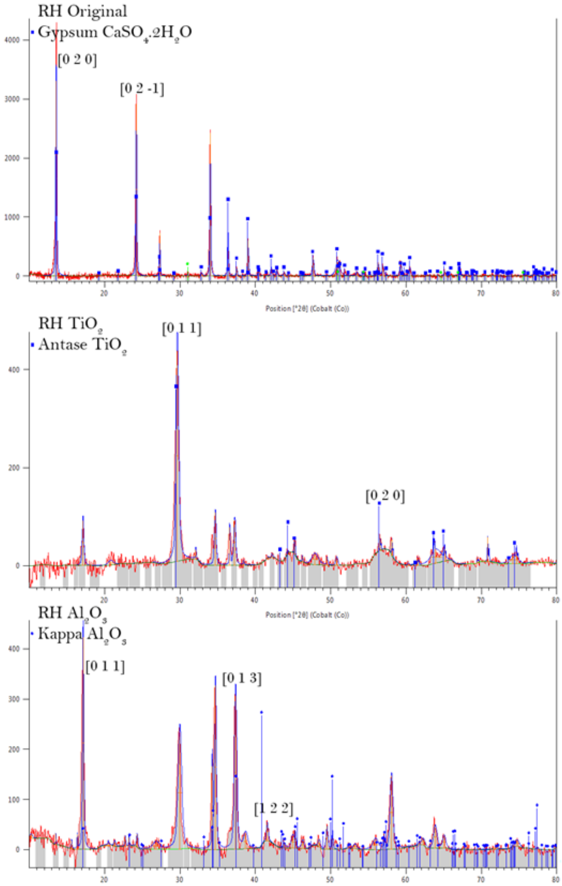

***Figure 2**. Figure 5. XRD profiles of unmodified and modified RH sorbents.*

Optimisation of adsorbent amount for AMD treatment

An optimal mass of modified sorbents for the maximum removal of metal ions and sulphates from synthetic AMD was found at 2 g L^{-1}, 20 times less than that of unmodified RH.

Contact time optimisation

Contact time optimisation of adsorbents and adsorbates was found under the following conditions: the initial concentration of SO_4^{2-} was 3470 mg L^{-1}; Ni^{2+}, Zn^{2+}, and Cu^{2+} was 100 mg L^{-1} and 1000 mg L^{-1} for Fe^{3+}. The initial amount of both adsorbents was 10 g L^{-1}. The equilibrium was reached after 48 h for both sorbents. The pollutants removals were similar for both modified sorbents and amounted around 70% for sulphate cations and 99% for metal ions (Figure 3). The solution pH was found to be changed from 3.5 to 4 slowly (Iakovleva et al. 2016; Silva et al. 2010; Tang et al. 2002).

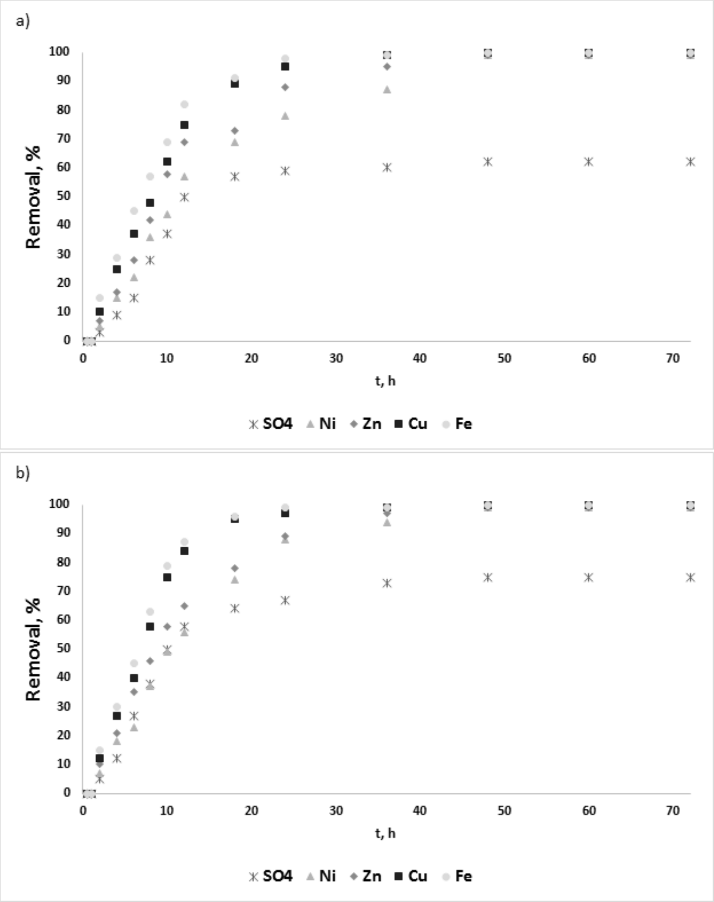

Figure 3. *Removal of sulphate and metal ions with modified adsorbents (a) RH_TiO2 and (b) RH_Al2O3 (c).*

A pH of initial solution was 2.5 and it increased during adsorption process after about 12 h to 5. The maximum adsorption efficiency for all ions was achieved in the same time. The pH affects to ionisation of metals and surface charge. All four metal ions removal increased when the solution pH higher than the pH of sorbents. Because initial sorbents pH is around 3 (Table 4), the pH of treated solution should be higher than this value for better removal of metal ions. However, better sorption capacity for sulphate ions was observed at 5 pH also. The similar effects were observed by many researchers (Bartczak et al. 2015; Boonamnuayvitaya et al. 2004; Genç-Fuhrman et al. 2016). It could be due to the effect of competitions between sulphate and metal ions in complex solution.

Adsorption isotherms

The equilibrium between the adsorption of pollutants on the sorbent surface at a constant temperature was described by Langmuir (Eq. 2) adsorption isotherm.

$$q_e = \frac{q_m K_L C_e}{1+K_L C_e} \qquad (2)$$

where q_e and q_m are sorption capacities (mmol g^{-1}) at equilibrium and maximum, respectively; C_e is concentration of pollutant ions in the solution (mmol L^{-1}) at equilibrium; K_L is Langmuir constant related to the sorption energy.

The parameters were calculated with minimisation of the error distribution between experimental and predicted data by Marquardt's percent standard deviation (MPSD):

$$\sum_{i=1}^{n} \left(\frac{q_{e,exp} - q_{e,calc}}{q_{e,exp}} \right)_i^2 \qquad (3)$$

Langmuir isotherm parameter q_m shows the number of adsorbent site that actively interacts with the pollutant ions (Allen et al. 2004). This parameter increases for all pollutants after modification of raw RH with both methods. The number of sites which participate in the adsorption of ions is much higher for SO_4^{2-} (around 600 mmol g^{-1}). For other ions it is around 200 mmol g^{-1}, expect for nickel ions (around 100 mmol g^{-1}) (Table 5).

The K coefficient is the affinity between sorbate and adsorbent. According to Langmuir theory the affinity between the adsorbents and adsorbates is:

$Fe^{2+} > Cu^{2+} > SO_4^{2-} > Zn^{2+} > Ni^{2+}$

This order is confirmed by many researchers (Alcolea et al. 2012; Aziz et al. 2008; Iakovleva et al. 2015a; Iakovleva et al. 2015b).

The complexation and ion-exchange mechanisms take place during the metal and sulphate ions removal in this experiments. The unmodified and modified RH contain silicate compounds, which can react with ions by following reactions:

$$\mathrm{SiO^- + H^+ + P^{n+} + OH^- \rightarrow SiOP + H^+ + OH^-} \qquad (4a)$$

$$\mathrm{Fe^{2+} + OH^- + SO_4^{2-} + \frac{Me^{n+}}{H^+} \rightarrow FeSO_4 + \frac{MeOH}{HOH}} \qquad (4b)$$

***Table 5**. Isotherm parameters for unmodified and modified RHs during AMD treatment process.*

		C_e (mmol L^{-1})	$q_{e\ exp}$ (mmol g^{-1})	$q_{e\ model}$ (mmol g^{-1})	q_m (mmol g^{-1})	K_L (L $mmol^{-1}$)	R^2
Langmuir							
RH	SO_4^{2-}	47.4	11.72	11.24	11.37	18.68	0.74
	Ni^{2+}	1.69	0.11	0.10	0.12	9.01	0.70
	Zn^{2+}	1.54	0.20	0.19	0.17	12.03	0.75
	Cu^{2+}	1.56	0.39	0.40	0.38	21.09	0.82
	Fe^{3+}	1.78	0.75	0.72	0.74	25.12	0.87
RH_Al_2O_3	SO_4^{2-}	47.4	650	622	637	20.15	0.82
	Ni^{2+}	1.69	98	100	99	10.17	0.85
	Zn^{2+}	1.54	150	145	152	12.05	0.84
	Cu^{2+}	1.56	201	204	199	20.22	0.87
	Fe^{3+}	1.78	225	215	218	26.30	0.90
RH_TiO_2	SO_4^{2-}	47.4	623	620	625	21.30	0.95
	Ni^{2+}	1.69	85	83	87	9.6	0.85
	Zn^{2+}	1.54	137	136	138	12.5	0.85
	Cu^{2+}	1.56	190	185	187	20.3	0.90
	Fe^{3+}	1.78	215	210	217	25.7	0.93

The addition of aluminium and titanium oxides onto the surface of sorbent allows a significant increase of ion removal. It can be due to the appearance of additional functional groups, which also participate in the removal of ions from solution. As it is known that activated alumina (Al_2O_3) is a highly porous commercial sorbent with a surface area more than 200 m^2 g^{-1} used for the removal of various pollutants (Gulshan et al. 2009; Han et al. 2013). Titanium dioxide has a lower chemical reactivity than activated alumina, however, its porosity and big surface area also contribute to application for the removal of various pollutants from water (Borai et al. 2015). Therefore, the increase of pollutant ion removal depends on the increase of the sorbent surface area and the presence of additional functional groups. Modified sorbent with alumina oxide has slightly better adsorption capacity for removal of sulphate and metal ions from synthetic AMD compared to the sorbent modified with titanium dioxide (Table 5). Wettability tests of unmodified and modified granules shows a better strength and stability of the modified granules to the aqueous medium compared to the unmodified ones.

Real AMD treatment with modified RHs

Removal of ions from real AMD was conducted by the batch method at ambient temperature for 720 h with 2 g L^{-1} of both modified sorbents. Removal efficiencies of sulphate, nickel, zinc, iron and copper ions for both sorbents were 50%, 75%, 80%, 99% and 90%, respectively which are lower compared to adsorption from the synthetic AMD (Fig. 4).

Increasing adsorbents concentration and sorption time did not increase removal efficiency. Equilibrium occurred at the optimal sorption time (48 h) and sorbents concentrations of 2 g L^{-1}. The lower sorption capacity of both sorbents for real AMD compared to synthetic solutions could be due to complex composition of real AMD. Other ions can act as competitors during the adsorption process, such as chloride, ammonium and some trace amount of metal ions.

Conclusions

Novel iron-containing sorbents from an industrial solid waste were produced with ALD technology for TiO_2 and Al_2O_3 coating. The optimal sorption parameters were estimated with synthetic AMD. The optimal time (48 h) and sorbent concentration (2 g L^{-1}) were determined with a batch method. The maximum sorption capacities of RH_Al_2O_3 and RH_TiO_2 were around 600, 200, 200, 150 and 100 mmol g-1 for removal of SO_4^{2-}, Fe^{3+}, Cu^{2+}, Zn^{2+} and Ni^{2+}, respectively. The sorption process was carried out using complexation and ion-exchange mechanism. The deposition of TiO_2 and Al_2O_3 on the surface of granules sufficiently increased the sorption capacities of raw material for real AMD treatment. The both produced sorbents could be used for real AMD treatment with a high capacity for some pollutants. The optimisation of modification process with ALD for cost decreasing while maintaining modified sorbents properties could be recommended for the further research. Increasing sulphate ions removal from complex solution should be taken into account also.

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