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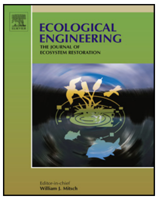

Acid mine drainage (AMD) treatment: Neutralization and toxic elements removal with unmodified and modified limestone

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ABSTRACT

Limestones and their modifications from Nordkalk Corporation (Finland) flotation fines (FF) and filter sand (FS) as potential adsorbents for AMD treatment and wastewater purification from Cu, Fe, Zn and Ni ions were studied. Limestones were capable of binding significant amounts of Cu and Fe from synthetic AMD solutions and wastewater, while unmodified limestones were not good for Zn and Ni removal. Two methods of surface area modification were suggested. The first one with 2 M solution of NaCl and the second one with wastewater from Norilsk Nickel Harjavalta. The structure of materials and their surface area were characterized by SEM, EDX, MIR spectroscopy and nitrogen adsorption methods. Optimal amount of adsorbents for different model and real solutions was found. Adsorption kinetics showed that the adsorption equilibrium was reached within approximately 8 h. The kinetic data fits to a pseudo second order model with correlation coefficients greater than 0.999. The adsorption capacity was the highest at solution pH range of 6–7. Langmuir, Toth and Sips models were used to fit the adsorption isotherms. Based on the parameters calculated from models, the adsorption capacity decreased in the order of Cu > Fe > Zn > Ni for FF and Fe > Cu > Zn > Ni for FS. The research showed that the proposed modified limestones can be successfully used for AMD neutralization and removal of Cu(II), Fe(III), Zn(II) and Ni(II).

1. Introduction

Each year global mining industry produces several billion tonnes of solid inorganic wastes or by-products, including liquid wastes through its mineral processing and metal production operations (Charbonier, 2001; Akcil and Koldas, 2006).

Composition of solid and liquid wastes in mining varies greatly depending on the process, methods of enrichments and treatments of ores. Mine waters can be categorized into three groups according to their acid-base properties: acid mine drainage (AMD) with pH 6 and below, neutral mine drainage with pH 6 and above, and saline mine drainage with pH above 6 containing more than 1000 mg L^{-1} of carbonates (Wolkersdorfer, 2008). AMD is formed by the decomposition of pyrites (Wolkersdorfer, 2008 After hydrothermal deposits of copper, lead, zinc, tin, and other nonferrous/colored metals into pyrites, substantial amounts of them are sent to landfill as they are economically inefficient to treat further.

Process of pyrites decomposition is hazardous because of mining water acidification and also because a large number of various toxic trace elements are released during the process, these are Ag, As, Bi, Cd, Co, Cu, Hg, Mo, Ni, Pb, Ru, Sb, Se, Sn, Te, and Zn (Abraitis et al., 2004; Chandra and Gerson, 2010; Deditius et al., 2011). The pyrite oxidation process has been extensively studied and can be summarized by the following reactions:

$$FeS_2 + \frac{7}{2}O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (1)$$

$$FeS_2 + \frac{7}{2}O_2 + H_2O \rightarrow Fe^{3+} + \frac{1}{2}H_2O \quad (2)$$

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$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 \downarrow + 3H^{+} \quad (3)$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^{+} \quad (4)$$

First, the oxidation of sulfide to sulfate is observed by the action of water and oxygen leaving Fe (II) unoxidized (Eq. (1)). Then the oxidation of Fe (II) to Fe (III) occurs (Eq. (2)) and part of Fe (III) is precipitated as ferric hydroxide (III) (Eq. (3)) while the other part reacts with pyrite oxidizing sulfide to sulfate in the presence of water reducing Fe (III) to Fe (II) (Eq. (4)). All four reactions above are parallel processes, which occur and last as long as there is access to water and oxygen. Ríos et al. (2008), described in detail the process of pyrite decomposition.

There are three main problems attributed to mining, such as AMD treatment, utilization of solid wastes and reusing of process water. Various adsorbents for mining wastewater purification have been recently reviewed (Iakovleva and Sillanpää, 2013). Recently interest has arisen to use solid wastes as adsorbents for waste water purification (Bhatnagar et al., 2014; Ahmaruzzaman, 2011;

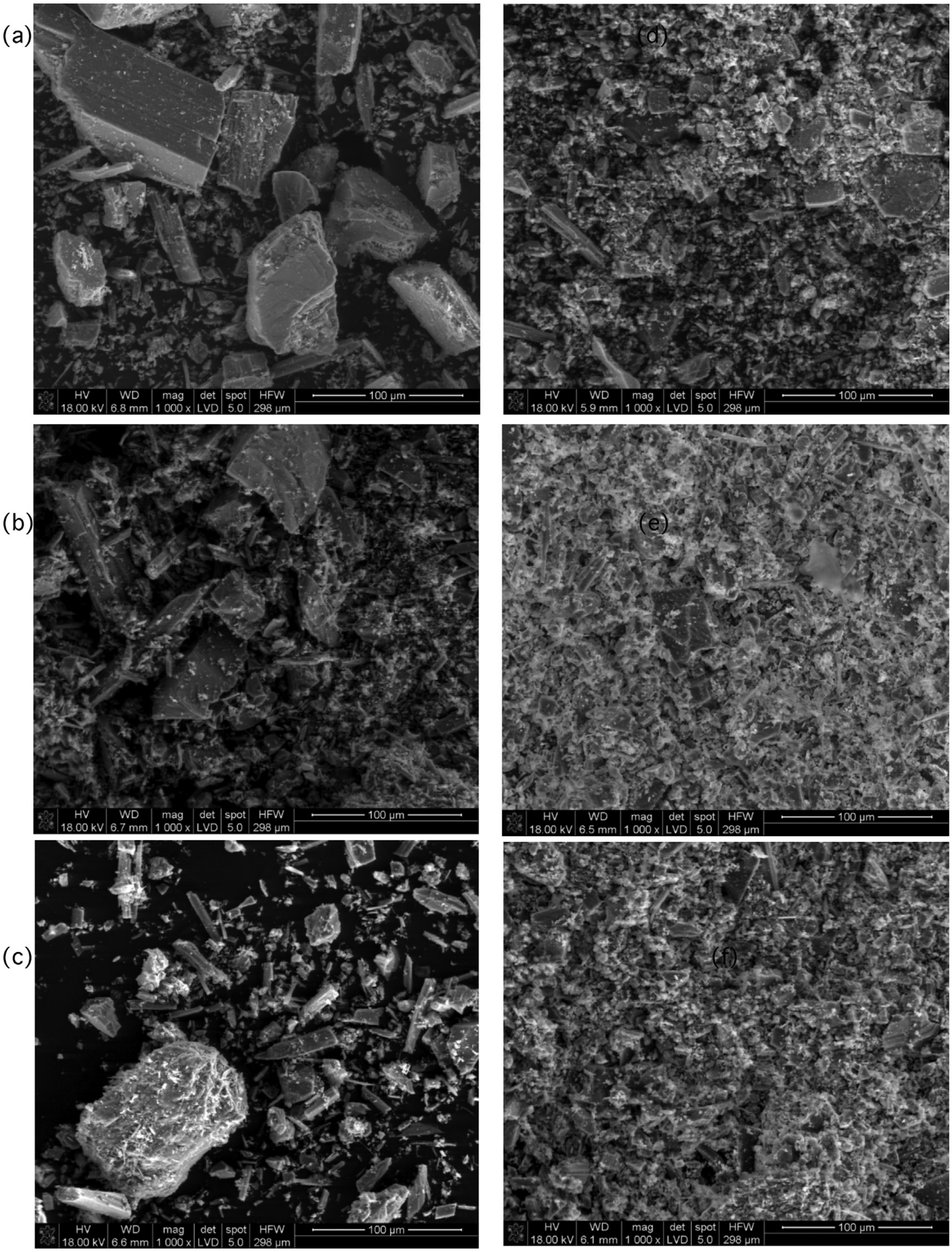

Fig. 1. SEM pictures of initial FS (a), modified FS with NaCl (b) and modified FS with MPW (c), initial FF (d), modified FF with NaCl (e) and modified FF with MPW (f).

Gupta et al., 2011; Oliveira et al., 2007; Wan Ngah et al., 2011; Zhang and Itoh, 2003). A number of AMD techniques of neutralization and recovery of toxic metal ions have been used, primarily including solid materials such as lime (Silveira et al., 2009) and limestone sand (Watten et al., 2005), fly ash (Gitari et al., 2008), natural clinker (Ríos et al., 2008), alkaline paper mill (Castillo et al., 2010) and lignite (Mohan and Chander, 2006). The above studies have shown good potential for the use of solid wastes as adsorbents for wastewater treatment. Some investigations (Repo et al., 2011; Yoğurtcuoğlu and Uçurum, 2011; Argun and Dursun, 2008; Zhao et al., 2013) showed that solid wastes are more efficient as adsorbents if pre-modified. For example, amino-polycarboxylic acids have been immobilized on solids to enhance their adsorption capacity (Repo et al., 2013). Modification method should be simple and inexpensive.

Limestones have been studied extensively as neutralizers for AMD and they are used mainly in passive wastewater treatment (Watten et al., 2005; Sibrell et al., 2006; Aziz et al., 2008; Strosnider and Nairn, 2010; Silva et al., 2012). In previous study, two limestones, FS and FF were investigated for purification of sulphates and chlorides from mining process water (MPW) (Iakovleva et al., 2015). In this study, MPW was used as a reagent for modifying of FS and FF the surface area. Three challenges were addressed; (1) AMD neutralization, (2) metal ions removal and (3) reuse of solid wastes using two solid wastes from limestone industry of Nordkalk Corporation (Finland).[1] Nordkalk produces limestone products, which are used, for example, for soil improvement in order to neutralize acidity. The products are used mainly in the paper, steel and building materials industries as well as in environmental care and agriculture (Nordkalk.com). Toxic metals, such as iron, copper, zinc and nickel, were chosen as targets metals since they can be found in mine wastewaters in large quantities. These metals are commonly present in substantial amounts in AMD and pose a serious threat to the environment and human health (Kemp et al., 2010). Moreover, if iron and copper ions can be removed from solution by precipitation, removal of nickel is much more complex task (Aziz et al., 2008; Sdiri et al., 2012; Alcolea et al., 2012). Electrochemical methods are most frequently used for the removal of nickel from solutions (Curteanu et al., 2011; Gao et al., 2007). The objective of this work was to find the least expensive way to purify water from metal ions specified above.The aim of this study was to investigate the performance of limestones for simultaneously AMD neutralization and the removal of Zn (II), Fe (III), Cu (II), Ni (II). Effect of competing ions on the adsorption process was studied. Removal of Cu (II), Zn (II), Fe (III), Ni (II) from real mine water was tested as well.

2. Materials and methods

2.1. Characterization of adsorbents

The particle size distribution and zeta potential of the samples were determined using dispersion analyzer LUMiSizer 610/611 (GmbH) and ZetaSizer Nano ZS, Malvern, UK, respectively. The zeta potential was calculated from electrophoretic mobility measurements using the Schmalukowski equation. A 1.5 g solid sample was conditioned in 50 mL of 0.001 M NaCl solutions at various final pHs for 24 h in a shaking bath. Each reported point value was an average of approximately 20 measurements. The pH of the suspension was adjusted using 0.01–1.0 M HCl. All solutions were prepared using ultrapure water. The pH of solutions was determined with a pH Electrode SenTix 81.

Table 1
Chemical composition of adsorbents (XRF and XRD analysis), RSDs at 3 times the detection limit were less than 10%.

Chemical composition, %	Commercial names of materials	
	FF	FS
Al	0.8	0.2
As	0.002	0.007
Ca	37.2	21.3
Cr	0.004	0.003
Cu	0.002	0.002
Fe	0.43	1.07
K	0.24	0.25
Mn	0.01	0.022
Ni	0.01	0.01
S	0.10	0.10
Si	10.3	42
Zn	0.002	0.006
Compounds formula	$(K,H_3O)Al_2Si_3AlO_{10}(OH)_2$ $CaSiO_3$	$CaMgSi_2O_6$ $CaCO_3$ $(K,H_3O)Al_2Si_3AlO_{10}(OH)_2$
Compounds name	Illite Parawollastonite	Diopside Calcite

The samples were characterized with nitrogen sorption at 196 °C using TriStar 3000 (Micromeritics Inc. USA). The specific surface area of samples was calculated using the Brunauer–Emmett–Teller (BET) theory.

FTIR spectra of adsorbents were recorded with a Bruker Vertex 70v spectrometer. Spectra were collected in the mid infrared region (4000–400 cm^{-1}) averaging 124 scans with 4 cm^{-1} resolution. Samples were prepared by the standard KBr pellets methods.

Microstructure of the produced materials was examined using of scanning electron microscope (SEM, Nova Nano SEM 200, FEI Company) with attached chemical analysis of specimen in microareas with energy dispersive X-ray spectroscopy (EDX, EDAX). The experiment was carried out at low vacuum condition in secondary electron mode. For the analysis samples were covered with a gold layer.

XRD data was collected with a PANalytical Empyrean powder diffractometer using Cu $K\alpha$ radiation. The configuration was a standard Bragg–Brentano (Θ/Θ) reflection setup with a Ni-filter placed prior to the detector. The measurements were performed between Θ scanning range of 3–90° with a 0.007° step size and the 69 s of measurement time for each step under ambient temperature and pressure.

2.2. Materials

Two limestones, FS and FF used in this study, were obtained from Nordkalk Corporation (Finland). Both materials are commercially used for pH increasing (from 1.5 to 9). Synthetic AMD solutions of Fe (II), Cu (II), Zn (II) and Ni (II) were prepared from analytical grade $Fe_2(SO_4)_3{\cdot}5H_2O$, $CuSO_4{\cdot}5H_2O$, $ZnSO_4{\cdot}H_2O$ and $NiSO_4{\cdot}6H_2O$, respectively (obtained from Merck). The required metal concentration was 100 mg L^{-1}. Real AMD were obtained from a sulfide mine in Finland from three depths (270, 500 and 720 m). Their compositions were tested with Inductively Compled Plasma Optical Emission Spectrometry (ICP-OES) spectrometer iCAP 6000 Series, Thermo (UK), with the detection limits for copper, zinc, iron and nickel at 0.4 ppb, 0.2 ppb, 0.1 ppb and 0.5 ppb, respectively. Cu was analyzed at 324.7 nm, Zn at 202.5 nm, Ni at 231.6 nm and Fe at 259.9 nm. MPW for surface area modification of adsorbents was obtained from Norilsk Nickel Harjavalta. MPW is process water from nickel chemical production after raw purification with diluted sodium sulfate solution. Then metal ions were precipitated using soda ash and caustic soda (Na_2CO_3 and NaOH).

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[1] Nordkalk.com, http://www.nordkalk.com/mine.

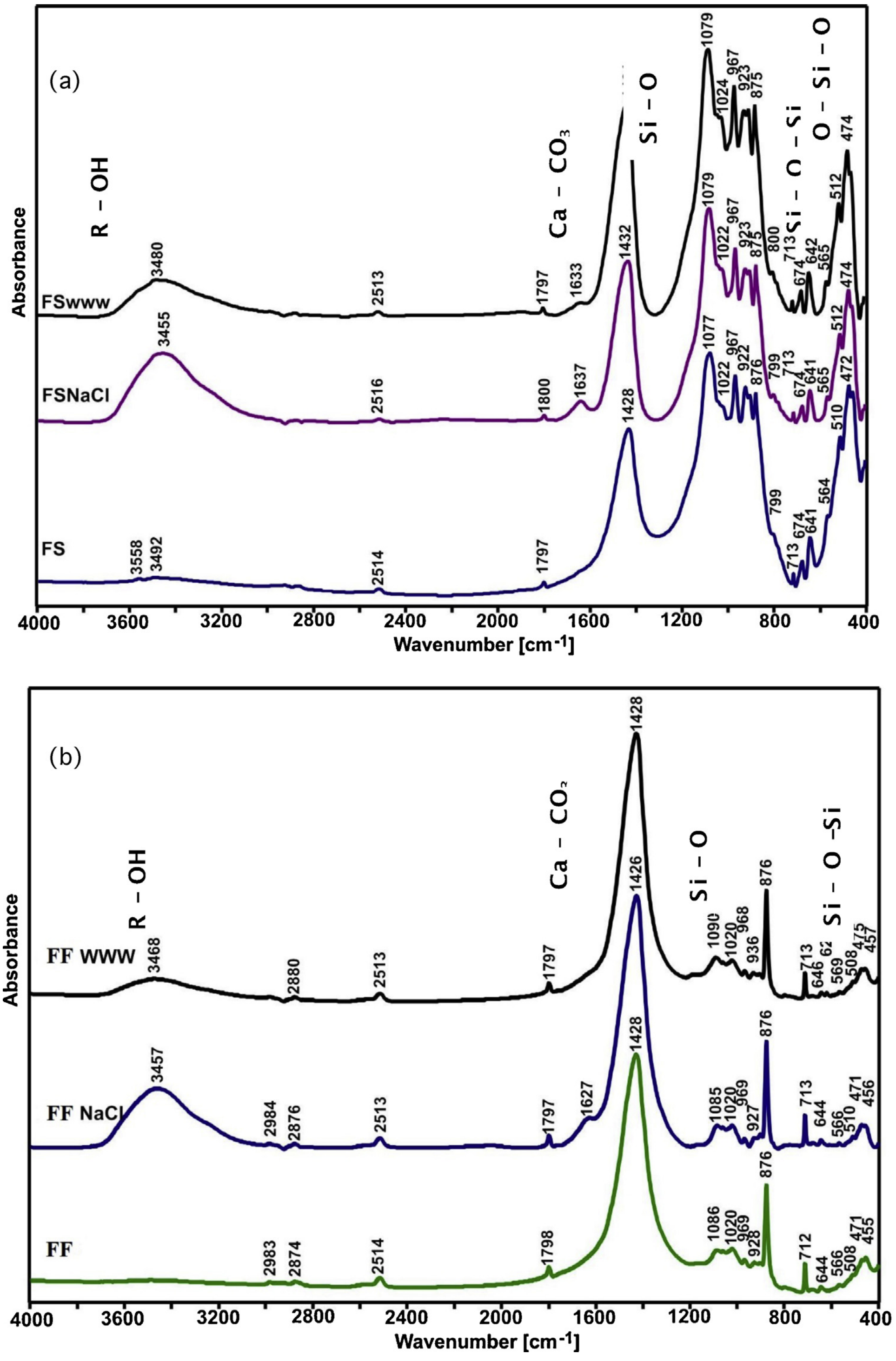

Fig. 2. MIR analysis of unmodified and modified FS (a) and FF (b).

2.3. Modification of adsorbents

To improve adsorption properties of the limestones, two modification methods were suggested. The first one with 2 M solution of NaCl and the second one with MPW from Norilsk Nickel Harjavalta. New modified adsorbents are (FS_NaCl, FS_ww, FF_NaCl and FF_ww). 100 g FS and FF were placed in 1 L of 2 M NaCl solution or 1 L alkaline MPW and then stirred at ambient temperature for 12 h. After preparation, the reaction mixtures were filtered and washed with distilled water and the modified adsorbents were oven-dried for 12 h at 80 °C. The dried adsorbents were stored in glass flasks.

2.4. Batch sorption

Batch adsorption tests were conducted by mixing known weight of FS and FF with 50 mL of synthetic and real AMD solution of known metal ions concentration. Metal ions concentrations in model solution were in range of 10–300 mg L^{-1}. The mixture was

Table 2
The particle size distribution, specific surface area and zeta-potential results of adsorbents.

	The particle size distribution, ηm					Specific surface area, $m^2\,g^{-1}$	zeta-potential, mV pH 11
	<90%	<75%	<50%	<25%	<10%		
FS	451	420	318	228	156	1.35	0
FS_NaCl	589	568	450	282	270	1.46	−15
FS_ww	273	134	131	91	90	1.29	−6
FF	599	567	354	185	177	1.82	−25
FF_NaCl	872	798	535	494	487	1.63	−20
FF_ww	492	421	188	87	88	1.58	−6

Table 3
Elemental composition of mining water from copper mine of Finland and process water (MPW) from Norilsc Nickel Harjavalta, RSDs at 3 times the detection limit were less than 3%.

	pH	Cu(II), ppm	Ni(II), ppm	Zn(II), ppm	Fe(III), ppm	Cl^-, ppm	Na^+, ppm
Level 270	2.6	108	13	2080	911	–	–
Level 500	2.3	76	1.7	5900	3400	–	–
Level 720	3.2	4.4	0.3	242	52	–	–
NorNikel	12	0.11	2.13	0.18	0.60	954	11570

shaked in a mechanical shaker ST5 (CAT M.Zipper GmbH, Staufen, Germany) from 30 min to 72 h, and 10 mL samples of the solution were taken from the flasks at known time intervals and then filtered, using 0.20 μm diameter polypropylene syringe filter. The temporal evolution of the solution pH was monitored.

The experiments were conducted to observe the effect of competitive metal ions by mixing model solutions containing Cu (II), Zn (II), Ni (II) and Fe (III). The final concentration of the pollutant ions in the aqueous phase then was determined by ICP-OES. The percentage adsorption (%) was calculated as

$$\%\text{Adsorption} = \frac{(C_i - C_t)}{C_i} \times 100 \tag{5}$$

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

2.4.1. Kinetic study

Amount of adsorbents was 40 g L^{-1} in a constant volume (50 mL) of synthetic solutions containing the different metal ions (Cu(II), Fe(III), Ni(II) and Zn(II)) with concentration of 20 ppm and 200 ppm. The agitation time was varied from 1 to 72 h. The sorption experiments were carried out in triplicate in order to observe the reproducibility of the results, and the mean value was used. In each case the standard deviation between the triplicate experiments was about ±5%.

2.4.2. Effect of solution pH

Effect of initial solution pH on adsorption was determined by mixing 0.8 g of adsorbent with 20 mL of Zn (II), Cu (II), Ni (II) and Fe (III) solutions with the concentration of 200 mg L^{-1} and multi element solution of 20 mg L^{-1} for each component at various pH values ranging from 1.5 to 9. Solution pH was adjusted with 1 M, NaOH and HCl solutions. The mixture was shaken for 48 h then the solution was filtered and analysed.

2.4.3. Neutralization of AMD

pH was monitored during the adsorption process (50 mL of solution was contacted with 2.5 g of all materials for 72 h).

3. Results and discussion

3.1. Adsorbents composition and characterization

The Fig. 1 shows the SEM pictures of original and modified adsorbents. Original surface has sufficiently pronounced crystalline structure of the adsorbents with different particle sizes. Surface modified adsorbents are more smooth and porous.

Chemical composition of studied materials is shown in Table 1. These results were obtained by XRF and XRD. Materials under investigation were found to have similar structure. The predominant exchangeable cations were found to be Ca and Si for both potential adsorbents. All chemical compounds similar in structure to calcite, jarosite, kaolite, diopside, illite, wollastonite and gypsum should have high adsorptive properties.

Spectroscopic studies in the Mid-infrared (MIR) (Fig. 2) confirm the results of XRD studies. The system of bands in each sample is characteristic for calcite (bands 1428 cm^{-1}, 875 cm^{-1}, and 713 cm^{-1}) and diopside (1077–1079 cm^{-1}, 1022–1024 cm^{-1}, 967 cm^{-1}, 922 cm^{-1}, 641–646 cm^{-1}, and 474–475 cm^{-1}). The difference is only in the proportions of these bands. Spectrum of

Table 4
Comparison of of the adsorption efficients on unmodified and modified adsorbents at room temperature.

Adsorbent	Metal	Contact time	pH	q_m (mmol g^{-1})	Removal, %
FF	Fe	5	4.5	3.4	98
	Cu	12	8	3.0	99
	Zn	12	8	2.5	80
	Ni	8	6	1.2	35
FF_NaCl	Fe	4	4	3.5	99
	Cu	8	6	3.1	99
	Zn	8	6	3.0	98
	Ni	12	8	3.3	97
FF_ww	Fe	4	4	3.5	99
	Cu	8	6	3.1	99
	Zn	8	6	3.0	98
	Ni	12	8	3.3	97
FS	Fe	8	6	3.1	87
	Cu	12	7	3.0	98
	Zn	24	7.5	2.4	78
	Ni	12	7	0.7	20
FS_NaCl	Fe	8	6	3.5	98
	Cu	12	7	3.0	98
	Zn	12	7	3.0	97
	Ni	8	6	3.2	96
FS_ww	Fe	8	6	3.5	98
	Cu	12	7	3.1	99
	Zn	12	7	3.1	97
	Ni	8	6	3.3	97

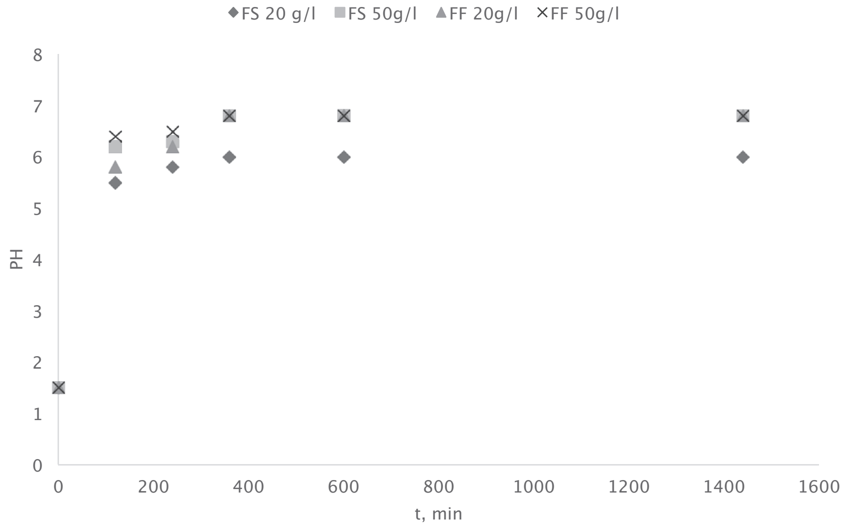

Fig. 3. Neutralization of AMD by FS and FF with concentration of 20 and 50 g/L in 24 h.

modified limestones indicate the presence of small amounts of hydroxyl groups (bands at 3558 and 3492 cm^{-1}), possibly a layered silicate or other silicate containing hydroxyl group (Yang et al., 2008). The comparison between initial and modified adsorbents shows that a new adsorption band around 3480–3455 cm^{-1} appears as a result of new hydroxide groups. It may be due to the introduction of sodium cation onto the structure of adsorbents surface in the form of sodium hydroxide.

The particle size distribution and specific surface area results of the original and modified materials are shown in Table 2. The surface areas of both adsorbents and their modified forms are approximately the same.

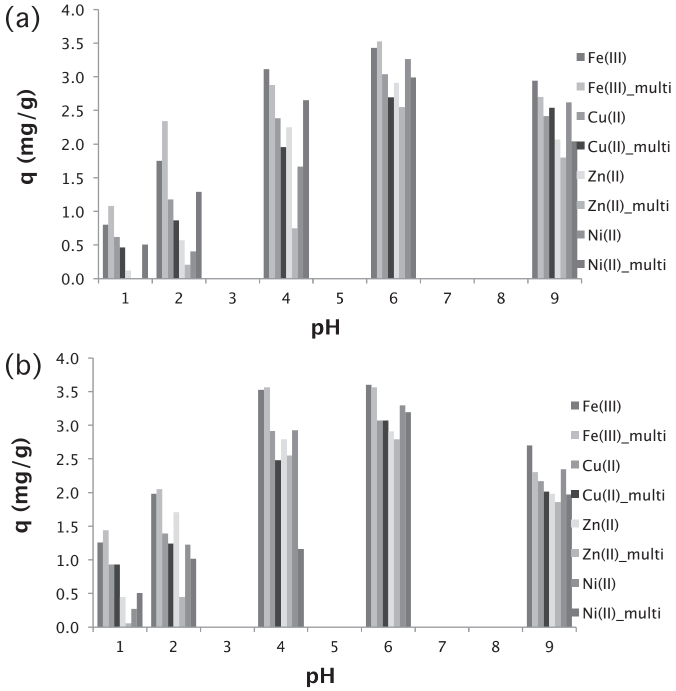

Fig. 4. Effect of pH on removal efficiency of Fe(III), Cu(II), Zn(II) and Ni(II) from single and multi ions solutions with FS_NaCl (a) and FF_NaCl (b). Initial concentration of metal ions in single and multi component solution is 20 ppm, dose of sorbent is 40 g L^{-1}.

Modification of FF and FS with 2 M NaCl solution resulting in increase and homogenization of the adsorbent particle size (Table 2). Despite the fact that the particle size increased, the surface area had not grown most probably due to the crystal structure of sodium chloride. Modification of FS and FF with MPW decreases and homogenizes the particle size of adsorbents. This may be due to the fact that MPW has a corrosive environment and during the modifications process, the expansion of the adsorbent surface may occur, which also leads to particle size reducing. The results for surface area of unmodified and modified adsorbents also confirm the change of the surface structure.

Zeta potential of each adsorbent does not exceed the value ±30 and was approximately −15 mV for FS, and −25 mV for FF. The zeta potential of the adsorbents tested in water is shown in Table 2. Furthermore, FF particles show slightly more negative zeta potential value compared to FS particles. If the zeta potential is low, attraction exceeds repulsion and the dispersion stability is violated. Thus, the colloids with high zeta potential are electrically stable, while colloids having low zeta potential tend to coagulate or flocculate (Viallis-Terrisse et al., 2001).

3.2. Sorbents modification

The contents of calcium and silicates in adsorbents were 20–35%. Thus, one can assume that suitable modification techniques should be similar to those used for calcite and silicates modification. Widely used, calcite and silicate modification techniques are not simple and cheap (Yoğurtcuoğlu and Uçurum, 2011; Gomari et al., 2006; Yuan et al., 2008). Based on the analysis of the surface area of the adsorbents the original calcite surface was smooth. To increase the surface area we tried to cover the adsorbent with a salt layer. This increases the surface area, as well as the number of functional groups to participate in ion exchange process. As an affordable modification method, sodium chloride treatment was chosen. Modification of materials with NaCl markedly improved the removal of nickel and zinc from the modeling solution. As alkaline matrix and high chloride ion content seem to be promising as the second approach for adsorbents modification, we decided to study MPW from Norilsk Nickel Harjavalta. Elemental composition of MPW and their pH are shown in Table 3. The concentration of chloride ions in this water is sufficient for the surface modification of calcite. The experimental

Table 5
Pseudo-first- and pseudo-second-order kinetic parameters for metal ions adsorption on FS and FF modified with NaCl.

		C_o ($\text{mmol}\,\text{L}^{-1}$)	$q_{e\ \exp}$ ($\text{mmol}\,\text{g}^{-1}$)		q_e ($\text{mmol}\,\text{g}^{-1}$)		K_2 (g mmol/min)		R^2	
			Pseudo-first-order	Pseudo-second-order	Pseudo-first-order	Pseudo-second-order	Pseudo-first-order	Pseudo-second-order	Pseudo-first-order	Pseudo-second-order
FS_NaCl	Cu (II)	0.22	0.058	0.057	0.049	0.064	1	0.28	0.23	0.97
	Zn (II)	0.99	0.039	0.042	0.039	0.044	1	1.15	0.74	0.98
	Ni (II)	0.71	0.048	0.054	0.048	0.06	1	0.37	0.68	0.92
	Fe (III)	0.053	0.075	0.086	0.075	0.096	1	0.19	0.6	0.98
FF_NaCl	Cu (II)	0.61	0.035	0.035	0.044	0.091	1	0.025	0.1	0.98
	Zn (II)	0.84	0.035	0.041	0.035	0.048	1	0.245	0.1	0.94
	Ni (II)	0.13	0.052	0.052	0.061	0.069	1	0.216	0.28	0.97
	Fe (III)	0.004	0.067	0.082	0.067	0.104	1	0.077	0.32	0.98

data showed that the best result was observed with adsorbent modified with NaCl, however, materials modified with MPW showed good adsorption capacity as well (Tab. 4). Removal of Ni(II) increase from 20 and 35% to 97% with modified FF and FS adsorbents, respectively. Use of such adsorbents modified with process water would solve several problems at the same time – modifications of adsorbents, purification of process water from the alkaline chlorides, as well as subsequent use of adsorbents with improved properties for metals removal and neutralization of AMD.

3.3. Selection of optimal conditions for AMD treatment

Neutralization of AMD and metal ions removal were studied by varying contact time of solution with adsorbents, adsorbents dosage and metal ion concentration.

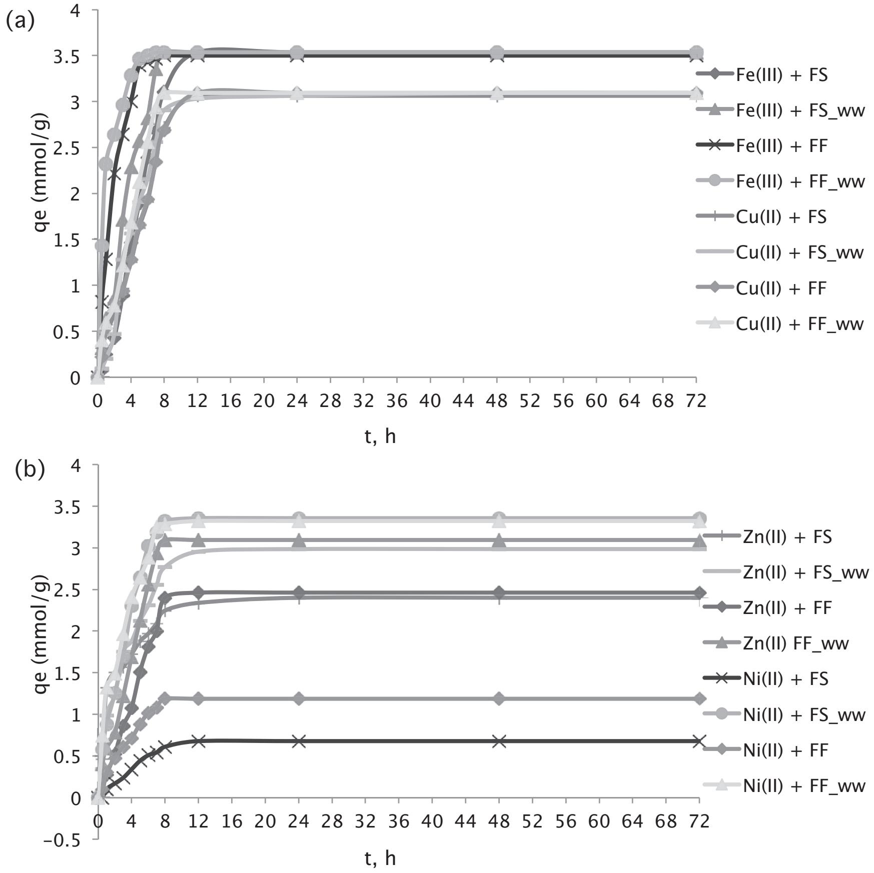

Fig. 5. Kinetic of Fe(III) and Cu(II) (a), Zn(II) and Ni(II) (b) adsorption with unmodified and modified FS and FF.

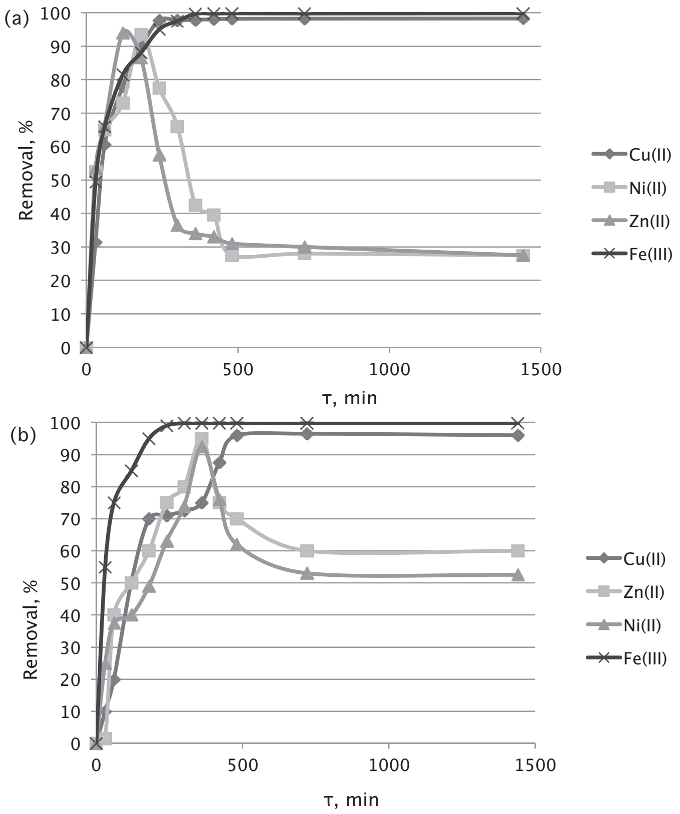

Fig. 6. Removal of copper, zinc, nickel and iron by modified FS with NaCl (a) and modified FF with NaCl (b) from multielement model solution with concentration of ions 0.3125 mmol L^{-1}, 0.3058 mmol L^{-1}, 0.3389 mmol L^{-1} and 0.3571 mmol L^{-1}, respectively.

3.3.1. Neutralization of AMD

Neutralization of AMD is generally the first step in mine water treatment. The acidity reduction properties of FS and FF were tested by batch method showing solution pH increased from 1.5 to 6.8 within 72 h. The results are presented in Fig. 3. FF and FS reduce the acidity of AMD fast. The increase of the initial pH (1.5) of the AMD occurred on contact with FS (20 and 50 g L^{-1}) and FF (20 and 50 g L^{-1}). After 2 h of shaking by the batch method, the pH reached 5.0–6.5. The reaction rates decrease as equilibrium was reached. The pH increase is the result of the progressive dissolution of the sorbent during the shaking process. The pH was stabilized after 6 h whereas the same time (6 h) was required using the modified materials as adsorbents for the metal ions removal. The final pH was 6.8, indicating that effective neutralization of AMD took place.

3.3.2. Effect of pH

pH is an important parameter in the sorption process optimization, since it affects not only the surface charge of adsorbents, but also the degree of ionization of the metal ions in solution. The effect of the initial pH of Cu (II), Ni (II), Fe (III) and Zn (II) solutions on the amount adsorbed was studied by varying the initial pH from 1.5 to 9, under constant temperature (Fig. 4). Maximum adsorption efficiency was achieved at pH 5–6 for each metal. At higher pHs the sorption capacity values decrease due to precipitation of hydroxide complexes especially for Zn (II) and Fe (III), and reduction in q_e value was observed at higher pHs (Sdiri et al., 2012). Initial pH of solution significantly affected adsorption characteristics of FF_NaCl and FS_NaCl, and removal of Cu (II), Ni (II), Fe (III) and Zn (II) was at maximum level in neutral solution. For example, in case of Cu (II) and Ni (II) sorption by FS the desorption of metal ions increased at the pH above 6. In multi ions solutions similar pattern was observed for FS_NaCl and FF_NaCl adsorbent (Fig. 4).

It seems that ion desorption takes place due to supersaturation of the solution. While as the part of ions precipitated and other of ions remain in solution. Ions partially precipitate and partially remain in the solution. Various researchers have also reported that the mechanism of sorption and precipitation depends on characteristic reactions of metals with calcite. Adsorption is occurring at metals concentrations lower than 2 mg L^{-1}, while at higher concentrations precipitation is dominating (Aziz et al., 2008; Sdiri et al., 2012; Alcolea et al., 2012; Macias et al., 2012).

3.3.3. Kinetic studies

The optimum dosage of the adsorbents for the best removal of most metals from model solutions was 40 g L^{-1}. The equilibrium occurs at 8 h at the concentration of 200 ppm. The results of the kinetic experiments of metals adsorption from synthetic solutions onto different adsorbents are shown in Table 5 and Fig. 5. Kinetics was studied using pseudo-first- (Eq. (6)) and second-order models (Eq. (7)).

The pseudo-first-order model is associated with the kinetics of one-site adsorption governed by the rate of the surface reaction. The equation is given as:

$$\frac{dq}{dt} = k_1(q_e - q) \qquad (6)$$

The pseudo-second-order model, which assumes that the adsorption process is governed by the surface reaction, has the form:

$$\frac{dq}{dt} = k_2(q_e - q)^2 \qquad (7)$$

where q_t and q_e (mmol g^{-1}) represent the amount of metals adsorbed at time t (min) and at equilibrium, respectively, and k_2 is the pseudo-second-order rate constant.

The adsorption process of metals from liquids was described best with the pseudo-second-order model. This model suggests that the system includes the formation of at least two compounds, or is a multi-component system with a complex compound of adsorbent with adsorbate.

3.3.4. Equilibrium study with adsorption isotherms

Removing metals from single metal solutions and the mixture was also conducted. Fig. 5 and Table 4 show that the modified adsorbents, FF_ww, FF_NaCl, FS_ww and FS_NaCl, have better adsorption properties for metals. Nickel and zinc are hardly removed with unmodified adsorbents. Apparently, this is due to the fact that the surface of unmodified adsorbent has a low affinity to these ions.

Study of multiple metal solution (Figs. 4 and 6) also shows that the best degree of removal takes place on modified materials, than on unmodified adsorbents. During the first six hours removal of all four metal ions is observed. Then desorption of Ni (II) and Zn (II) into the solution taces place. After approximately 12 h the equilibrium is observed in the system. Both adsorbents have exhibited greater affinities to iron and copper ions. While strong bonds are formed on the surface area of the adsorbents due to iron and copper ions, bonds of zinc and nickel ions with the adsorbent surface are weakened, and Zn (II) and Ni (II) desorb into solution. The desorption of zinc and nickel ions might be associated with supersaturation of solution, as is observed above. Apparently, iron and copper ions formed more stable complexes, than zinc and nickel ions. The same pattern was observed by other researchers (Aziz et al., 2008; Sdiri et al., 2012; Alcolea et al., 2012).

Adsorption capacity, equilibrium concentration of the adsorbate and affinity of adsorbates to adsorbents were fitted with the Langmuir (Eq. (8)), Sips (Eq. (9)) and Toth (Eq. (10)) adsorption

Table 6
Isotherm parameters for FS_NaCl and FF_NaCl during adsorption process of metal ions from model solution.

		C_o(mmol L^{-1})	$q_{m\ exp}$(mmol g^{-1})	q(mmol g^{-1})	K_L(L/mmol)	R^2
Langmuir model						
FS_NaCl	Cu (II)	0.068	0.391	0.066	472	0.895
	Zn (II)	0.068	0.391	0.076	19	0.905
	Ni (II)	0.038	1.864	0.043	8.26	0.968
	Fe (III)	0.089	8.9×10^{-4}	0.13	3010	0.969
FF_NaCl	Cu (II)	0.071	0.004	0.083	745	0.977
	Zn (II)	0.119	0.033	0.247	15	0.931
	Ni (II)	0.075	0.366	0.107	3.52	0.985
	Fe (III)	0.006	0.089	0.17	203	0.944

		C_o(mmol L^{-1})	$q_{m\ exp}$(mmol g^{-1})	q(mmol g^{-1})	n	K(L/mmol)	R^2
Sips model							
FS_NaCl	Cu (II)	0.068	0.391	0.129	0.246	1.972	0.988
	Zn (II)	0.068	0.391	0.073	1.062	21	0.907
	Ni (II)	0.038	1.864	0.06	0.52	1.744	0.988
	Fe (III)	0.089	8.9×10^{-4}	0.131	1.01	3052	0.969
FF_NaCl	Cu (II)	0.071	0.004	0.078	1.217	886	0.937
	Zn (II)	0.119	0.033	0.129	4.298	44	0.846
	Ni (II)	0.075	0.366	0.089	1.874	5.313	0.951
	Fe (III)	0.006	0.089	0.183	0.913	164	0.940

		C_o (mmol L^{-1})	$q_{m\ exp}$ (mmol g^{-1})	q_m (mmol g^{-1})	a_T	m_T (L/mmol)	R^2
Toth model							
FS_NaCl	Cu (II)	0.068	0.391	0.066	0.002	0.985	0.914
	Zn (II)	0.068	0.391	0.076	0.052	1.028	0.903
	Ni (II)	0.038	1.864	0.067	0.242	1.264	0.845
	Fe (III)	0.089	8.9×10^{-4}	0.506	0.03×10^{-2}	3.766	0.372
FF_NaCl	Cu (II)	0.071	0.004	0.055	0.001	1.136	0.953
	Zn (II)	0.119	0.033	0.03×10^{-2}	2.7×10^{-5}	4.189	0.967
	Ni (II)	0.075	0.366	0.548	1.005	2.419	0.92
	Fe (III)	0.006	0.089	–	–	–	–

isotherms for modified adsorbents (FS_NaCl and FF_NaCl). Coefficients of sorption isotherms equations and graphs of the adsorption isotherms are showed in Table 6.

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{8}$$

$$q_e = \frac{q_m (K_S C_e)^{n_S}}{1 + (K_S C_e)^{n_S}} \tag{9}$$

$$q_e = \frac{q_m c_e}{(a_t + C_e^{m_t})^{1/mT}} \tag{10}$$

where q_e and C_e are sorption capacity (mmol g^{-1}) and concentration of metal ions in the solution (mmol L^{-1}) at equilibrium, respectively; q_m is the maximum uptake capacity; K_L and K_S are Langmuir and Sips constants related to the energy of sorption, respectively; n_s is coefficient of Simps isotherm describes the surface heterogeneity; a_t is the adsorptive potential constant (mmol L^{-1}) and m_T the heterogeneity factor of the Toth isotherm.

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

Langmuir adsorption model allows us to describe the sorption of substances in a single homogeneous layer of sorbent with finite number of active binding sites. The coefficient q_e, that reflects the amount of sorption sites in the sorbent molecule that actively interact with sorbate, and the coefficient K, which indicates the degree of affinity between the sorbate and sorbent, can be calculated with Langmuir model. Affinity shows the increasing degrees for metal ions to the surface of the adsorbent on the basis of coefficient K values as follows:

FS: Ni(II) < Zn(II) < Cu(II) < Fe(III)

FF: Ni(II) < Zn(II) < Fe(III) < Cu(II)

Both adsorbents show less affinity for nickel and zinc ions. It was difficult to find a suitable model of adsorption isotherm for adsorption process description. Apparently, this is due to the heterogeneous structure of adsorbents, alongside with their complex structure. Some of the isotherms fit the description of the rare cases of adsorption system presented in literature (Erkey, 2011).

The Toth isotherm is an empirical equation, which was derived to improve the Langmuir model fittings at both low and high concentrations. The Toth model assumes an asymmetrical quasi-Gaussian energy distribution and is useful in the cases of heterogeneous adsorption. These models were used to describe the adsorption on FF and FS. It was found that Toth model was inappropriate to describe iron adsorption process on FF. The Sips isotherm is a combination of the Langmuir and Freundlich isotherms and can be derived using either equilibrium or thermodynamic approach and was used to describe of FF and FS adsorbents.

Correlation coefficients (R^2) were calculated to estimate the relevant patterns and are given in Table 6. The R^2 values of the isotherms described by Langmuir, Sips and Toth models are relatively close. However, it can be concluded that Toth model is better for FS and Sips model for FF, both involving the sorption on a

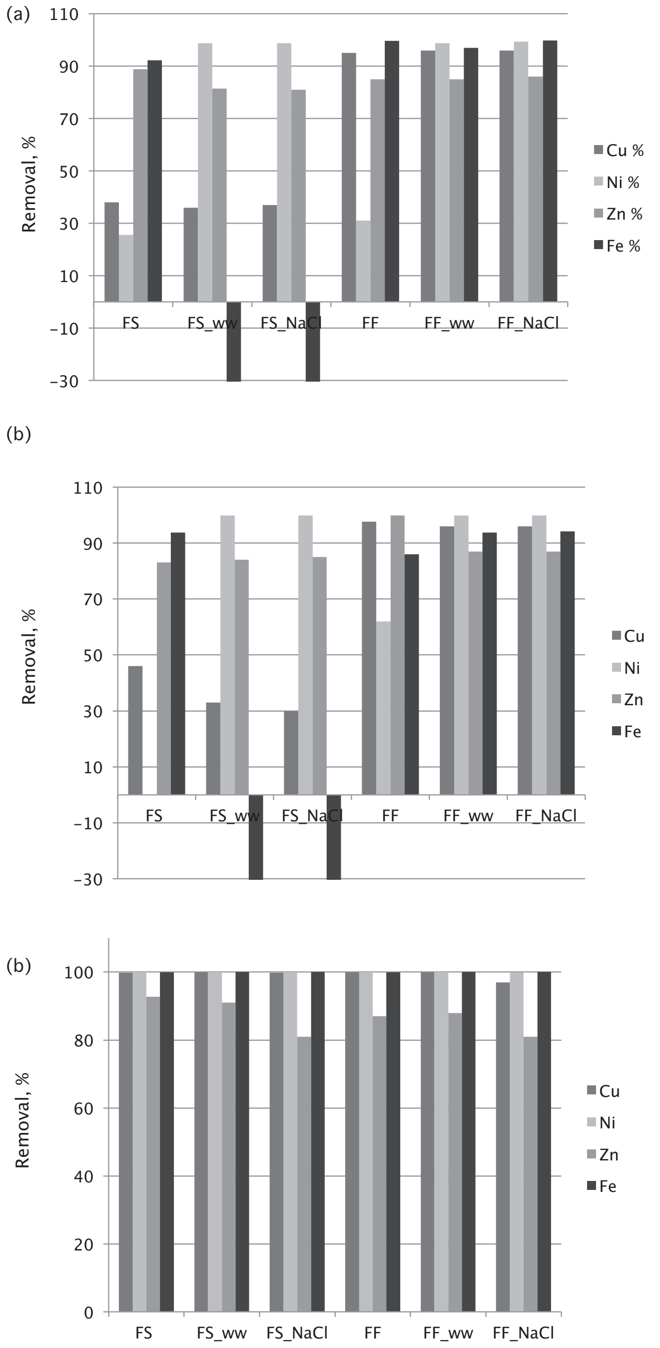

Fig. 7. Mining water treatment with unmodified and modified FS and FF from different mining depths: (a) 270 m, (b) 500 m, (c) 720 m. Contact time is 24 h, agitation speed is 50 rpm.

heterogeneous surface. When the first active positions with lower energy are filled, a continuous variation of sorption energy occurs.

3.4. Mine water treatment

Mine water treatment is a very complex process and depends on several factors, such as waters matrices, composition and pH. In this study, waters from different mining depths were investigated. pH was 2.3–3.2 and the chemical composition is presented in Table 3. AMD neutralization and metal ions removal were studied. The experiments were carried out at ambient temperature for 12 h with 40 g L^{-1} unmodified and modified FS and FF. After 8 h pH increase to 6.5–6.8. Both unmodified and modified FFs shows better adsorption properties in mine waters treatment compared to FSs (Fig. 7). Unmodified FF showed good affinity for Zn and Fe in all waters and better affinity than FS for Cu in waters from 1st and 2nd depths. Desorption of Fe (III) for levels 1 and 2 on unmodified and modified FS was observed. Modified FF adsorbed nearly 100% of all metal ions (Zn (II), Fe (III), Cu (II) and Ni (II)).

3.5. Removal mechanism of metal ions

There are two mechanisms of metal ions removal from acidic solutions. These mechanisms are sorption, include complexation and ion-exchange mechanism (Aziz et al., 2008; Yuan et al., 2008; Aziz et al., 2004; Christensen et al., 2001; Martin et al., 2005; Miller et al., 2011) and precipitation (Watten et al., 2005; Wang et al., 2013; Allende et al., 2012; Miller et al., 2013). In these experiments, ion-exchange is much more likely than precipitation. Since, like most silicates, unmodified and modified FS and FF shows a negative surface charge at high pH (as given in Eqs. (11–13)) and it will be changed due to the adsorption of ions on to the surface. Dissociation equilibrium of silicate sites due to the pH increase is given in (Eq. (11)). Calcium ion should be exchanged with hydrogen ion and attached to the surface of the adsorbent to form a complex compound (Eq. (12)). Further interaction in solution leads to an ion exchange between calcium and metal ion, while pH of the solution increased (Eq. (13)).

$$\equiv \mathrm{SiOH} \leftrightarrow \mathrm{SiO}^{-} + \mathrm{H}^{+} \tag{11}$$

$$\equiv \mathrm{SiOH} + \mathrm{Ca}^{2+} \leftrightarrow = \mathrm{SiOCa} + \mathrm{H}^{+} \tag{12}$$

$$= \mathrm{SiOCa} + \mathrm{M}^{e+} + 2\mathrm{HOH} \rightarrow = \mathrm{SiOM} + \mathrm{Ca}^{+} + 2\mathrm{OH}^{-} \tag{13}$$

Iron compounds, such as oxides and hydroxides are known to be effective sorbents for various ion metals (Iakovleva and Sillanpää, 2013), including nickel and zinc. Since iron is a component of FF and FS materials, nickel and zinc could be removed by complexation of these ions with iron compounds onto surface area of sorbents.

During removal of ion metals from multicomponent solutions, the removal of zinc and nickel increased to approximately 10% in comparison to single component solution. It could be because some of iron precipitated and secondary metal removal could be observed. Major mechanism of secondary metal removal is adsorption and co-precipitation with newly formed iron compound particulates. After treatment of multicomponent system, the color of adsorbents was changed from white to dirty yellow, that also could indicate a certain level of iron precipitation as hydroxide. Precipitation of $Fe(OH)_3$ on the limestone particles was also observed by Wang et al. (2013).

Modified adsorbents removed nickel and zinc ions approximately four times more effective than unmodified ones (Fig. 5, Table 3). Possible explanation of these results is that the metal ions could create a surface complex, and the ternary complexation of nickel and zinc with carbonate or chloride were formed. For example complexation of nickel and zinc with carbonate was observed by Miller et al. (2011). However, in the next study, the same authors suggested the benefit of co-precipitation of these metals under the same conditions (Miller et al., 2013).Batch experiments show that the removal effectivity of nickel and zinc ions is heavily affected by presences the carbonates and chlorides on the surface area of modified adsorbents and somewhat by the iron content in solution. Therefore, besides an adsorption mechanism, co-precipitation of iron, zinc and nickel ions could be have place during the removal process of metals from acidic solutions.

4. Conclusions

Modification of limestones surface area by sodium chloride and process water with high content of chlorides, sodium hydroxide and sodium carbonate seems effective and inexpensive methods of modification.

It was found that unmodified and modified materials exhibit good adsorption properties for Zn (II), Fe (III), Cu (II). Both unmodified adsorbents were better to copper and iron, however FF can be used for removal of zinc and nickel as well. These adsorbents neutralized the solution acidic and changed pH from 1.5 to 6. Both limestones can be effectively used after modification as adsorbents for AMD treatment and removal of iron, cooper, zinc, and nickel as well. For industrial application of these adsorbents, further experiments in their selectivity to different kinds of pollutants, such as cations and anions are required. Preliminary experiments using the pilot plant are required.

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References

Abraitis, P.K., Pattrick, R.A.D., Vaughan, D.J., 2004. Variations in the compositional, textural and electrical properties of natural pyrite: a review. Int. J. Miner. Process. 74, 41–59.

Ahmaruzzaman, M., 2011. Industrial wastes as low-cost potential adsorbents for the treatment of wastewater laden with heavy metals. Adv. Colloid Interface Sci. 166, 36–59.

Akcil, A., Koldas, S., 2006. Acid mine drainage (AMD): causes, treatment and case studies. J. Clean. Prod. 14, 1139–1145.

Alcolea, A., Vazquez, M., Caparros, A., Ibarra, I., Garcia, C., Linares, C., Rodriguez, R., 2012. Heavy metal removal of intermittent acid mine drainage with an open limestone channel. Miner. Eng. 26, 86–98.

Allende, K.L., Fletcher, T.D., Sun, G., 2012. The effect of substrate media on the removal of arsenic, boron and iron from an acidic wastewater in planed column reactor. Chem. Eng. J. 179, 119–130.

Argun, M.E., Dursun, S., 2008. A new approach to modification of natural adsorbent for heavy metal adsorption. Bioresour. Techol. 99, 2516–2527.

Aziz, H.A., Adlan, M.N., Ariffin, K.S., 2008. Heavy metals (Cd, Pb, Zn, Ni, Cu and Cr(III)) removal from water in Malaysia: post treatment by high quality limestone. Bioresour. Techol. 99, 1578–1583.

Aziz, H.A., Yusoff, M.S., Adlan, M.N., Adnan, N.H., Alias, S., 2004. Physico-chemical removal of iron from semi-aerobic landfill leachate by limestone filter. Waste Manage. 24, 353–358.

Bhatnagar, A., Kaczala, F., Hogland, W., Marques, M., Paraskeva, C.A., Papadakis, V.G., Sillanpää, M., 2014. Valorization of solid waste products from olive oil industry as potential adsorbents for water pollution control—a review. Environ. Sci. Pollut. Res. 21, 268–298.

Castillo, P.-L., Quispe, D., Nieto, J.M., 2010. Neutralization of acid mine drainage using the final product from CO_2 emissions capture with alkaline paper mill waste. J. Hazard. Mater. 177, 762–772.

Chandra, A.P., Gerson, A.R., 2010. The mechanisms of pyrite oxidation and leaching: a fundamental perspective. Surf. Sci. Rep. 65, 293–315.

Charbonier, B., 2001. Management of Mining, Quarryng and Ore-processing Waste in the European Union. EU.

Christensen, T.H., Kjeldsen, P., Bjerg, H.J., Jensen, D.L., Chrestensen, J.B., Braun, A., Albrechsten, H.J., Heron, G., 2001. Biogeochemistry of landfill leachate plumes. Appl. Geochem. 16, 659–718.

Curteanu, S., Piuleac, C.G., Giodini, K., Azaryan, G., 2011. Modeling of electrolysid process in wastewater treatment using different types of neutral network. Chem. Eng. J. 172, 267–276.

Deditius, A.P., Utsunomiya, S., Reich, M., Kesler, S.E., Ewing, R.C., Hough, R., Walshe, J., 2011. Trace metal nanoparticles in pyrite. Ore Geol. Rev. 42, 32–46.

Erkey, C., 2011. Chapter 4 – thermodynamics and dynamics of adsorption of metal complexes on surfaces from supercritical solutions. Supercritical Fluid Science and Technology. Elsevier, pp. 41–77.

Gao, B., Yue, Q., Wang, Y., 2007. Coagulation performance of polyaluminum silicate chloride (PASiC) for water and wastewater treatment. Sep. Purif. Technol. 56, 225–230.

Gitari, W.M., Petrik, L.F., Etchebers, O., Key, D.L., Iwuoha, E., Okujeni, C., 2008. Passive neutralisation of acid mine drainage by fly ash and its derivatives: a column leaching study. Fuel 87, 1637–1650.

Gomari, K.A.R., Denoyel, R., Hamouda, A.A., 2006. Wettability of calcite and mica modified by different long-chain fatty acids (C18 acids). J. Colloid Interface Sci. 297, 470–479.

Gupta, V.K., Ganjali, M.R., Norouzi, P., 2011. Electrochemical analysis of some toxic metals by ion-selective electrodes. Critic. Rev. Anal. Chem. 41, 282–313.

Iakovleva, E., Mäkilä, E., Salonen, J., Sitartz, M., Sillanpää, M., 2015. Industrial products and wastes as adsorbents for sulphate and chloride removal from synthetic alkaline solution and mine process water. Chem. Eng. J. 259, 364–371.

Iakovleva, E., Sillanpää, M., 2013. The use of low-cost adsorbents for wastewater purification in mining industries. Environ. Sci. Pollut. Res. 20, 7878–7899.

Kemp, D., Bond, C.J., Franks, D.M., Cote, C., 2010. Mining, water and human rights: making the connection. J. Clean. Prod. 18, 1553–1562.

Macias, F., Caraballo, M.A., Nieto, J.M., Rötting, T.S., Ayora, C., 2012. Natural pretreatment and passive remediation of highly polluted acid mine drainage. J. Environ. Manage. 104, 93–100.

Martin, S., Zhu, C., Rule, J., Nuhfer, N.T., Ford, R., Hedges, S., Soong, Y., 2005. A high-resolution TEM-AEM, pH titration, and modeling study of Zn^{2+} coprecipitation with ferrihydrite. Geochim. Cosmochim. Acta 69, 1543–1553.

Miller, A., Figueroa, L., Wildeman, T., 2011. Sinc and nickel removal in simulated limestone treatment of mining influenced water. Appl. Geochem. 26, 125–132.

Miller, A., Wildeman, Th., Figuroa, L., 2013. Zinc and nickel removal in limestone based treatment of acid mine drainage: the relative role of adsorption and co-precipitation. Appl. Geochem. 37, 57–63.

Mohan, D., Chander, S., 2006. Removal and recovery of metal ions from acid mine drainage using lignite—a low cost sorbent. J. Hazard. Mater. 137, 1545–1553.

Oliveira, L.C.A., Goncalves, M., Oliveira, D.Q.L., Guerreiro, M.C., Guilherme, L.R.G., Dallago, R.M., 2007. Solid waste from leather industry as adsorbent of organic dyes in aqueous-medium. J. Hazard. Mater. 141, 344–347.

Repo, E., Petrus, E.R., Sillanpää, M., Warchoł, J.K., 2011. Equilibrium studies on the adsorption of Co(II) and Ni(II) by modified silica gels: one-component and binary systems. Chem. Eng. J. 172, 376–385.

Repo, E., Warchoł, J.K., Bhatnagar, A., Mudhoo, A., Sillanpää, M., 2013. Aminopolycarboxylic acid functionalized adsorbents for heavy metals removal from water. Water Res. 47, 4812–4832.

Ríos, C.A., Williams, C.D., Roberts, C.L., 2008. Removal of heavy metals from acid mine drainage (AMD) using coal fly ash, natural clinker and synthetic zeolites. J. Hazard. Mater. 156, 23–35.

Sdiri, A., Higashi, T., Jamoussi, F., Bouaziz, S., 2012. Effect of impurities on the removal of heavy metals by natural limestone in aqueous systems. J. Environ. Manage. 93, 245–253.

Sibrell, P.L., Watten, B.J., Haines, T.A., Spaulding, B.W., 2006. Limestone fluidized bed treatment of acid-impacted water at the Craig Brook National Fish Hatchery Maine, USA. Aquacult. Eng. 34, 61–71.

Silva, A.M., Lima, R.M.F., Leão, V.A., 2012. Mine water treatment with limestone for sulfate removal. J. Hazard. Mater. 221–222, 45–55.

Silveira, A.N., Silva, R., Rubio, J., 2009. Treatment of acid mine drainage (AMD) in South Brazil: comparative active processes and water reuse. Int. J. Miner. Process. 93, 103–109.

Strosnider, W.H., Nairn, R.W., 2010. Effective passive treatment of high-strength acid mine drainage and raw municipal wastewater in Potosí, Bolivia using simple mutual incubations and limestone. J. Geochem. Explor. 105, 34–42.

Viallis-Terrisse, H., Nonat, A., Petit, J., 2001. Zeta-potential study of calcium silicate hydrates interacting with alkaline cations. J. Colloid Interface Sci. 244, 58–65.

Yang, X., Roonasi, P., Holmgren, A., 2008. A study of sodium silicate in aqueous solution and sorbed by synthetic magnetite using in situ ATR-FTIR spectroscopy. J. Colloid Interface Sci. 328, 41–47.

Yoğurtcuoğlu, E., Uçurum, M., 2011. Surface modification of calcite by wet-stirred ball milling and its properties. Powder Technol. 214, 47–53.

Yuan, P., Cheng, Z., Zhou, Z., Yuan, W., Semiat, R., 2008. Zeta potential on the anti-scalant modified sub-micro calcite surface. Colloids Surf. A: Physicochem. Eng. Asp. 328, 60–66.

Wang, Y., Sikora, S., Townsed, T.G., 2013. Ferrous iron removal by limestone and crushed concrete in dynamic flow columns. J. Environ. Manage. 124, 165–171.

Wan Ngah, W.S., Teong, L.C., Hanafiah, M.A.K.M., 2011. Adsorption of dyes and heavy metal ions by chitosan composites: a review. Carbohydr. Polym. 83, 1446–1456.

Watten, B.J., Sibrell, P.L., Schwartz, M.F., 2005. Acid neutralization within limestone sand reactors receiving coal mine drainage. Environ. Poll. 137, 295–304.

Wolkersdorfer, C., 2008. Water Management at Abandoned Flooded Underground Mines. Springer.

Zhao, Y., Yang, S., Ding, D., Chen, J., Yang, Y., Lei, Z., Feng, C., Zhang, Z., 2013. Effective adsorption of Cr(VI) from aqueous solution using natural Akadama clay. J. Colloid Interface Sci. 395, 198–204.

Zhang, F.-Sh., Itoh, H., 2003. Adsorbents made from waste ashes and post-consumer PET and their potential utilization in wastewater treatment. J. Hazard. Mater. 101, 323–337.