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Industrial products and wastes as adsorbents for sulphate and chloride removal from synthetic alkaline solution and mine process water

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HIGHLIGHTS

- The solid wastes and limestone were tested to removal of sulphates and chlorides.
- Their alkaline mine process water treatment capacity were compare.
- Tests were conducted with synthetic and real mining process water.

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ABSTRACT

Two limestones and two solid wastes were tested as adsorbents for chloride and sulphate ion removal from synthetic and real alkaline process mining water. The composition and surface structure of the adsorbents were analysed by ED-XRF, XRD, SEM and MIR spectroscopy and the nitrogen adsorption method. The optimal adsorption time and amount of adsorbent were determined by batch analysis with an anion concentration of 20 mg/L. In synthetic solution adsorbents removed 99% of SO_4^{2-} and 96% of Cl^- and in real process water the removal rate was 85% and 74% for SO_4^{2-} and Cl^-, respectively. It was found that equilibrium could successfully be fitted to the Langmuir, Toth and BiLangmuir adsorption isotherms.

1. Introduction

Water is a vital factor in many industrial processes, including mining. Water is much more than a medium for cooling, creating steam, transport or cleaning; it is often an essential component of the process or product [1,2].

As water shortages increase, so does the need to use unconventional supplies such as seawater or wastewater for industrial processes. The water deficit may also be met by energy intensive water recovery systems such as cooling water systems for industrial processes. With the right treatment technologies, water can be reused over several cycles which helps to bridge the gap between water supply and demand [1,3].

Process water treatment problems can be solved using a variety of treatment technologies, such as the electro-chemical method [4–7], biological degradation [8], membrane filtration [9,10], coagulation [11–13], adsorption or ion exchange [10,14–17]. Low-cost process water recovery is one of the most significant issues facing industry today. Ion exchange is considered to be one of the best and most efficient methods for removing anions from water due to its high efficiency, simplicity and low cost.

Process water content depends on the type of industrial process. Alkaline mining process waters require special treatment mainly due to the combination of a high concentration of anions, such as Cl^-, SO_4^{2-}, NO_3^-, NO_2^-, NH_4^+, and a low concentration of metal ions [1].

The removal of anions from highly alkaline process water is expensive and quite challenging. Sulphate and chloride removal is often accomplished thorough an ion exchange mechanism with limestone [10,18,19]. This process involves ion exchange between OH^- on the adsorbent surface and removed anions. Natural lime is often used for process and wastewater treatment [20–24]. Sulphate removal from water by adsorption has not always been successful, for example, in A. Darbi et al.'s research on sulphate removal from drinking and groundwater by bentonite [10]. Solid waste, however, is similar in composition to limestone and has a demonstrably high capacity to adsorb anions from wastewaters,

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yet it has received the least amount of research attention [25,26]. This work took a novel approach to the removal of sulphate and chloride ions from alkaline process water. Two limestone products and two solid wastes from various industries were used as adsorbents. Two challenges were faced; real mining process water treatment forms SO_4^{2-} and Cl^-, and it is difficult to reuse solid wastes. The adsorption capacities of unmodified solid wastes were studied and the effect of both competing ions on the adsorption process was also investigated.

2. Materials and methods

2.1. Materials

Two solid wastes, iron sand (RH) and pulp and paper waste (DI-60), were used. RH and DI-60 were obtained from Ekokem Company and Metsä Tissue Corporation (Finland), respectively. Two limestone products, filter sand (FS) and flotation fines (FF), obtained from Nordkalk Corporation (Finland) were applied as adsorbents. Before use all the adsorbents were milled, washed with distilled water, and oven dried for 12 h at 80 °C. The dried adsorbents were stored in glass flasks. Sodium sulphate (Merck) and sodium chloride (Sigma–Aldrich) were used for the preparation of sulphate and chloride solutions. Solution pH adjustment was carried out with 0.1 M NaOH and HCl (Merck). Milli-Q ultrapure water was used to prepare the stock and dilute solutions.

2.2. Characterisation of adsorbents

The particle size distribution and zeta potential of the samples were determined using dispersion analyser LUMiSizer 610/611 (LUM GmbH) and ZetaSizer Nano ZS (Malvern Instruments Ltd., UK), respectively. 1.5 g of solid sample was conditioned in 50 ml of 0.001 M NaCl solutions at various final pH for 24 h in a shaking bath. Zeta potential was calculated from electrophoretic mobility measurements using the Smoluchowski equation; each 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 and solution pH was determined with a pH Electrode SenTix 81.

The physical structure of the samples was analysed with N_2 adsorption at −196 °C with TriStar 3000 (Micromeritics Inc.). The specific surface area was calculated from the adsorption isotherm using Brunauer-Emmett-Teller (BET) theory [27].

Infrared spectroscopic measurements in middle infrared (MIR) spectra of adsorbents were recorded with a Bruker Vertex 70v spectrometer. MIR: transmission technique, samples were prepared by the standard KBr pellets method. Spectra were collected in the mid infrared region ($4000–400\ cm^{-1}$) averaging 124 scans with $4\ cm^{-1}$ resolution. Samples were prepared according to the standard KBr pellets method.

The microstructure of the materials were examined using scanning electron microscopes (SEM, Nova Nano SEM 200, FEI Company and Hitachi S-4800), with energy dispersive X-ray spectroscopy (EDX, EDAX) for micro-area analysis. The experiment was carried out at low vacuum conditions in secondary electron mode and samples were covered with a layer of gold.

X-ray diffraction (XRD) data were collected with a PANalytical Empyrean powder diffractometer using Cu Kα radiation. The configuration was a standard Bragg–Brentano (θ/θ) reflection setup with a Ni-filter placed in front of the detector. The measurements were performed in a θ scanning range of 3–90° with a 0.007° step size and 69 s of measurement time for each step at ambient temperature and pressure.

The chemical composition of materials was determined by an energy dispersive X-ray fluorescent (ED XRF) analyser X-Art (Joint Stock Company Comita, St. Petersburg, Russia) [28].

2.3. Batch adsorption experiments

Ion exchange tests were conducted by mixing a known weight of FF, FS, RH and DI-60 with 15 ml of synthetic sulphate and chloride ions in alkaline solution. The ion concentrations of the synthetic solution ranged from 20 to 2000 mg/l. The solutions were shaken in a mechanical shaker ST5 (CAT M.Zipper GmbH, Staufen, Germany) from 1 to 720 h. 2 ml samples of the solution were taken from flasks at known time intervals and then filtered using a 0.20 μm diameter polypropylene syringe filter. All tests were performed at ambient temperature (22 ± 2 °C) and pressure. The final concentrations of sulphate and chloride anions in the solutions were determined with high-performance liquid chromatography (HPLC). A Shimadzu HPLC equipped with a conductivity detector (Shimadzu Model CDD-10A) was used (column: 4.0 mm ID × 250 mmL Shodex IC SI-50 4E; mobile phase: solution of 3.2 mM Na_2CO_3 and 1 mM $NAHCO_3$ in ultrapure water; flow rate: 0.7 ml/min; temperature:ambient). Adsorption was calculated as:

$$A = \frac{C_i - C_t}{C_i} * 100, \tag{1}$$

where A is adsorption (%), C_i and C_t (mg/l) are the ion concentrations in the initial and post treatment solutions, respectively.

2.3.1. Sorbent optimisation

The optimum amount of sorbent was determined by mixing 15 ml of SO_4^{2-} and Cl^- synthetic solutions with different amounts of sorbent (2, 5, 10, 20, 30, 40, and 50 g/l). Each result is the average of three samples.

2.3.2. Contact time optimisation

The optimum contact time was determined by mixing 40 g/l of FF, FS DI-60, and RH in 15 ml flasks tumbled at 100 rpm from 1 to 720 h with an initial concentration of SO_4^{2-} and Cl^- of 20 mg/L. Samples were taken after 1, 2, 4, 8, 24, 48, 96, 120, 240, 480, and 720 h.

3. Results and discussion

3.1. Adsorbent characterisation

The chemical compositions of the studied materials are shown in Table 1. These results were obtained by ED-XRF and XRD. Each material contains calcium (12–37%). RH contains more than 17% sulphur. Such a high sulphur concentration could affect the removal of sulphate ions, because sulphur on the adsorbent surface can initiate competition in the ion exchange process [13]. All chemical compounds structurally similar to calcite should have high adsorptive properties for sulphate and chloride ions.

The particle size distribution and specific surface area of the original materials are shown in Table 2. The particle size of FS and FF adsorbents are approximately the same (approximately 500 μm). The particle size for DI-60 is about three times larger (≈1500 μm), and for RH it is four times smaller (≈125 μm). Unexpectedly, the active surface area of RH is significantly larger than that of other adsorbents, which may be explained by its relatively high porosity. The results of spectroscopic analysis of the adsorbent are shown in Fig. 1. Each image presents two spectra, before (1) and after (2) washing and drying the adsorbents. As can be seen, pretreatment does not change the distribution and location

Table 1
Chemical composition of adsorbents (XRF and XRD analysis).

Element (%)	FS	FF	RH	DI-60
Ca	21.3	37.2	14.4	12.0
Fe	1.07	0.43	7.2	0.46
K	0.254	0.241	0.3	0.329
Mn	0.0216	0.0100	0.27	0.0043
S	0.100	0.105	17.6	0.039
Si	42	10.3	0.2	4.4
Sr	0.026	0.074	0.021	0.016
Ti	0.052	0.042	2.3	0.059
Rb	0.0013	0.0005	0.001	0.0020
Compounds formula	$CaMgSi_2O_6$ $CaCO_3$ $(K,H_3O)Al_2Si_3AlO_{10}(OH)_2$	$(K,H_3O)Al_2Si_3AlO_{10}(OH)_2$ $CaSiO_3$	$Ca(SO_4)(H_2O)$ $Ca(CO_3)$	$Ca(CO_3)$ $Al_2(Si_2O_5)(OH)_4$
Compounds name	Diopside Calcite	Illite Parawollastonite	Calcium sulphate hydrate Calcite	Calcite Kaolinite

Table 2
Characteristic of the surface of adsorbents.

Name of adsorbent	Particle size (μm)	Specific surface area (m^2/g)	Zeta-potential (mV) pH = 11
FF	599	1.35	0
FS	451	1.82	−25
RH	180	62.5	−7
DI-60	1390	3.29	−14

of functional groups on the adsorbent surface. Spectroscopic studies in the mid-infrared (MIR) region confirm the results of the XRD studies. The spectra of each adsorbent show two additional bands characteristic of water molecules, at about 1620–1640 and 3450–3480 cm^{-1} (Fig. 1). The OH^- stretch vibrations of the SiOH group adsorb at 3200–3700 cm^{-}, and strong Si–O bands at 830–1100 cm^{-} are observed in the spectra of DI-60 (Fig. 1c). The spectra of sulphones show strong adsorption bands at 1120–1160 cm^{-} for RH (Fig. 1d). These bands arise from symmetric SO_2 [29]. Adsorbent

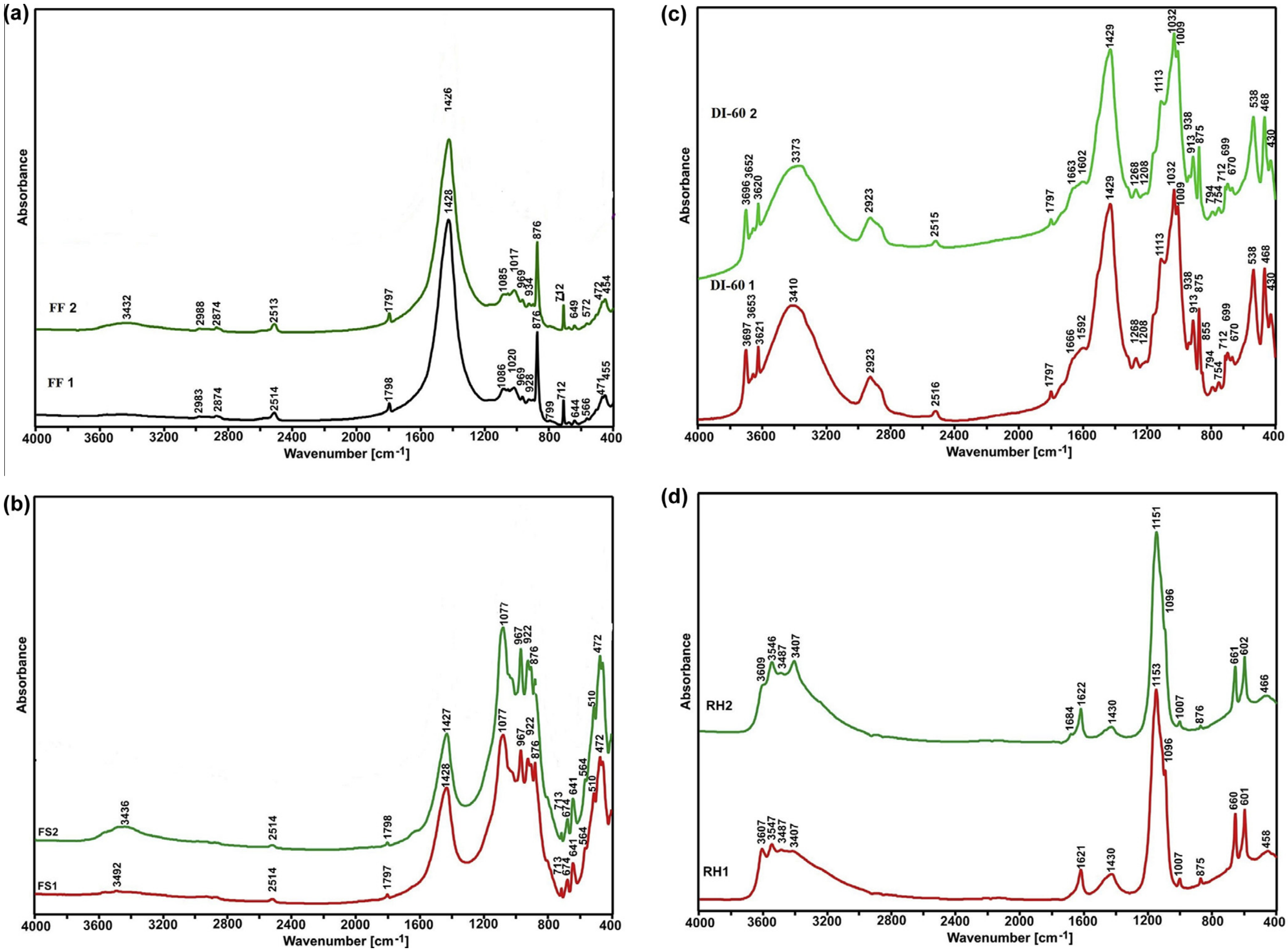

Fig. 1. MID spectrums of FF (a), FS (b), DI-60 (c) and RH (d).

surfaces were studied by XRD (Table 1) and MRI (Table 2). Both methods showed the presence of sulphur on the RH surface and silicone on the FF, FS, and DI-60 surfaces.

SEM images are presented in Fig. 2. The structure of RH is the finest, which is partly due to its highly specific surface area. This is confirmed by data on the active surface of adsorbents obtained by the BET method (Table 2); RH has the largest active surface area.

3.2. Optimisation of adsorbent amount and ion competition

The optimal amount of adsorbent for chloride and sulphate removal with an initial concentration of 20 mg/l is shown in Fig. 3. This indicates that initially Cl^- and SO_4^{2-} removal increased with increasing amounts of adsorbent, with equilibrium reached at an adsorbent concentration of 40 g/l. The highest removal percentage of sulphate (99%) was achieved with DI-60; sulphate removal was 88.5%, 90%, and 92% with RH, FS, and FF, respectively. Kolics et al. described the competition between sulphates and chlorides during the adsorption on aluminium [30]. They found that chlorides were adsorbed better than sulphates. Our experiments show that in case of adsorption with DI-60 and RH, ion competition was not observed: Cl^- ion removal reached approximately 96% with DI-60 and RH. With limestone-like adsorbents (FF and FS), however, this was not the case. Chloride removal was substantially lower than that of sulphates; only 66% and 54% were removed with FF and FS, respectively. Chloride was adsorbed better than sulphate with RH, which had the highest adsorption capacity. This phenomenon can consider as one of the factor influencing for better adsorption of Cl^- ions than SO_4^{2-} ions, because chloride ions are smaller than sulphate [12]. Since RH has a porous surface structure it was better able to adsorb chloride.

3.3. Contact time optimisation

It was found that the removal percentage increases with time, reaching the maximum at 480 h (Fig. 4). The maximum amount of Cl^- and SO_4^{2-} adsorbed to FF, FS, DI-60, and RH was 65% and 92%; 90% and 54%; 96% and 99%; 95% and 89%, respectively. It was observed that the ion exchange process does not change the initial pH of the solution [12,13].

3.4. Adsorption isotherms

Equilibrium of the adsorbate sorption on the adsorbent surface at a constant temperature is described with empirical models known as adsorption isotherms. Mathematical modelling of adsorption isotherms gives us information about the adsorption mechanism. A rigorous theory of adsorption isotherms was proposed by Langmuir for monolayer adsorption on specific homogeneous sites without attractive forces between the adsorbate

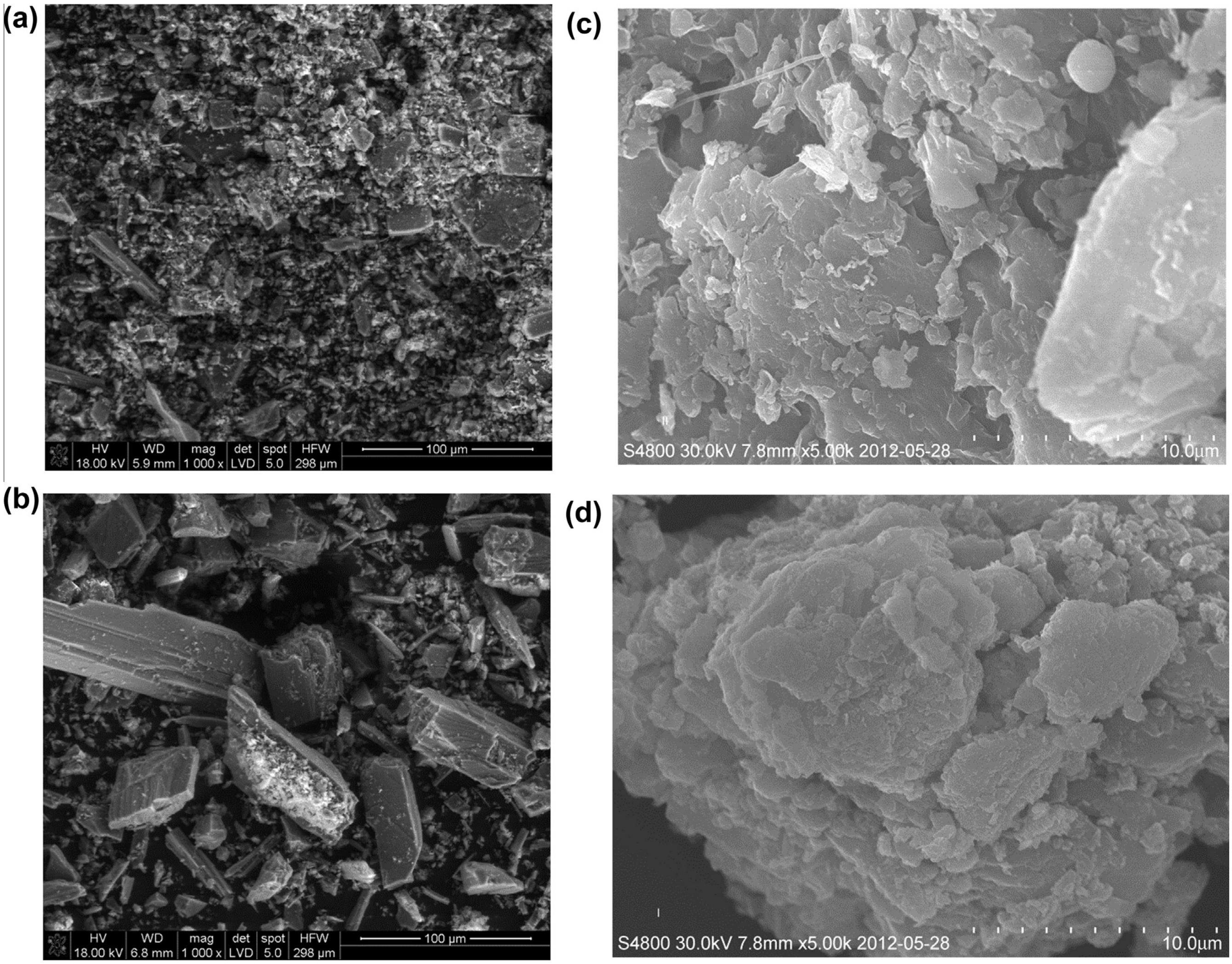

Fig. 2. SEM images of FF (a), FS (b), DI-60 (c) and RH (d).

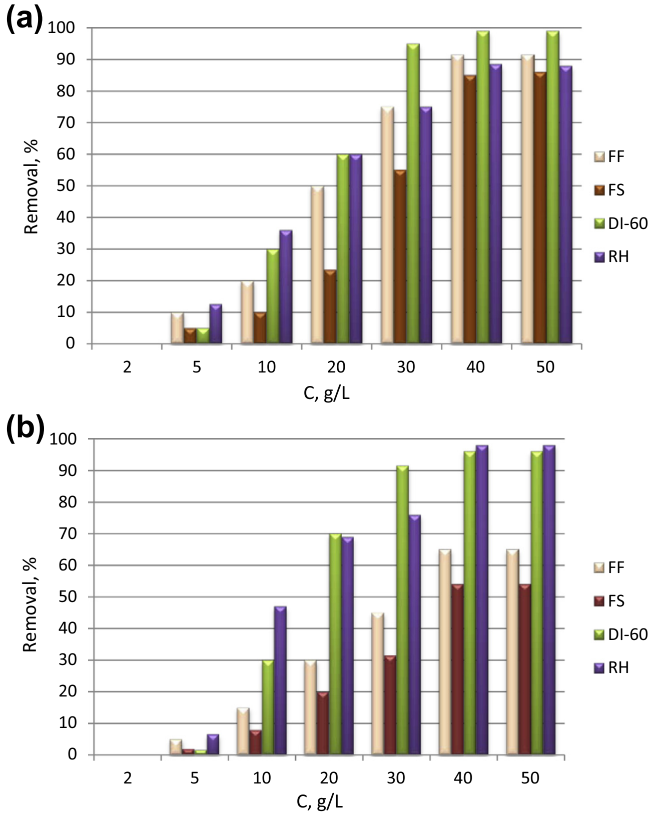

Fig. 3. Effect of dosage of FF, FS, DI-60 and RH for removal of SO_4^{2-} (a) and Cl^- (b) with initial concentration of ions 20 mg/l.

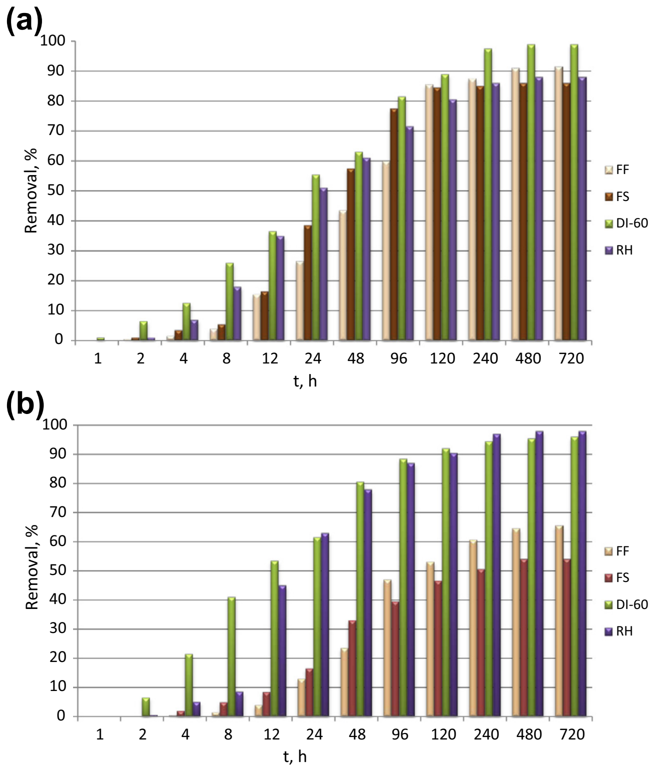

Fig. 4. Kinetics of SO_4^{2-} (a) and Cl^- (b) ions removal with FF, FS, DI-60 and RH, at pH 12. Initial ions concentration is 20 mg/L.

molecules and their mobility along the surface [31]. Further development of the theory eliminates assumptions made by Langmuir. Since the adsorbents have a complex structure, homogeneous as well as heterogeneous adsorption mechanisms are possible. Two-parameter Langmuir isotherm (Eq. (2)) was used to describe a classic case of adsorption in a homogeneous system. Three-parameter (Toth Eq. (3)) and four-parameter (BiLangmuir Eq. (4)) models were selected to describe adsorption process in the case of a heterogeneous system:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{2}$$

$$q_e = \frac{q_m C_e}{(a_T + C_e^{m_T})^{\frac{1}{m_T}}} \tag{3}$$

$$q_e = \frac{q_{m1} K_{L1} C_e}{1 + K_{L1} C_e} + \frac{q_{m2} K_{L2} C_e}{1 + K_{L2} C_e} \tag{4}$$

where q_e and C_e are anion-exchange capacity (mmol/g) and concentration of anions in the solution (mmol/L) at equilibrium, respectively; q_m is the maximum uptake capacity; K_L is Langmuir, K_{L1} and K_{L2} are the BiLangmuir constants related to the energy of anion-exchange; a_T is the adsorptive potential constant (mmol/L) and m_T the heterogeneity factor of the Toth isotherm.

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

$$\sum_{i=1}^{n} \left(\frac{q_{\mathrm{e,exp}} - q_{\mathrm{e,calc}}}{q_{\mathrm{e,exp}}} \right)_i^2 \tag{5}$$

The Langmuir isotherm is the most frequently used theory [32]. A basic assumption is that one molecule occupies a site and no further adsorption can take place at that site. In the other words, at equilibrium, saturation point is reached where no further adsorption can occur. Parameter q_m shows the number of adsorbent sites that actively interact with anions of the sorbate. The K coefficient is the affinity between sorbate and adsorbent. According to Langmuir theory the affinity between the studied adsorbents and adsorbates is:

$$\mathrm{RH;\ FS;\ DI\text{-}60:}\ \ SO_4^{2-} > Cl^-$$

$$\mathrm{FF:}\ \ Cl^- \geqslant SO_4^{2-}$$

The number of sites (q_m) which participate in the adsorption of Cl^- is much greater than in the adsorption of SO_4^{2-}. This could be because chloride molecules are smaller than sulphate molecules; Langmuir theory implies that the amount of adsorbed chloride will be much greater [33]. Yet since the affinity (K) of adsorbents to sulphate ions is higher, better removal of sulphate could be observed with FF, FS and DI-60. Chloride was more effectively removed with RH, since its pores are significantly larger than those of other sorbents (Table 2). The combination of large RH pores and small chloride ions allows for near complete chloride removal (Fig. 3b). Comparison with published data was difficult, because very few studies of the concurrent removal of chloride and sulphate ions exist; however, Hendricks found the same relationship between sulphate and chloride ions [34].

The Toth isotherm (three-parameter equation) is an adaptation of Langmuir theory to allow for a heterogeneous system. The Toth equation is obtained by adding two parameters, (a_T) and (m_T), to the Langmuir equation [35]. Those two parameters allow for heterogeneity of system. The Toth isotherm fits adsorption of both anions with DI-60 slightly better than the Langmuir one (Fig. 5), apparently because DI-60 is more heterogeneous.

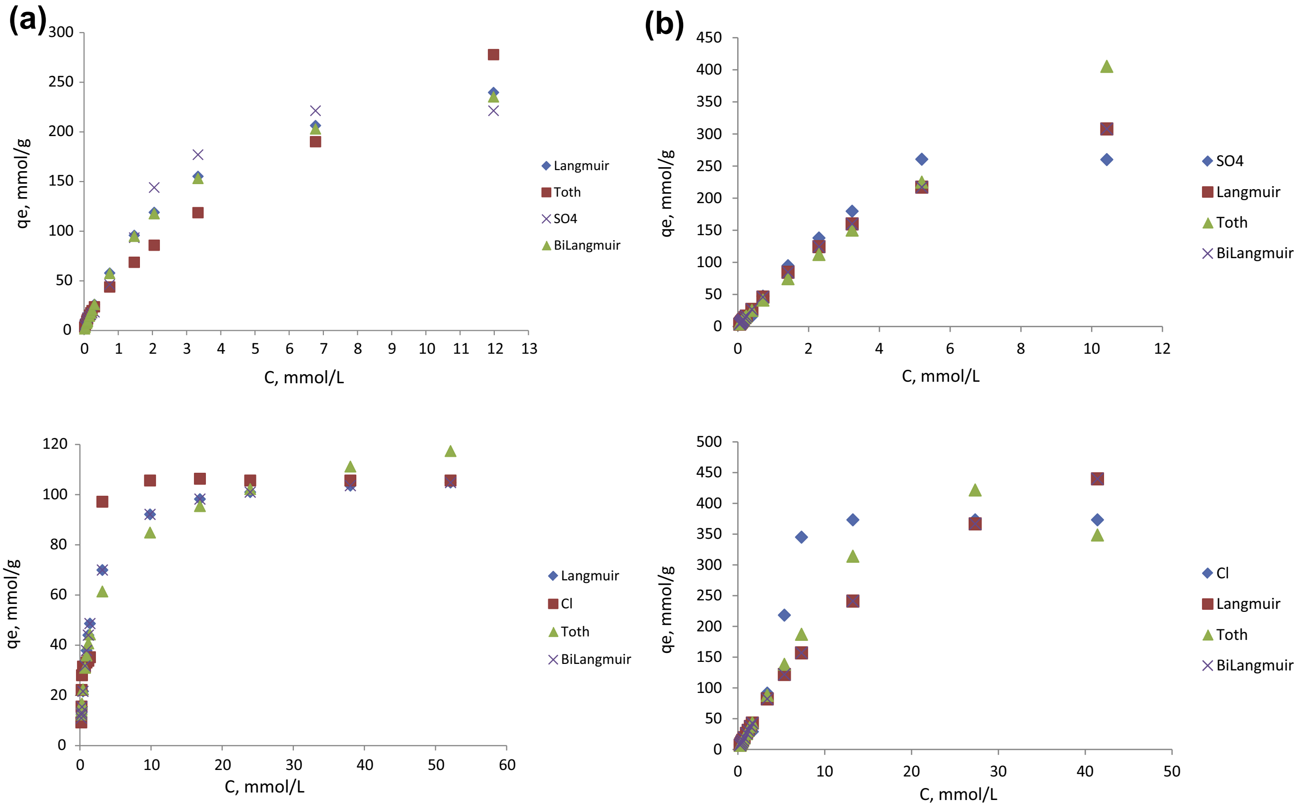

Fig. 5. Adsorption isotherms for SO_4^{2-} and Cl^- with FF (a), FS (b), DI-60 (c) and RH (d) (40 g/L). Contact time is 480 h, initial ions concentration is 20 mg/L.

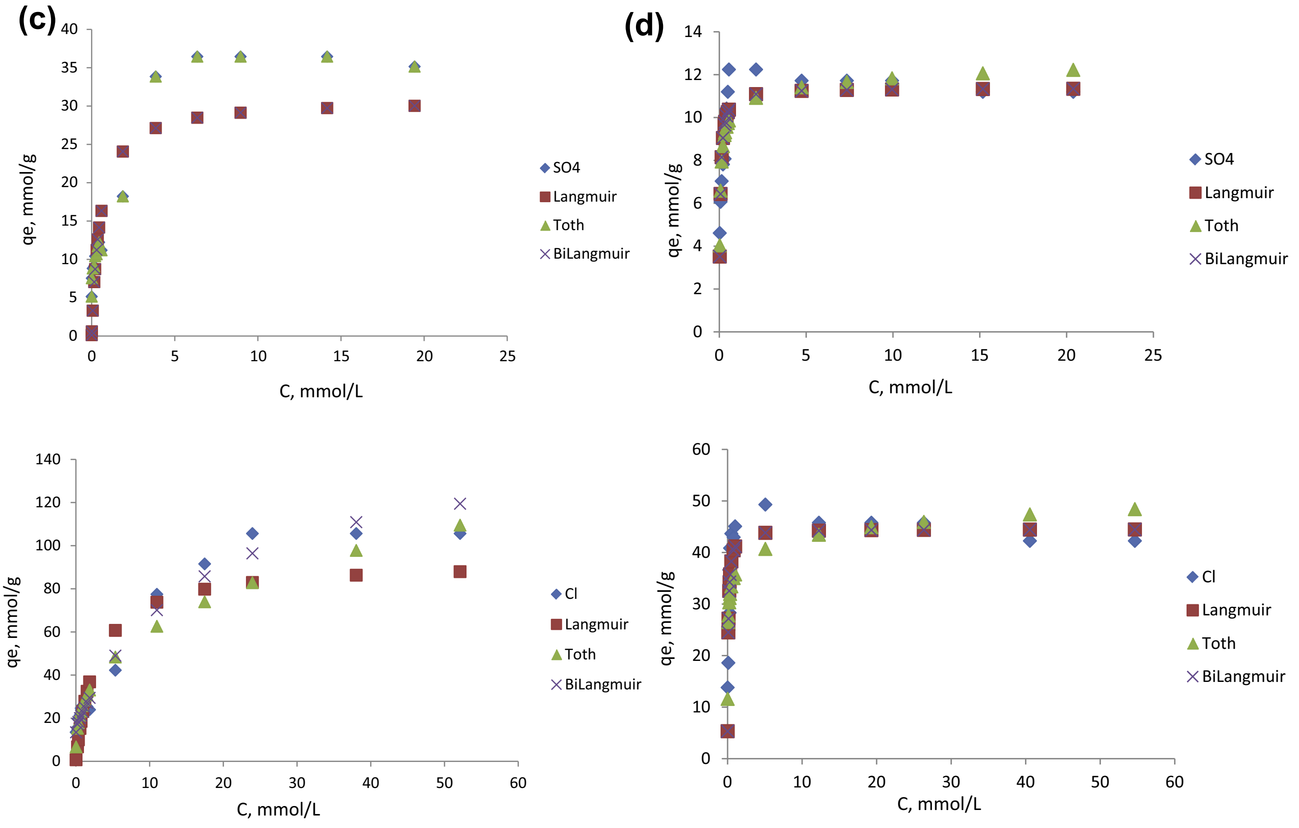

Fig. 5 (*continued*)

Table 3
Isotherm parameters for FS, FF, DI-60 and RH during adsorption process of anions from synthetic solution.

		C_e (mmol/L)	$q_{e\ exp}$ (mmol/g)	$q_{e\ model}$ (mmol/g)	q_m (mmol/g)		K_L (L/mmol)		R^2
Langmuir									
FF	SO_4^{2-}	6.77	221	215	285		0.453		0.998
	Cl^-	16.9	106	104	115		0.583		0.984
FS	SO_4^{2-}	5.2	261	217	526		0.135		0.998
	Cl^-	13.2	373	241	718		0.038		0.997
DI-60	SO_4^{2-}	8.96	29.13	36.46	30.85		1.895		0.928
	Cl^-	23.94	105	83	93		0.355		0.928
RH	SO_4^{2-}	4.74	11.72	11.24	11.37		18.68		0.728
	Cl^-	5.07	49.3	43.8	44.5		12.06		0.757
		C_e (mmol/L)	$q_{e\ exp}$ (mmol/g)	$q_{e\ model}$ (mmol/g)	K (L/mmol)		a_T (mmol/L)	m_T	R^2
Toth									
FF	SO_4^{2-}	6.8	221.4	190.2	10,936		0.019	0.338	0.995
	Cl^-	16.9	106.3	102.2	141.5		0.821	0.854	0.997
FS	SO_4^{2-}	5.2	260.7	225	114.5		0.207	0.177	0.999
	Cl^-	13.2	373.3	314.1	35.8		10,149	2.67	0.997
DI-60	SO_4^{2-}	6.4	36.5	25.9	29.2		14.3	0.941	0.985
	Cl^-	23.9	105.6	82.8	60,389		0.001	0.641	0.981
RH	SO_4^{2-}	0.55	12.2	9.9	616		0.035	0.957	0.897
	Cl^-	5.07	49.3	40.7	3810		0.019	0.929	0.961
		C_e (mmol/L)	$q_{e\ exp}$ (mmol/g)	$q_{e\ model}$ (mmol/g)	q_{m1} mmol/g	q_{m2} (mmol/g)	K_1 (L/mmol)	K_2 (L/mmol)	R^2
BiLangmuir									
FF	SO_4^{2-}	6.8	221.4	218	118.5	166.4	0.162	0.101	0.995
	Cl^-	16.9	106.3	98.2	95	32.9	0.133	16.7	0.989
FS	SO_4^{2-}	5.2	260.7	217.2	139.8	123.5	0.089	0.033	0.998
	Cl^-	13.2	373.3	241.2	271.4	120.5	0.038	0.213	0.997
DI-60	SO_4^{2-}	6.4	36.5	28.5	37.7	8.03	0.257	78.9	0.991
	Cl^-	23.9	105.6	96.4	17.6	132.1	140.9	0.154	0.991
RH	SO_4^{2-}	0.55	12.2	10.4	11.0	0.106	20.7	0.107	0.775
	Cl^-	5.07	49.3	43.8	3.7	42.3	1.7	14.1	0.825

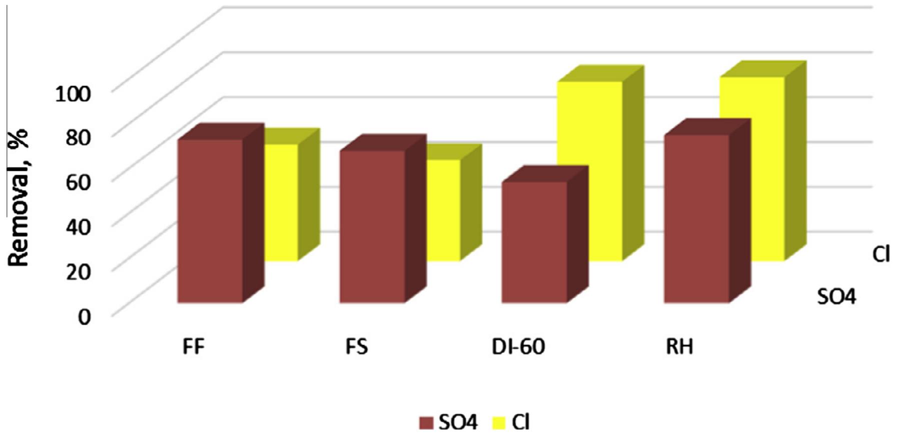

Fig. 6. Removal of SO_4^{2-} and Cl^- with FF, FS, DI-60 and RH from real process water. Initial concentration of SO_4^{2-} and Cl^- was 30 and 2.5 g/L, respectively. Amount of adsorbents is 40 g/L.

The BiLangmuir isotherm assumes that the surface contains two divergent active sites having different affinities towards the target compound [36]. BiLangmuir isotherms for both anions fit better to the FF, FS, and DI-60 adsorbents (Fig. 5), possibly because these adsorbents have at least two anion adsorption sites. The BiLangmuir model was rather efficient in reflecting the adsorption process.

3.5. Anion removal from real process water

Chloride and sulphate ion concentrations in real mining process water were 2.5 and 30 g/L, respectively. The chemical composition of the process waster is presented in Table 3. The removal of anions was conducted by batch method at ambient temperature for 480 h with 40 g/L of each adsorbent. The experiment was carried out in three steps, using fresh adsorbent at each stage, and the total process took 60 days. Chloride removal with FF, FS, DI-60, and RH was 52%, 45%, 80%, and 82%, respectively; sulphate removal with the same adsorbents was 73%, 68%, 54%, and 75%, respectively (Fig. 6). Increasing adsorbent concentration and time did not increase anion removal, as might be expected. Equilibrium occurred at the optimal adsorption time (480 h) and adsorbent concentration (40 g/L). The lower removal of anions from the real process water could be due to its complex composition. It contains other ions beside Cl^- and SO_4^2 which can act as competitors during the adsorption process.

4. Conclusions

The efficiency of four solid wastes used as anion exchangers to remove chloride and sulphate ions from alkaline mining process water was investigated. The optimal adsorption parameters were estimated with synthetic solution. The optimal time (480 h) and adsorbent concentration (40 g/L) were determined by batch method. The maximum adsorption capacities of FF, FS, DI-60 and RH ranged from 221, 261, 29 and 12 mmol/g for SO_4^{2-} removal, to 106, 373, 105 and 49 mmol/g for Cl^- removal, respectively. All three isotherms (Langmuir; Toth; BiLangmuir) described both anion exchange processes well. The FF and FS removed more than 50% of both anions and RH removed approximately 80% of sulphate ions. The DI-60 removed more than 80% of both sulphate and chloride ions. All adsorbents could be used industrially for alkaline process water treatment: although the removal process is long (around 2 months), the treatment requires a minimum amount of energy and is low in cost due to the use of solid wastes as adsorbents.

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