Integrated absorption-adsorption process for waste-free decontamination of gases from sulfur dioxide. Part 1. Choice of ion-exchange resin and adsorption and desorption parameters

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One of the most hazardous atmospheric air pollutants is sulfur dioxide. Its main anthropogenic source is the burning of fossil fuels with high sulfur content. A waste-free new technology is proposed for decontamination of sulfur dioxide-containing gases that uses its absorption by water, followed by adsorption by ion-exchange resin, subsequent desorption and further processing of the contaminant. As a first step for detailed investigation of the technology a screening for the appropriate resin is conducted. Seven different ion exchange resins and a zeolite are presented in this study. After the initial evaluation Dowex® 66 is selected as the most promising one and further experiments regarding adsorption and desorption times, as well as variation of the concentration of desorbing agent, are performed. Lastly, consecutive adsorption/desorption is conducted to determine the number of cycles the resin can operate at peak performance.

Keywords: Ion-exchange resin, adsorption, desorption, sulfur dioxide

INTRODUCTION

Many technologies for gases purification from SO_2 are known [1,2]. A wide class of methods uses alkaline absorbents [3-8]. The products obtained from the absorption process in most cases have to be subjected to additional oxidation that increases the expenses for the whole process [9-11]. The final products - sulfates (Na_2SO_4 and $CaSO_4$) have limited practical application and they present a problem for their disposal.

There are few articles dedicated to the adsorption of gaseous sulfur dioxide by ion-exchange resins and zeolites [12-14]. Information for adsorption of sulfurous acid by ion-exchange resins wasn't found.

For the gas purification from SO_2, a practically waste-free technology should be used. In view of the above, we propose a new absorption-adsorption approach for flue gas SO_2 decontamination by direct water absorption, followed by adsorption by ion-exchange resin and subsequent desorption from the resin by dilute ammonia solution. The resultant solution, treated appropriately, can be used as precursor in the chemical industry. The proposed absorption-adsorption method includes absorption of SO_2 in water with the simultaneous adsorption of the SO_2 from the water solution by ion-exchange resin. The adsorbent desorption is accomplished with a solution of NH_3, followed by decomposition of the resulting $(NH_4)_2SO_3$ with HNO_3. The products of the processes are pure - gaseous SO_2 and aqueous solution of NH_4NO_3.

Sulfur dioxide has application in the chemical industry, and NH_4NO_3 is also a commercially viable product - nitrogen fertilizer.

MATERIALS AND METHODS

Ion-exchange resins choice

The ion-exchange resins used in this study are all commercially available and were chosen based on their size, functional groups and mechanism of adsorption. Sulfurous acid with concentration of 1.6 ± 0.2 g l^{-1} was used to simulate the water-adsorption process of SO_2 flue gas decontamination. This concentration is consistent with the maximum concentration of sulfur dioxide in the flue gases [12] and Henry's law.

Adsorption of contaminant

The initial screening of the resins was conducted by mixing a set amount of resin (1-5 g) and 100 ml of sulfurous acid in a closed flask. The mixture was stirred for a fixed time and at a constant rate (400 rpm). In order to evaluate the time needed for adsorption experiments were carried out varying the stirring time (0 - 60 min). After the stirring the mixture was left to settle, the aqueous phase was removed and the remaining sulfurous acid analyzed, while the loaded ion-exchange resin proceeded for desorption.

Desorption of contaminant

Desorption of sulfurous acid was performed by adding 50 ml of aqueous solution of NH_3 to the ion-exchange resin.

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The mixture was stirred for a fixed time at a constant rate (400 rpm). In order to evaluate the time needed for desorption experiments were carried out varying the stirring time (0 - 60 min). Afterwards, the mixture was left to settle, the aqueous phase was removed and the solution analyzed. The amount of NH₃ used was chosen to be in great excess (2.5 % v/v) or near (0.8 % v/v) the stoichiometric amount needed for the complete desorption of the initial amount of sulfurous acid. The volume used was half that of the initial sulfurous acid in order to achieve additional increase of the acid concentration, which in turn will ease further processing of the contaminant.

The concentrations of sulfurous acid before and after the absorption and after regeneration were determined iodometrically.

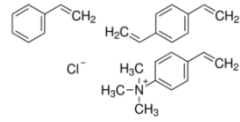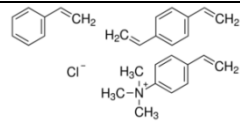*Ion-exchange resin cycle life*

In order to determine the viability of the ion-exchange resin for continuous use 10 adsorption/desorption cycles were performed on the same resin sample, according to the above methodology. Due to a gradual decrease in the performance of the resin 5 additional cycles were performed with a "water rinsing" step between the end of the desorption and before the next adsorption. This "rinsing" step constituted of removing the desorption solution, adding 50 ml of distilled water and stirring at constant rate (400 rpm) for 60 min.

RESULTS AND DISCUSSION

Screening for the appropriate resin

For this study seven ion-exchange resins were chosen as appropriate, taking into account the resin particle size, the functional groups present, as well as their mechanism of adsorption.

Table 1. Ion-exchange resins characteristics

Resin trade name	pH range	Composition of the resin	Resin size	Resin application	Sign
Zeolite	0-14	$(SiO_2)_x(Al_2O_3)_y$	2.2 – 4 mm	Zeolite is a naturally occurring volcanic rock used for its ability to bind with ammonias	Zeolite
Dowex® 1×8 Chloride form	1-14		20-50 mesh	Dowex® 1×8 is a strongly basic anion exchange resin which is used as an absorbent in solid phase extraction	Dowex ①
Dowex® 1×8 Chloride form	1-14		200-400 mesh	Dowex® 1×8 is a strongly basic anion exchange resin which is used as an absorbent in solid phase extraction	Dowex ②
AmberLite® FPA66 (formerly Dowex® 66) free base	0-14	Styrene-divinylbenzene (macroporous) matrix active group	50-125 mesh	Weakly basic anion exchange resin for deashing and mixed bed polishing of high fructose corn syrups.	Dowex ③
Ionac SR 7	1-14	Crosslinked polystyrene matrix; quaternary amine functional group	24-28 mesh	Very high selectivity for nitrate ions; selective removal of nitrates	IonacSR7
AmberLite™ FPX66	0-14	Macroreticular aromatic polymer	24-28 mesh	Non-functionalized, adsorbent resin	Amberlite ①
Amberlite® XAD7HP	0-14	Matrix: acrylic	20-60 mesh	Nonionic macroreticular resin that adsorbs and releases ionic species through hydrophobic and polar interactions; usually used under isocratic conditions.	Amberlite ②
Amberlite® I RA-96 free base	0-7	Styrene-divinylbenzene (macroporous) matrix active group	20-27 mesh	Weakly basic anion exchange resin, useful for deionization, chromate recovery, formaldehyde deacidification, ammonium nitrate removal and recovery.	Amberlite ③

Additionally, a zeolite was also tested as it is proven that zeolites have the capacity to adsorb contaminants [14]. A list of the resins and some of their characteristics are presented in Table 1. The adsorption capacity of each resin was investigated separately and all experiments were performed in triplets, except one for the zeolite. Each experiment was performed as described above and consisted of mixing a fresh sample (5 ± 0.1 g) of ion-exchange resin and 100 ml of sulfurous acid ($C_{H2SO3} = 1.6 \pm 0.2$ g.l^{-1}), stirred for 60 min for the adsorption step and 50 ml of 2.5 % v/v aqueous NH_3, stirred for 30 min for the desorption step. Results are presented in Table 2, Fig. 1a) (adsorption) and 1b) (desorption).

The experiments showed that the zeolite sample was too brittle and was reduced to dust during the adsorption step. Moreover, no sulfurous acid was recovered, so a decision was made to eliminate it from further testing.

Of the rest of the samples all showed over 75 % adsorption of the contaminant, except for Amberlite 1 and Amberlite 2, which performed poorly and adsorbed only about 20 %.

For the desorption of the acid none of the ion-exchange resins showed consistent results over 60%. We attribute some of these lower results to oxidation of the sulfite to sulfate ions due to the prolonged time of the experiment. A note should be made that the presented percent of desorption is a ratio of adsorbed to desorbed sulfurous acid.

As can be seen from the figure Dowex 2, Dowex 3 and Amberlite 3 adsorb all the quantity of the acid. This is not the case with the regeneration. Only Dowex 3 shows about 60% desorption of the initial quantity of the acid and this is the reason why further experiments were carried with this ion-exchange resin.

Determination of the time for adsorption and desorption

The next step was to examine the influence of the adsorption and desorption time on the selected ion-exchange resin (Dowex 3). In order to achieve this goal, the time for adsorption and desorption was varied between 0 and 60 min. The results are presented in Fig. 2 (Fig. 2a) for adsorption and Fig. 2b) for regeneration).
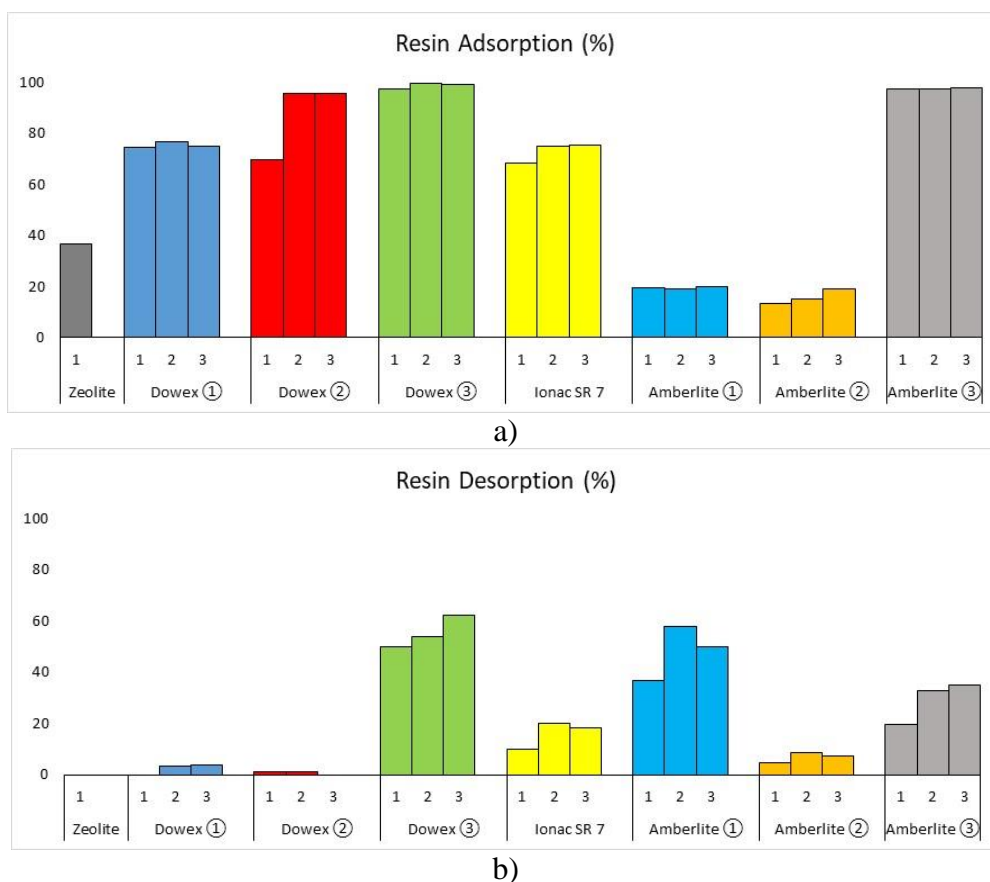

a)

b)

**Fig. 1.** Adsorption-desorption capacity of the resins investigated.

Table 2. Ion-exchange resin experimental results

Resin	Exp. №	Mass (g)	C_{H2SO3} (g.l^{-1})	$C_{Ads\ H2SO3}$ (g.l^{-1})	Adsorbed %	$C_{Des\ H2SO3}$ (g.l^{-1})	Desorbed %
Zeolite	1	5.0030	1.6851	0.6199	36.79	0.0000	0.00
Dowex ①	1	5.0033	1.6851	1.2546	74.45	0.0000	0.00
	2	5.0032	1.6789	1.2915	76.92	0.0807	3.12
	3	5.0032	1.6789	1.2591	74.99	0.0968	3.84
Dowex ②	1	5.0057	1.8401	1.2808	69.61	0.0242	0.95
	2	5.0049	1.4854	1.4209	95.65	0.0320	1.13
	3	5.0018	1.4854	1.4209	95.65	0.0000	0.00
Dowex ③	1	5.0779	1.6531	1.6144	97.66	1.6195	50.16
	2	5.0010	1.6789	1.6757	99.81	1.8081	53.95
	3	5.0032	1.6789	1.6628	99.04	2.0664	62.14
Ionac SR 7	1	5.0013	1.8401	1.2620	68.58	0.2558	10.14
	2	5.0017	1.6379	1.2320	75.22	0.4945	20.07
	3	5.0007	1.6379	1.2361	75.47	0.4572	18.49
Amberlite ①	1	5.0057	1.8040	0.3514	19.48	0.2583	36.76
	2	5.0040	1.7240	0.3292	19.10	0.3809	57.85
	3	5.0051	1.7240	0.3452	20.02	0.3456	50.06
Amberlite ②	1	5.0087	1.8040	0.2382	13.20	0.0225	4.73
	2	5.0106	1.7240	0.2647	15.35	0.0467	8.83
	3	5.0110	1.7240	0.3292	19.10	0.0467	7.10
Amberlite ③	1	5.0796	1.6531	1.6144	97.66	0.6355	19.68
	2	5.0052	1.6379	1.5974	97.52	1.0525	32.94
	3	5.0025	1.6379	1.6022	97.82	1.1283	35.21

Experimental conditions: V_{H2SO3} = 0.1 L, T_{ads} = 60 min; V_{NH3} = 0.05 L, T_{des} = 30 min.
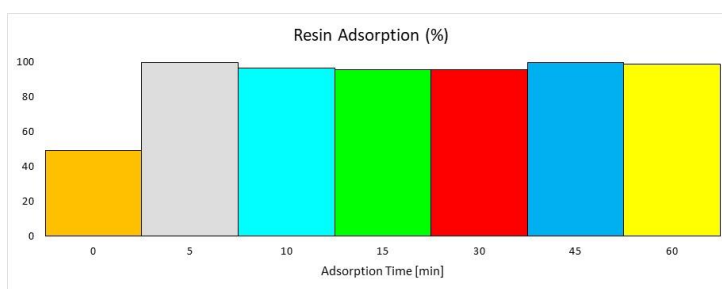
a)
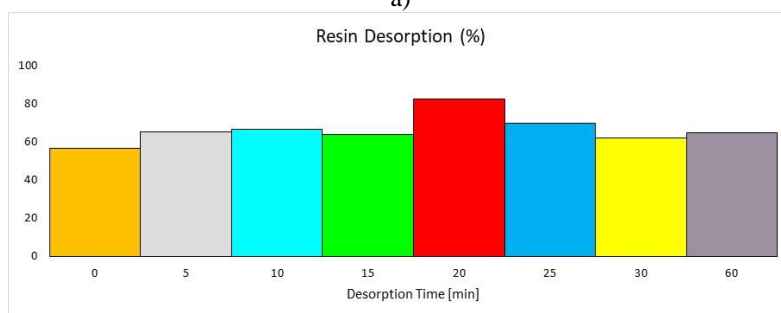
b)

Fig. 2. Dependence of the adsorption and desorption on time.

The figures show that the adsorption process is practically independent of time while maximum desorption is achieved at the 20th minute mark. The results for the regeneration exceed those in Fig. 1 (reaching more than 70%) probably because the prolonged time of desorption in the initial experiments results in higher oxidation of the sulfites to sulfates. So the conditions for further experiments were set at five min for adsorption and twenty min for desorption.

Determination of the capacity of the resin

Experiments with different quantity of resin (1, 2, 3, 4 and 5 g) were conducted next. The results are given in Fig. 3.

Figure 3 shows that the whole quantity of acid is adsorbed by about 4 g of resin. The results are sufficiently repeatable and will be used for further mathematical modeling of the proposed technology.

Ion-exchange resin cycle life

Determination of the concentration of ammonia used. In order to test the effect of ammonia concentration on the desorption cycles experiments with 2.5 % v/v and 0.8 % v/v ammonia were performed. The results are presented in Fig. 4.
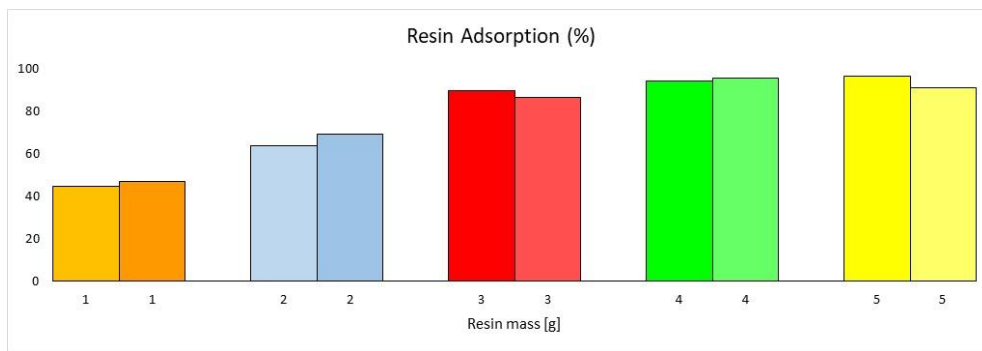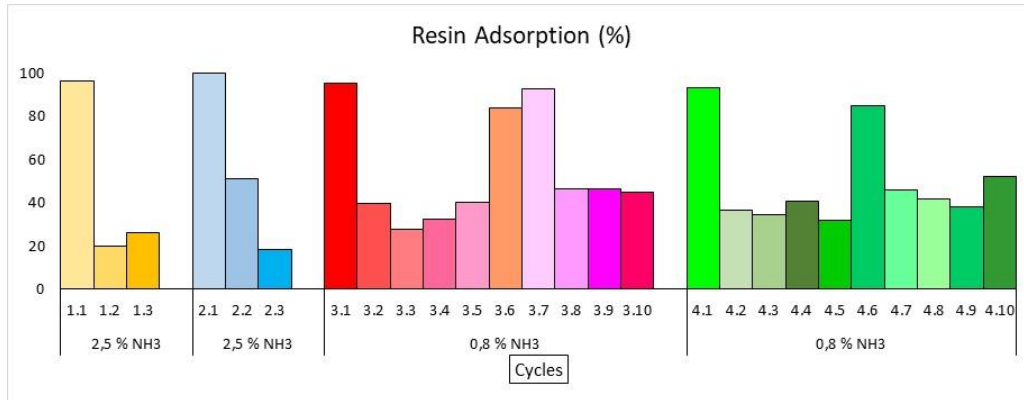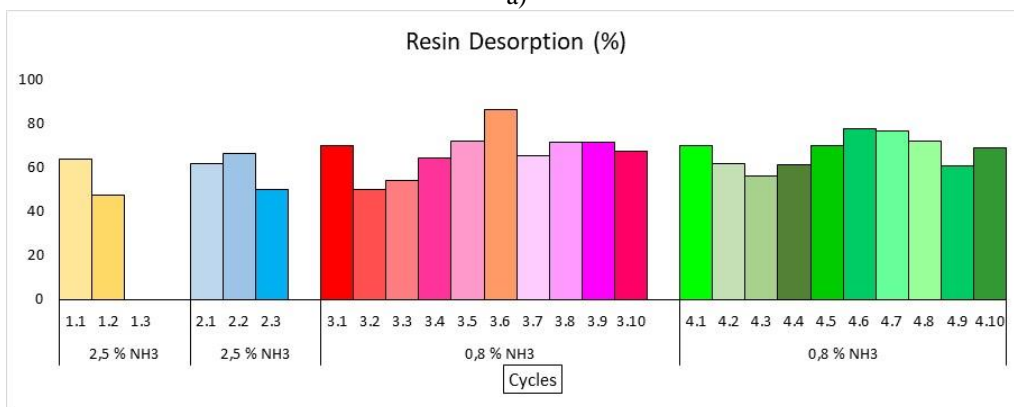

Fig. 3. Capacity of the resin

a)

b)

Fig. 4. Cycles for multiple use of one and the same resin sample. Comparison of the regeneration with 2.5 % v/v and 0.8 % v/v NH$_3$

As can be seen the adsorption capacity (amount of adsorbed sulfurous acid) of the resin rapidly decreases with every cycle. Taking into account this decrease with every cycle the desorption capacity (amount of desorbed acid relative to the amount adsorbed) expressed as percent, seemingly remains stable, but actually the amount desorbed decreases with each cycle as well.

An interesting conclusion can be made by comparing the experiments with 2.5 % v/v and 0.8 % v/v NH_3 - the adsorption of each consecutive cycle declines much more rapidly when using the solution with higher ammonia concentration. We attribute this to irreversible chemical reactions between the desorbent and the ion-exchange resin which is avoided in the case of the lower concentration used. Hence, we decided to continue further experiments with 0.8 % v/v NH_3 used as desorbent. Another hypothesis for the steady decrease in the adsorption capacity of the resin is that some of the products remain on the active sites of the resin after the desorption cycle. In an effort to bring the resin in its initial state we performed a conditioning with distilled water, as explained in "Materials and methods", between the fourth and fifth cycle (between 3.4 - 3.5 and 4.3 - 4.5 from Fig. 4.). As the figure shows this conditioning regenerated the ion-exchange resin to performance comparable to the first cycle of use that gradually declined over the next cycles. These results inclined us to perform another set of experiments to further examine this "rinsing" method. The results are presented in Fig. 5.

Sulfates and a small quantity of sulfites are proved qualitatively in the conditioning water by addition of $BaSO_4$. This coincides with the hypothesis that some of the sulfites are oxidized to sulfates and remain in the resin as larger ions.
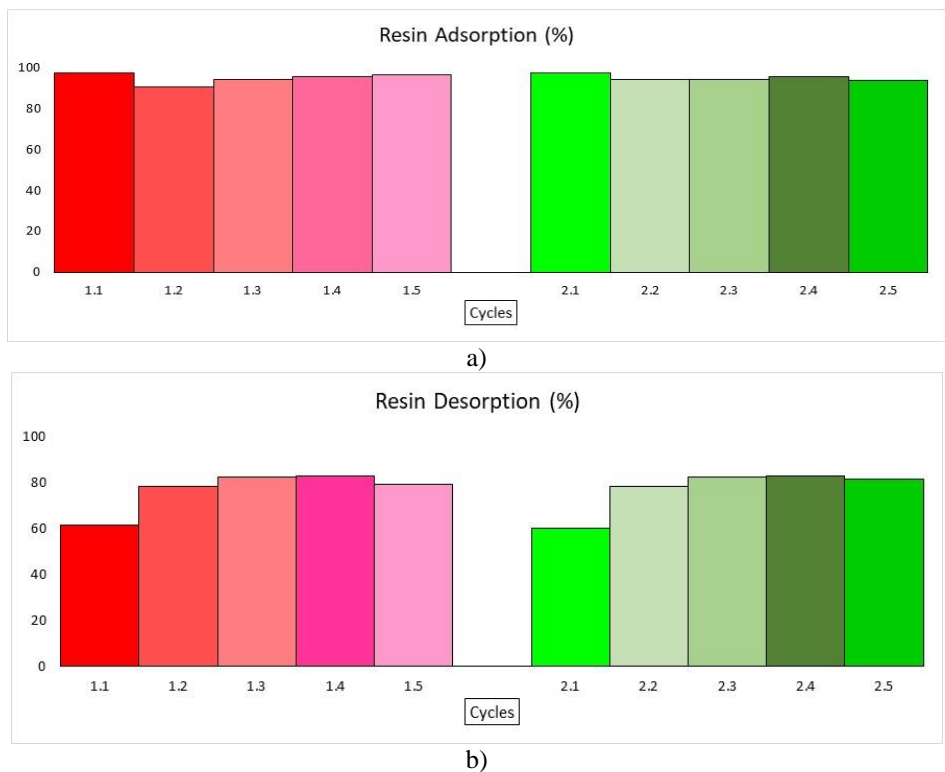

a)

b)

Fig. 5. Ion-exchange resin cycle life with conditioning

Ion-exchange resin cycle life with conditioning

As can be seen from the figures, the conditioning with distilled water after each desorption drastically improves the performance of the resin to the point that there is no noticeable decrease in both adsorption and desorption capacity after 5 consecutive cycles. This supports our hypothesis that some of the products with bigger molecules (sulfates) are not removed from the surface of the ion-exchange resin and "rinsing" it with water removes most, if not all, of said products. This relatively simple (technologically) process substantially increases the cycles the ion-exchange resin can be used, thus improving the overall efficiency of the whole process being investigated as the ion-exchange resin itself is usually a large portion of the maintenance cost.

Detailed information about the cycles is presented in Table 3.

Table 3. Ion-exchange resin cycle life experimental results

Exp. set	Exp. №	Mass (g)	C_{H2SO3} (g.l^{-1})	$C_{Ads\ H2SO3}$ (g.l^{-1})	Adsorbed %	$C_{Des\ H2SO3}$ (g.l^{-1})	Desorbed %
①	1.1	5.0891	1.6331	1.5860	97.12	1.9471	61.39
	1.2	5.0891	1.6174	1.4604	90.29	2.2926	78.49
	1.3	5.0891	1.6174	1.5232	94.17	2.5125	82.47
	1.4	5.0891	1.7273	1.6488	95.45	2.7323	82.86
	1.5	5.0891	1.7273	1.6645	96.36	2.6381	79.25
②	2.1	5.1150	1.6331	1.5860	97.12	1.9032	60.00
	2.2	5.1150	1.6174	1.5232	94.17	2.3869	78.35
	2.3	5.1150	1.6174	1.5233	94.18	2.5120	82.45
	2.4	5.1150	1.7273	1.6488	95.45	2.7402	83.10
	2.5	5.1150	1.7273	1.6174	93.64	2.6381	81.55

Experimental conditions: V_{H2SO3} = 0.1 L, T_{ads} = 5 min; V_{NH3} = 0.05 L, T_{des} = 20 min, $V_{H2O\ rinsing}$ = 0.05 L, T_{rins} = 60 min.

CONCLUSIONS

The ion-exchange resin Dowex® 66 was chosen out of eight candidates for the novel technology being investigated in this study. Important technological parameters such as quantity of the resin for nearly total adsorption of the sulfurous acid (4 g of resin adsorb 0.1517 g of acid, 96% of total), time for adsorption (5 min) and desorption (20 min), concentration of the desorbing NH_3 (0.8 % v/v) were determined. Additionally, it was found that the conditioning of the resin with water can prolong its cycle life substantially (insignificant (< 2%) decrease after 5 cycles).

These parameters can be used for further scaling, implementation and investigation of the new technology for waste-free decontamination of gases from sulfur dioxide.

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