REMOVAL OF ANIONS FROM SOLUTION BY CALCINED HYDROTALCITE AND REGENERATION OF USED SORBENT IN REPEATED CALCINATION–REHYDRATION–ANION EXCHANGE PROCESSES

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Synthetic hydrotalcite calcined at 350–550 °C was used for the removal of arsenate, chromate, and vanadate ions from water solutions. The initial anion concentrations were 0.002 mol l^{-1}. The sorption isotherms were measured at 20 °C and at neutral pH. The Langmuir adsorption isotherm was used for the sorption capacity evaluation. The ability of the calcined hydrotalcite to remove the anions from solution decreased in the order of vanadate – arsenate – chromate. The hydrotalcite calcined at 450 °C exhibited the best sorption ability for all the anions. The sorbed anions were released by anion exchange in a carbonate-containing solution and the hydrotalcite after subsequent calcination was used again for the removal of anions. The repeating cycles calcination–rehydration–anion exchange gradually reduced the adsorption capacity of the hydrotalcite. The sorption capacity decreased by 50% after the first two cycles but it did not change significantly in the subsequent cycles. When chromate anions were adsorbed, the decrease in sorption capacity was not observed during repeated calcination–rehydration–anion exchange cycles. The change in the sorption capacity was influenced by the ability of calcined hydrotalcite to regenerate the layered crystal structure during the rehydration process.

Key words: Hydrotalcite; Thermal decomposition; Rehydration; Crystal structure reconstruction; Waste water treatment; Anion exchangers.

Hydrotalcite, the mineral of chemical composition $Mg_6Al_2(OH)_{16}CO_3\cdot 4\,H_2O$, has been taken as a reference name for many other isomorphous materials. They are also referred to as anionic clays or layered double hydroxides. Hydrotalcite-like compounds can be represented by the general formula $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}[A^{n-}_{x/n}\cdot y\,H_2O]^{x-}$, where M^{II} and M^{III} are divalent and trivalent metal ions (Mg^{2+}, Zn^{2+}, Fe^{2+}, Ca^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+}, Al^{3+}, Cr^{3+}, Fe^{3+}, *etc.*), A is an *n*-valent anion (*e.g.* CO_3^{2-}, SO_4^{2-}, Cl^-, NO_3^-), and x can have values between approximately 0.25 and 0.33. Their structure is similar to that of brucite ($Mg(OH)_2$), and hydrotalcite-like compounds crystallize in a layer-type lattice[1,2]. In the brucite, each Mg^{2+} ion is octahedrally surrounded by six OH^- ions and the different octahedra share edges to form infinite sheets. The sheets are stacked one on top of the other and are held together by weak interactions through hydrogen. If some Mg^{2+} ions are replaced isomorphously by cations with higher charge, but similar radius, the brucite-type sheets become positively charged and the electrical neutrality is maintained by the interlayers composed of anions and water molecules (Fig. 1). The OH-sheets may exhibit two stacking sequences, rhombohedral and hexagonal. These two forms can be distinguished only by XRD analysis. Their physical properties and chemical composition are the same.

These materials have found a variety of uses as prepared or after calcination at high temperatures. Many catalysts based on mixed oxides can be obtained by a controlled decomposition of the hydrotalcite-like compounds[3]. Catalytic applications of these mixed oxides include condensation[4–6], alkylation[7,8], dehydrogenation[9], and oxidation[10] reactions, nitrogen oxide reduction[11,12], *etc.* Hydrotalcite-like compounds are often used in polymer processing as halogen scavengers or in PVC stabilizer compositions. They are also known as good sorbents and anion exchangers. The exchange affinity is greater for divalent than for monovalent anions, the exchange affinity for CO_3^{2-} being the highest[2].

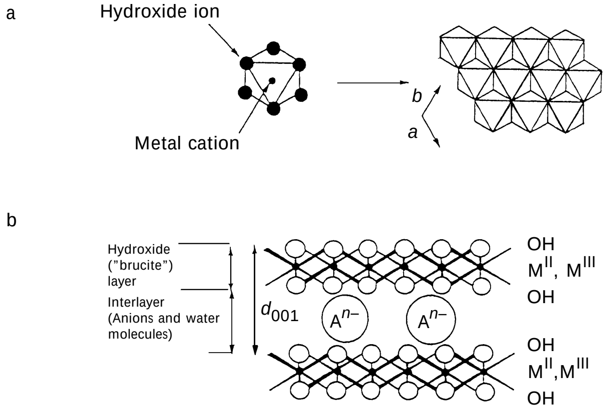

FIG. 1

Schematic representation of the hydrotalcite crystal structure: a brucite-like layers with M^{II}/M^{III} isomorphous substitution in octahedral sites, b interlayers composed of anions and water molecules neutralising a net positive charge of hydroxide sheets

Interlayer anions are incorporated into the hydrotalcite structure either by synthesis or by anion exchange. In both cases, the preferential incorporation of CO_3^{2-} is observed. The presence of carbonates in solution prevents the incorporation of other anions into the solid phase. The alternative procedure to incorporate other anions into the hydrotalcite structure is *via* the rehydration of calcined hydrotalcite. The interlayer water is released at 150–250 °C. During the subsequent heating at 350–600 °C, the hydroxyl and carbonate groups are simultaneously transformed into water and carbon dioxide, respectively. The layered crystal structure of hydrotalcite collapses to form a predominantly amorphous mixture of Mg and Al oxides. Further increase in temperature up to 900 °C results in crystallization of $MgAl_2O_4$ (spinel)[13–16]. Calcined hydrotalcite can be rehydrated in water. During the rehydration, reconstruction of the layered hydrotalcite structure with incorporation of anions from the solution takes place. This method can be applied to intercalate large anions (*e.g.* organic or polyoxometalate anions)[17–21]. The rehydration of calcined hydrotalcite can be also used for the removal of undesirable anions from solutions[22–25]. Regeneration of hydrotalcite enriched with sorbed anions can be carried out by anion exchange with CO_3^{2-} and following calcination[26]. The calcined hydrotalcite can be used again for removal of undesirable anions from solution.

The presented work deals with a possible utilization of the synthetic hydrotalcite in waste water purification processes. Adsorption of anions in calcined hydrotalcite is higher and faster than in uncalcined one[22,24]. Arsenate, chromate, and vanadate removal by hydrotalcite calcined at different temperatures is studied in the presented work and the optimum calcination temperature is found. The influence of repeated regenerations of sorbent (by anion exchange with carbonate and calcination) on the sorption capacity and crystal structure of the used hydrotalcite is also examined.

EXPERIMENTAL

Materials

Hydrotalcite was prepared by coprecipitation. An aqueous solution (450 ml) containing magnesium sulfate (153.06 g $MgSO_4 \cdot 7\,H_2O$, 0.621 mol) and aluminium sulfate (92.96 g $Al_2(SO_4)_3 \cdot 18\,H_2O$, 0.139 mol), molar ratio Mg : Al = 2.23, total metal ion concentration of 2 mol l^{-1}, was added dropwise under vigorous stirring into solution containing 145.73 g (1.375 mol) of Na_2CO_3 (500 ml). The addition took about 1 h. During the synthesis, the temperature was maintained at 85 °C and pH at about 10 by a simultaneous addition of a 10 M NaOH solution. The resulting slurry was then maintained at 85 °C, under stirring, for 4 h. The product was filtered off and washed several times with hot distilled water (until free of SO_4^{2-}). The washed product was dried at 130 °C in air. Elemental analysis confirmed the

Al/(Mg + Al) ratio in hydrotalcite of 0.31. The calcination of dried hydrotalcite was carried out at 350, 400, 450, and 550 °C in air for 3 h.

Rehydration Procedures

The anion sorption isotherms were measured for hydrotalcite calcined at 350, 400, 450, and 550 °C. Different weights of calcined hydrotalcite (0.01–0.4 g) were added to 150 ml of a solution containing 0.002 mol l^{-1} of arsenate, chromate, or vanadate anions prepared from $Na_2HAsO_4 \cdot 7\ H_2O$, K_2CrO_4, or NH_4VO_3 of analytical-grade quality and decarbonized distilled water. The suspension was placed in sealed 250 ml polyethylene bottles, shaken at room temperature (20 °C) for 72 h and then filtered. The anion concentration was determined in the filtrate.

Calcination–Rehydration–Anion Exchange Cycle

The dried hydrotalcite was calcined at 450 °C for 3 h. After cooling, 40 g of calcined hydrotalcite was added to 3 000 ml of solution with anion concentration 0.1 mol l^{-1} (prepared from $Na_2HAsO_4 \cdot 7\ H_2O$, K_2CrO_4, or NH_4VO_3 of analytical-grade quality and decarbonized distilled water). The suspension was shaken in a sealed 5 000 ml polyethylene bottle at room temperature (20 °C) for 72 h, then filtered and washed with decarbonized water. The washed filtration cake was dispersed in 2 700 ml of 0.5 M Na_2CO_3 solution and again shaken in a sealed polyethylene bottle at room temperature for 72 h. The time of 72 h was sufficent for total anion exchange. The exchanged product was filtered off, washed with distilled water, dried at 130 °C, and then calcined at 450 °C for 3 h. The procedure was repeated five times. Before starting each procedure, 1.5 g of calcined hydrotalcite was sampled. This sample was used for sorption isotherm measurements (as described above), in solutions with initial anion concentration of 0.002 mol l^{-1} to determine the sorption capacity of calcined hydrotalcite in each cycle.

Methods

The concentration of anions in solution was determined by photometry using a UV/VIS spectrophotometer UNICAM 5625. The concentration of arsenate was determined as As^V by the Molybdenum Blue method at 825 nm, chromate concentration was determined from the absorption intensity of acidified solution (pH 1) at 350 nm and the vanadate was determined as V^V with hydrogen peroxide at 460 nm (ref.[27]).

Powder X-ray diffraction patterns were recorded using a Seifert XRD 3000P instrument with CoKα radiation ($\lambda = 0.179026$ nm, graphite monochromator, goniometer with Bragg–Brentano geometry) in 2θ range 12–75°, step size 0.05° 2θ.

BET surface area measurements were carried out on a PulseChemisorb 2700 instrument (Micromeritics) by dynamic chromatographic method. The samples were pretreated in air at 120 °C for 2 h. Specific surface areas were evaluated following the three-point method by nitrogen adsorption at 77 K. The N_2 concentrations of 5, 15, and 30 vol.% in the nitrogen–helium mixture were used.

Thermogravimetric analysis was carried out on air using TG-750 Stanton–Redcroft with a heating rate of 10 K min^{-1} and a flowing rate 10 ml min^{-1}.

RESULTS AND DISCUSSION

Rehydration of Calcined Hydrotalcite and Anion Removal

The X-ray diffraction patterns for hydrotalcite calcined at temperatures 400 °C and higher showed only one peak corresponding to magnesium oxide – periclase (Fig. 2). Hydrotalcite calcined at 350 °C still had the layered structure and the carbonate was not lost at this temperature. The value of specific surface area (BET) measured for a sample calcined at 350 °C changed only little in comparison with that of hydrotalcite dried at 130 °C (64.2 and 57.5 $m^2\ g^{-1}$, respectively). The value of 253.4 $m^2\ g^{-1}$ was measured for hydrotalcite calcined at 400 °C. This considerable increase in specific surface area indicated decomposition of hydrotalcite, which is accompanied by the destruction of the layered crystal structure and release of water and carbon dioxide. The higher calcination temperature decreased the value of specific surface area (Table I). TG/DTA analyses presented in Fig. 3 also indicate the decomposition of hydrotalcite at 400 °C. The first endothermic peak observed at *ca* 230 °C is caused by the lost of interlayer water. The mass loss observed at this temperature was about 15 wt.%. The second endothermic peak observed at 400 °C was caused by the dehydroxylation of OH bound with Mg and Al and the main CO_2 evolution. The layered crystal structure of hydrotalcite collapsed at this temperature but the mass loss continued to about 600 °C to reach more than 40 wt.%.

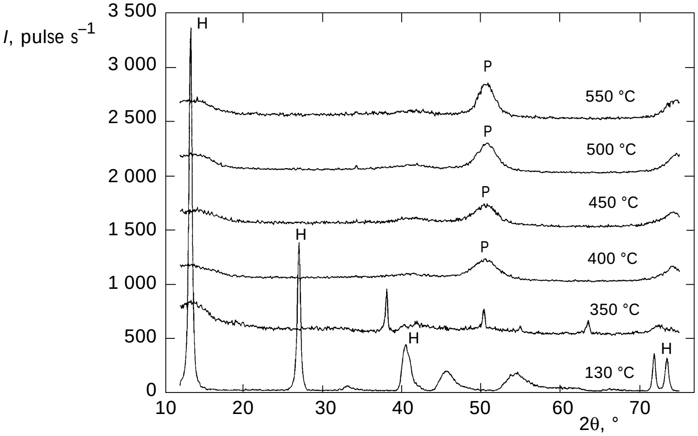

FIG. 2

Powder X-ray diffraction patterns for hydrotalcite as function of calcination temperature. H Hydrocalcite, P periclase

The time of 72 h chosen for rehydration reaction is sufficient to reach equilibrium conditions (anion concentrations in solution did not change significantly after 10–12 h of the reaction). The nature of the sorption isotherms is demonstrated in Figs 4a–4c. For all the observed anions, the sorption isotherms measured with hydrotalcite calcined at 350 °C show a marked diference in comparison with those measured with hydrotalcite calcined at higher temperatures. The experimental results of sorption isotherms were fitted to the Langmuir adsorption isotherm

$$q_e = \frac{QKc_e}{1 + Kc_e} , \qquad (1)$$

TABLE I
Specific surface area (BET), anion sorption capacity *Q* of calcined hydrotalcite and equilibrium constant *K* in dependence on calcination temperature for observed anions

Calcination °C	BET $m^2 g^{-1}$	As^{V}		Cr^{VI}		V^{V}	
		Q mmol g^{-1}	*K* l $mmol^{-1}$	*Q* mmol g^{-1}	*K* l $mmol^{-1}$	*Q* mmol g^{-1}	*K* l $mmol^{-1}$
350	64.2	0.99	0.83	0.43	0.47	1.38	0.34
400	253.4	2.38	4.51	0.71	3.78	3.34	6.45
450	240.8	3.05	11.66	1.17	113.85	3.90	13.77
550	199.1	2.63	16.31	1.16	210.32	3.72	36.55

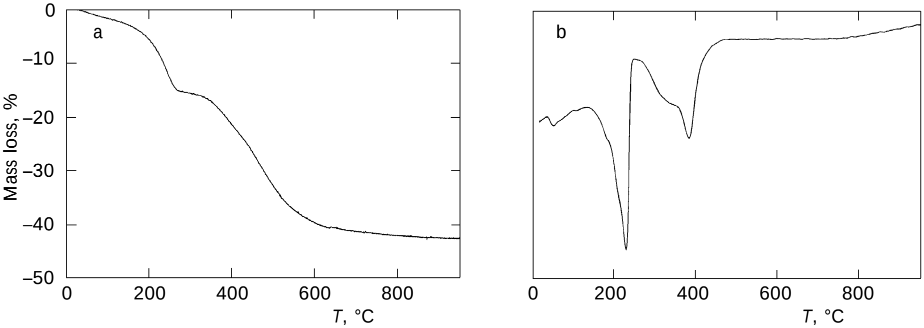

FIG. 3
TG (a) and DTA (b) curves of hydrotalcite

where q_e is the content of anion sorbed in the solid phase at equilibrium (apparent adsorbed amount) in mmol g^{-1}, c_e is concentration of anion in solution in mmol l^{-1} at equilibrium, K is the equilibrium constant in l $mmol^{-1}$, and Q is the sorption capacity in mmol g^{-1}. The amount of anion adsorbed in the solid phase q_e was calculated from Eq. (*2*) using experimental data:

$$q_e = \frac{V_0(c_0 - c_e)}{m} , \tag{2}$$

where V_0 is the solution volume in litres, c_0 is the initial anion concentration in mmol l^{-1}, and m is the amount of added hydrotalcite in grams. The experimental relationships were expressed through values q_e *vs* c_e (Figs 5a–5c) and the sorption capacity Q and the equilibrium constant K for the anion adsorption were calculated from Eq. (*1*). The calculated Q and K values are shown in Table I. The sorption selectivity of the calcined hydrotalcite decreases in the order: vanadate > arsenate > chromate. Table I shows the in-

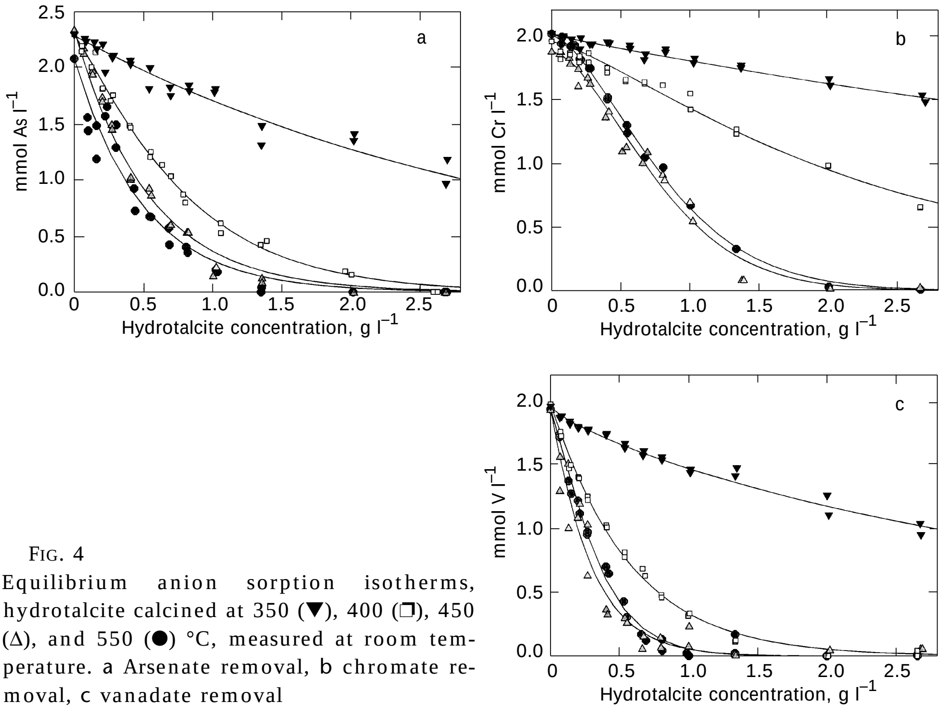

FIG. 4

Equilibrium anion sorption isotherms, hydrotalcite calcined at 350 (▼), 400 (❐), 450 (Δ), and 550 (●) °C, measured at room temperature. a Arsenate removal, b chromate removal, c vanadate removal crease in the sorption capacity of hydrotalcite after its decomposition for all the anions. The *Q* values for hydrotalcite calcined at 400 °C are lower in comparison to those for hydrotalcite calcined at 450 °C and 550 °C. Hydrotalcite calcined at 450 °C had the best sorption ability for all the observed anions. The q_e *vs* c_e dependences in Figs 5a–5c showed a poor agreement of Eq. (*1*) for anion adsorption in hydrotalcite calcined at 350 °C. The carbonate was not lost at this temperature and occupied anion positions in the crystal structure. Therefore it prevents the anion adsorption. Equation (*1*) describing a chemisorption of anions on the surface of calcined hydrotalcite is in a good agreement with experimental data measured with hydrotalcite after its thermal decomposition at higher temperatures. The calculated *K* values showed the most intensive interaction between the calcined hydrotalcite and chromate anions.

X-Ray diffraction, specific surface area, and TG/DTA measurements showed collapse of layered crystal structure and decomposition of hydrotalcite at 400 °C. However, this temperature was not sufficient to reach the maximum sorption ability. This fact indicates that a higher calcination temperature (about 450 °C) is necessary for complete decomposition

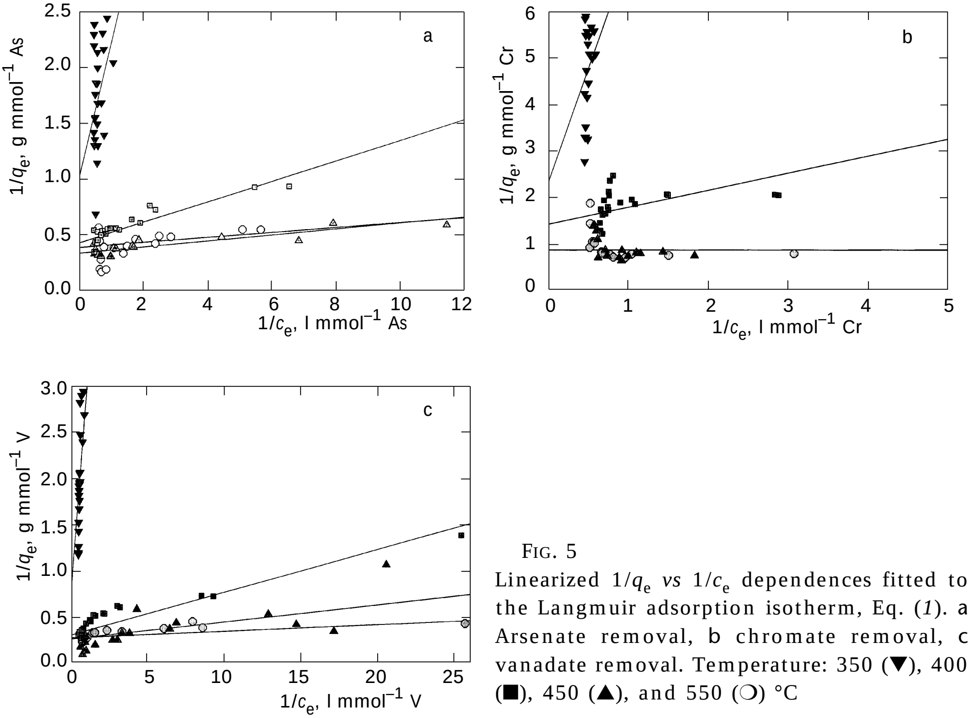

FIG. 5

Linearized $1/q_e$ *vs* $1/c_e$ dependences fitted to the Langmuir adsorption isotherm, Eq. (*1*). a Arsenate removal, b chromate removal, c vanadate removal. Temperature: 350 (▼), 400 (■), 450 (▲), and 550 (○) °C of hydrotalcite. The course of sorption isotherms in Figs 4a–4c and the calculated *Q* values showed a decrease in sorption ability of hydrotalcite calcined at 550 °C. Probably the higher calcination temperature caused changes in internal arrangement of the calcined product and decreased its rehydration and sorption capacity.

Repeated Calcination–Rehydration–Anion Exchange Cycles

The theoretical value of anion exchange capacity of hydrotalcite corresponds to its chemical composition as defined by the Al^{3+} content in brucite type layers. Thermal decomposition of hydrotalcite can be expressed by following reactions:

$$Mg_6Al_2(OH)_{16}CO_3 \cdot 4\,H_2O \xrightarrow[\substack{-\,4\,H_2O\ (\approx 200\ ^\circ C) \\ -\,(CO_2 + 8\,H_2O)\ (\approx 400\ ^\circ C)}]{} 6\,MgO \cdot AlO_3 \qquad (3)$$

The theoretical anion capacity of the calcined hydrotalcite corresponded to the chemical composition as above and was calculated as 5.8 meq g^{-1}. A higher theoretical capacity, about 7.1 meq g^{-1}, was calculated for the hydrotalcite with the ratio Al/(Mg + Al) equal 0.31 used in these experiments. The experimentally found values of the sorption capacity were significantly lower than those theoretically calculated (Table I).

The regeneration of hydrotalcite with sorbed anions and the use of regenerated sorbent has not been previously examined. Parker *et al.*[26] described sorption of F^-, Br^-, $B(OH)_4^-$, NO_3^-, and HPO_4^{2-} by hydrotalcite. Preparation of their anion sorbent involved calcination, anion sorption, exchange with carbonate, and repetition of the cycle. Ulibarri *et al.*[22] demonstrated the repeated use of hydrotalcite for sorption of trinitrophenol and trichlorophenol. A U.S. patent[23] mentioned the removal of heavy metal ions (Zn^{2+}, Ni^{2+}, and Cr^{VI} as chromate) by a sorbent containing calcined hydrotalcite and its regeneration in an alkaline medium.

This work discusses the use of hydrotalcite for removal of arsenate, chromate, and vanadate anions from water solutions. Each cycle includes anion sorption by hydrotalcite calcined at 450 °C, anion exchange of the sorbed anion for carbonate in Na_2CO_3 solution and recalcination. The sorption capacity of calcined hydrotalcite for the anion in each cycle was calculated from an experimental sorption isotherm by means of the Langmuir equation (*1*). The changes in the sorption capacity as a function of the number of cycles are shown in Table II. The sorption capacity was reduced to *ca* 80% in the first cycle and to *ca* 50% after the second cycle when arsenate or vanadate anions were sorbed. The subsequent cycles decreased the capacity only little. Similar results were published by Parker *et al.*[21]. The reduction in sorption capacity of hydrotalcite probably depends on retention of the hydrotalcite lattice structure. This is degraded with every sorption/reactivation and the sorption capacity of calcined hydrotalcite decreases. Powder X-ray diffraction analyses of hydrotalcite after anion exchange in Na_2CO_3 solution during repeated calcination–rehydration–anion exchange cycles are shown in Figs 6a–6c. The samples of hydrotalcite after the first cycle are well crystallized in comparison with the hydrotalcite after the fourth or fifth cycles. The height and area of the first diffraction peak decreased to *ca* 40% after the fifth cycle during arsenate sorption (Fig. 6a). This fact confirmed the worse crystallinity of used hydrotalcite. During vanadate sorption, the height and area of the first diffraction peak decreased to *ca* 25% after the fourth cycle. The powder X-ray diffraction pattern after the fifth cycle was almost amorphous (Fig. 6c). Other relationships were observed in the case of chromate sorption. The value of sorption capacity of CrO_4^{2-} was the lowest after the first cycle (about half of

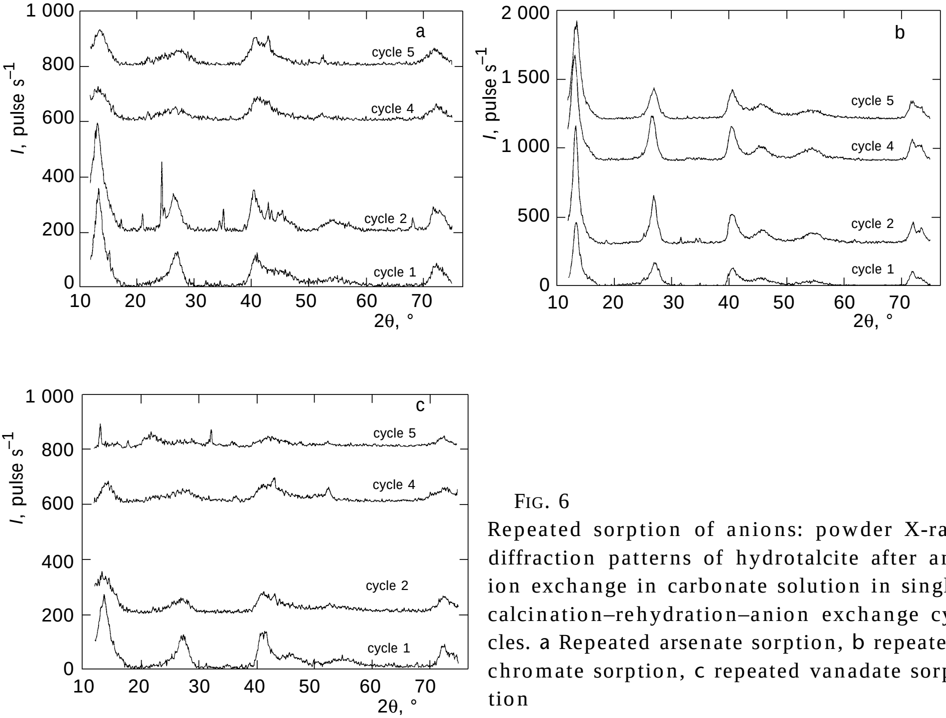

FIG. 6

Repeated sorption of anions: powder X-ray diffraction patterns of hydrotalcite after anion exchange in carbonate solution in single calcination–rehydration–anion exchange cycles. a Repeated arsenate sorption, b repeated chromate sorption, c repeated vanadate sorption the sorption capacity found for arsenate and vanadate). However, further cycling did not significantly change the sorption capacity. Powder X-ray diffraction analysis (Fig. 6b) confirmed a good regeneration of the crystal structure of hydrotalcite used for chromate sorption.

CONCLUSIONS

Experimental measurements showed a decrease in anion concentration in aqueous solutions by use of calcined hydrotalcite as an anion sorbent. The calcination temperature must be high to decompose the carbonate anions and remove them from the hydrotalcite structure. This process is accompanied by destruction of the layered crystal structure of hydrotalcite. The ability of calcined hydrotalcite to sorb the anions decreased in the order of vanadate – arsenate – chromate. The sorbed anions are displaced by carbonate-containing solution. Thermal decomposition of carbonate hydrotalcite could be used for further anion uptake. The first two calcination–rehydration–anion exchange cycles reduced the sorption capacity of calcined hydrotalcite to about 50%, but further cycles had little effect. When chromate anions were sorbed, a decrease in the sorption capacity was not observed during repeated calcination–rehydration–anion exchange cycles. The sorption capacity was influenced by the ability of the calcined hydrotalcite to regenerate as a layered crystal structure during the rehydration process.

TABLE II
Anion sorption capacity of hydrotalcite calcined at 450 °C as a function of the number of calcination–rehydration–anion exchange cycles

Number of cycles	Sorption capacity, mmol g^{-1}		
	As^{V}	Cr^{VI}	V^{V}
1	3.21	1.52	3.65
2	2.65	1.27	2.92
3	1.71	1.31	2.15
4	1.48	1.47	2.08
5	1.42	1.49	1.94

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