A study on the removal of heavy metals by carbonatation cake discarded in sugar industry

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Abstract

The removal of chromium (III) and cadmium ions by precipitation from synthetic wastewater samples by using I.carbonatation cake discarded in sugar production was investigated. The dried carbonatation cake (DCC) containing 75-80 % $CaCO_3$ precipitates chromium (III) and cadmium by neutralising the acidity of solution. However, organic substances in the cake cause an increase in the chemical oxygen demand (COD) of the water in contact with the cake. It was observed that the calcined forms obtained by heating the carbonatation cake above 600°C precipitate the chromium and cadmium ions most effectively without increasing organic pollution of water treated. It was concluded that the calcined carbonatation cakes (CDCC) can be used in heavy metals removal instead of calcium carbonate and/or lime in water treatment.

Introduction

Heavy metals are a significant source of pollution. The pollution potential of heavy metals is, to a large extent, dependent on the solubility of their salts. All metal salts are soluble to some extent in water. A small amount of some heavy metals has a vital activity-regulating role for living organisms in aquatic systems. However, since these metals do not degrade in the environment into harmless end-products, they can accumulate in living tissue and cause acute and chronic poisoning (Whol & Goodhart,1968; Casarett & Doull, 1975, Moore & Ramomoorthy 1984; Peavy *et al.*, 1985). For that reason, the amounts of heavy metals in drinking and surface waters have been restricted (EPA, 1995; Förstner & Wittmann, 1983).

Chemical precipitation processes are commonly used to remove heavy metals from wastewaters. By these processes, heavy metals are converted into their insoluble salts such as hydroxide, sulphide and carbonate. The hydroxide precipitation process is generally preferred because the materials used - such as lime, soda ash and sodium hydroxide - are cheap and quite abundant (Dean *et al.*, 1972; Patterson,1975; Lanouette, 1977). It is stated that the use of limestone instead of lime in order to neutralise excessive acidity from acidic mine drainages, plating industry wastes and rinse waters is economically attractive (Dean *et al.*, 1972; Maree *et al.*, 1992). However, excessive amounts of limestone must be used for acidic wastes since it may not be effective as theoretically indicated owing to particle coating, the need for fine grinding and pH limitation of calcium carbonate (Dean *et al.*, 1972). A study by Maree *et al.*, (1992) indicated that the use of limestone is approximately 70 % cheaper than lime.

In sugar production, a sludge which is known as carbonatation cake with high $CaCO_3$ content, about 70 % on dry basis, is discarded in significant quantities during the carbonatation process. Besides its high $CaCO_3$ content, the carbonatation cake with fine particles is a no cost waste and does not need to be ground. Because of the advantages mentioned above, the carbonatation cake may be used as cheap precipitation agent for the removal of heavy metals from aqueous solution. The fact that the carbonatation cake contains organic materials released from sugarbeet during extraction process may lead to an increase in the amount of organic contaminants in the water to be contacted with the cake. However, the organic materials can be eliminated by heating the carbonatation cake at elevated temperatures. In addition, the removal of organics from the cake causes an increase in the fraction of $CaCO_3$ in the calcined forms, which increases their neutralisation capacity.

For that reason, in this study, carbonatation cake in both its dried form (DCC) and calcined form (CDCC) were used to precipitate Cd(II) and Cr(III) ions from aqueous solutions. A series of experiments were carried out using pure $CaCO_3$ in order to compare the results obtained from the DCC and CDCC samples. To measure the amount of organic pollutants to be released from precipitants, chemical oxygen demand (COD) was determined in the water treated with DCC and CDCCs.

Materials and methods

Materials

I.carbonatation cake used as a precipitation agent was provided from a sugar plant in Elazı?, Turkey. This material was dried on a polyethylene sheet at atmospheric conditions. Cake lumps formed during drying process were ground and sieved to obtain –200 mesh fraction (<74 mm). The fraction was dried in an oven at 70°C until its weight became constant. It was then stored in a capped glass jar.

To determine the chemical composition of dried cake DCC, a weighed sample was dissolved in nitric acid solution and then the mixture was filtered to remove the organic residue from the supernatant. The analysis of calcium in the solution was performed by complexometric titration (Gülensoy, 1977). The concentrations of sodium and potassium were determined by flame photometry (Jeffery *et al.*, 1989) (Eppendorf), iron and

Table 1. Chemical composition of dried I.carbonatation cake (DCC).

Constituent	Composition, %
CaO	44.80
MgO	3.86
Na_2O	0.18
K_2O	0.13
FeO	0.38
Weight loss (70-800°C)	46.09

Table 2. Weight losses of dried I.carbonatation cake (DCC) at different calcination temperatures

Calcination temperature, °C	Weight loss, %
300	10.84
400	12.38
500	13.25
600	15.76
700	25.65
800	46.09

magnesium concentration in the solution were determined by atomic absorption spectrophotometry (Perkin Elmer, 370 model).

The DCC samples were calcined in an oven at temperatures ranging from 300 to 800°C for 6 hours. The samples were mixed every 30 minutes. The resulting products were denoted as CDCC.

Preparation of solutions

Cr(III) and Cd stock solutions in the concentration of 10 g l^{-1} were prepared separately by dissolving $Cr_4(SO_4)_5(OH)$ (Riedel-de Haen 12243) and $3CdSO_4.8H_2O$ salts (Merck 102027) in distilled water, respectively. All working solutions were prepared by diluting stock solutions to obtain a concentration of 100 mg-metal ion l^{-1}. The pH of all working solutions were adjusted to 2.0±0.05 by the addition of sulphuric acid.

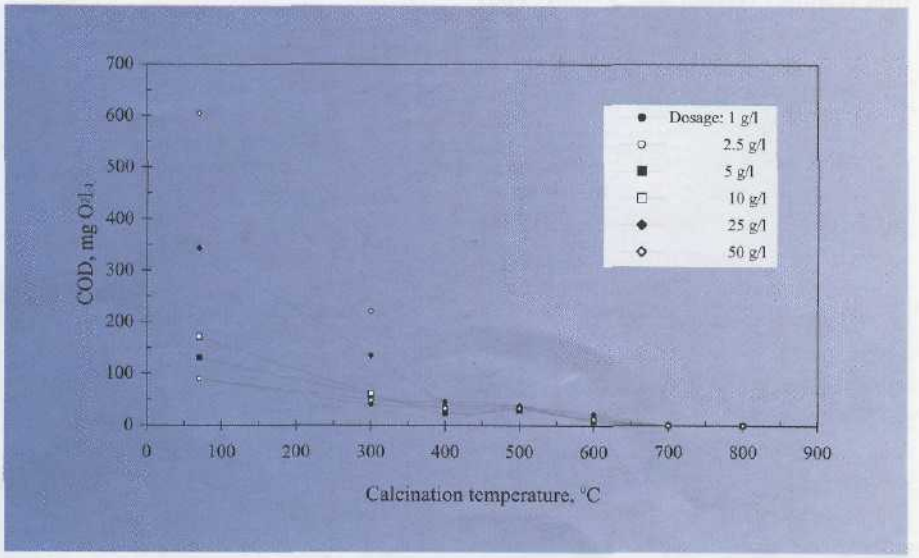
Experimental study

100 ml of the working solutions were transferred into 250 ml glass flasks containing various amount of DCC samples (0.25-1.00g). After the flasks were capped tightly, they were shaken at the rate of 400±50 rpm at 25°C for a contact period varying from 15 to 120 minutes using a flask shaker (Stuart Scientific, SF1 model) equipped with a temperature controlled water bath. Also, a series of experiments were carried out at the same conditions mentioned above by using pure $CaCO_3$ (Merck 2069) and calcined DCC produced at different temperatures. At the end of the predetermined contact time, the suspensions were filtered by using filter paper (Advantec Toyo 6) and the supernatants were acidified with 0.5 ml of concentrated nitric acid to prevent the precipitation of metal ions.

Concentration of Cr(III) and Cd ions in the supernatants were determined using a Perkin Elmer 370 model atomic absorption spectrophotometer (APHA *et al.*, 1975). All experiments were performed in duplicate, and results within ±5% were considered acceptable.

To estimate the organic pollution potential of DCC and CDCCs to be contacted with water, a series of experiments were carried out by contacting these precipitants with distilled water. The chemical oxygen demand (COD) of the samples, which is a measure of organic pollution, was determined by dichromate method (APHA *et al.*, 1975).

Figure 1. The variation of chemical oxygen demand (COD) of the water contacted with carbonatation cake(DCC) and CDCCs obtained at different temperatures (First values belong to carbonatation cake dried at 70°C) (Conditions: contact time,120 min.; temperature, 25°C.)

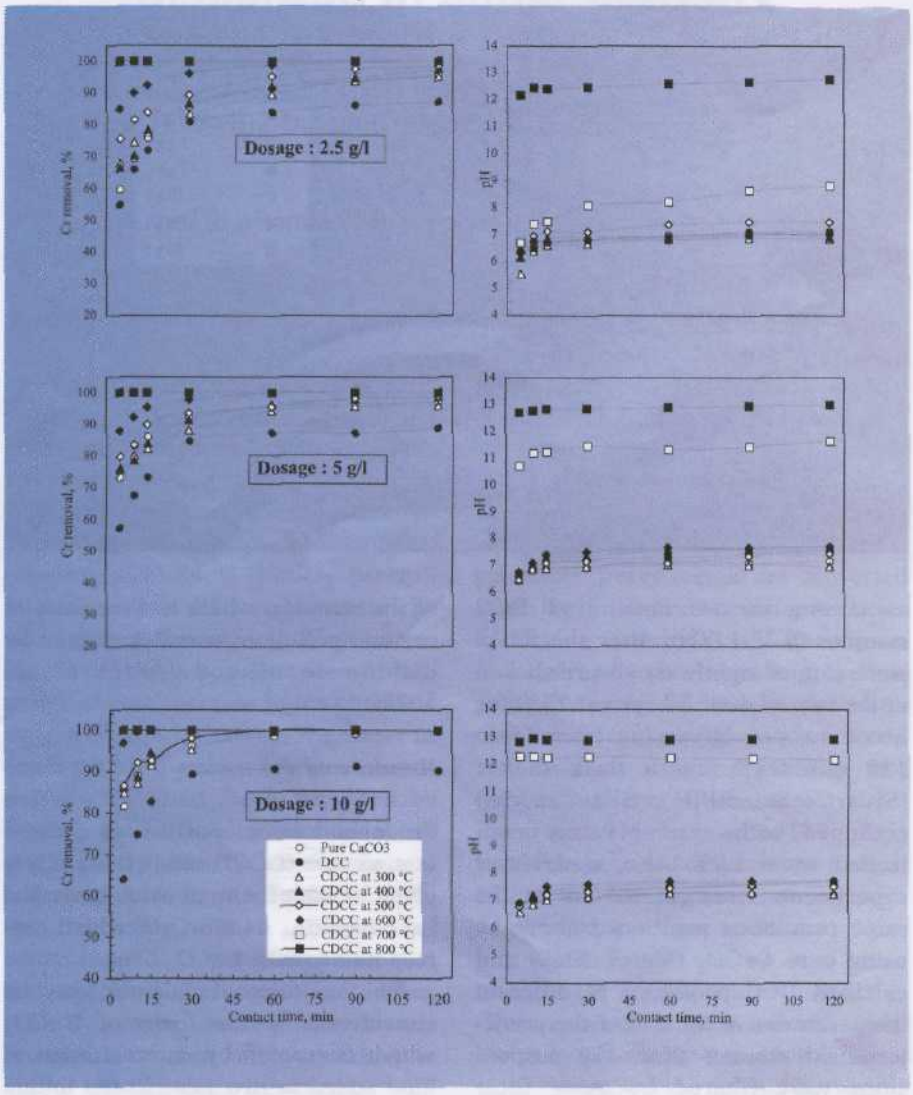


Results and discussion

The chemical composition of carbonatation cake (DCC) used in this study is given in Table1. On an oxide basis, the cake contains 44.8% CaO, which corresponds to 80% $CaCO_3$.

The majority of calcium may be considered in the form of $CaCO_3$ which is formed by carbonatation of lime added to raw juice in the liming process. The pH of I.carbonatation process is quite high (10.8-11.2), hence, a small amount of calcium in the cake may be in the form of $Ca(OH)_2$. However, a small amount of calcium may be in different forms such as sulphate, phosphate, oxalate and other organic salts stemming from sugarbeet. As a result, it can be stated that the DCC mostly consists of $CaCO_3$ which has an important role in metal precipitation process. The weight losses in the CDCC samples obtained by heating DCC are tabulated (Table 2). The weight loss is dependent on calcination temperature. For example, while weight loss at 300°C was 10.84%, it increased to 46.09% at

Figure 2. Effect of contact time on the removal of Cr(III) by pure $CaCO_3$, carbonatation cake (DCC) and CDCCs obtained at different temperatures (Conditions: initial pH, 2.00±0,05; initial concentration of solution, 100 mg-Cr(III) l^{-1}; temperature, 25°C)



800°C. In addition, it was observed that the colour of CDCCs turned gradually from grey to black tone as temperature increased from 300 to 600°C. Above 600°C, CDCCs got lighter and lighter and white-coloured product was obtained at 800°C. The change in the colours of CDCCs can be attributed to the carbonisation and incineration of organic materials present in DCC.

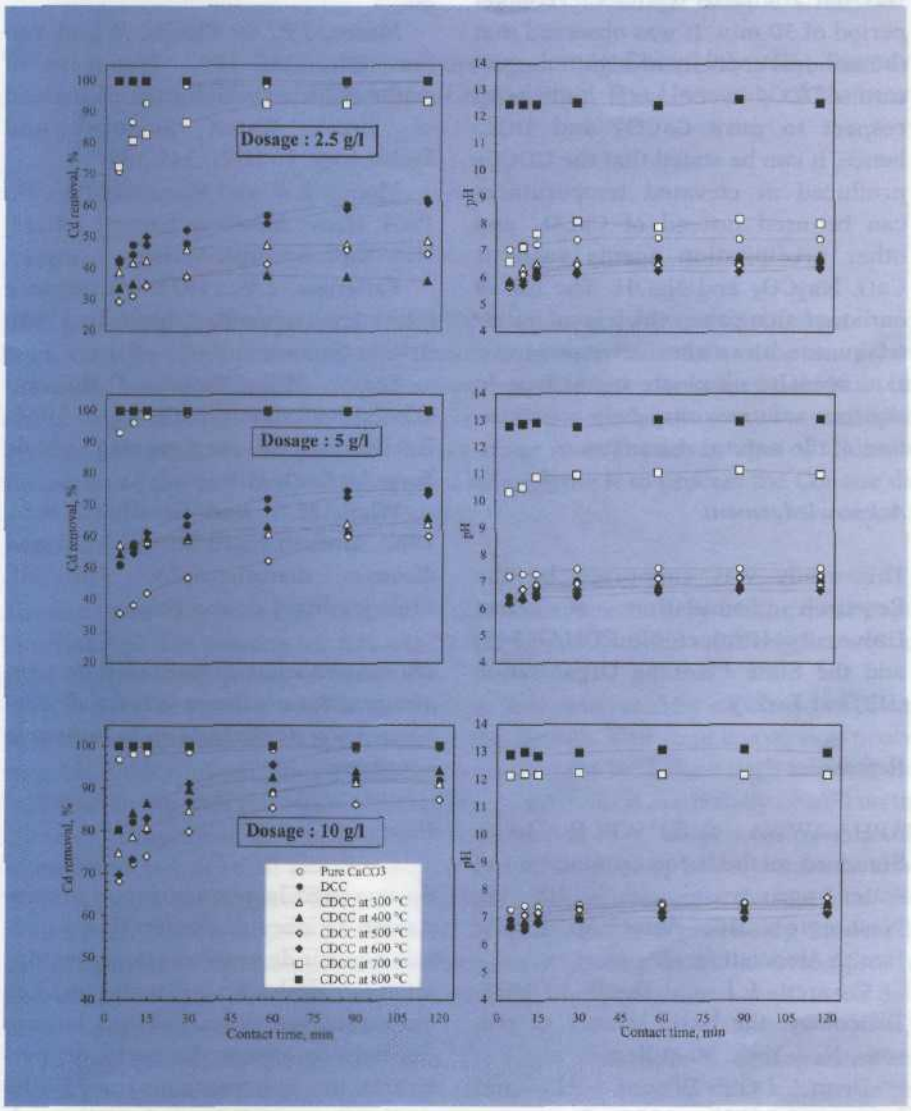
The results of the experiments carried out to estimate chemical oxygen demand (COD) of water contacted with DCC and CDCC samples produced at different temperatures are shown in Figure 1. In these experiments, various amounts of the DCC and CDCCs (0.1-5.0 g) were contacted with 100 ml distilled water for 120 min. COD was determined in the supernatants. As seen from the Figure, when the dosage of the DCC increased, the values of COD of water contacted with the cake increased. For the dosage of 2.5, 5.0 and 10.0 g l^{-1}, the COD of water samples were determined as 90, 130 and 170 mg-O_2 l^{-1}, respectively. When a high dosage of 50 g l^{-1} was used, the COD of supernatants reached to 600 mg-O_2 l^{-1}. As expected, the higher cake dosage, the greater the amount of organics released from the cake into the water.

In experiments using the CDCCs, the COD of the water decreased with a rise in the temperature of calcination. The COD value of water contacted with the CDCC obtained at 400 ∞C was about 40 mg-O_2 l^{-1} for all the dosages. There was no significant difference among the values of CODs of water treated with CDCCs obtained at 500 and 600°C. The CDCCs produced at 700 and 800°C did not, to a considerable extent, introduce any organic pollution to the water. This confirms that the organic materials in the cake decomposed during calcination at high temperatures.

Figure 2 shows the removal yield of Cr(III) ions by various dosages of pure $CaCO_3$, DCC and CDCCs produced by heating the DCC at different temperatures (300-800°C) as a function of contact time for an initial concentration of 100 mg Cr(III) l^{-1} at 25°C. Figure 2 also includes the change in the final pH of the solutions with contact time.

It can be seen that the Cr(III) removal efficiency of all precipitation agents used increased with contact time for all dosages. The removal percentage of Cr(III) did not show a remarkable increase after a contact time of 30 min, especially for the higher dosages. The removal capacity of DCC was lower compared with the other agents. When the DCC were contacted with a 100 ml Cr(III) solution (100 mg Cr-(III) l^{-1}) at dosages of 2.5, 5.0, 10.0 g l^{-1} for 30 min the amounts of Cr(III) removed was 80.9%, 84.8% and 89.3%, respectively. While pure CaCO3 e removed 85.7, 92.3 and 96.2% Cr(III), with CDCCs at high temperatures (700, 800°C), the removal of Cr(III) was complete. The removal efficiencies of the CDCCs produced at lower temperatures (300-600°C) were comparable to that of pure CaCO3. As expected, with increasing the dosage of the precipitating agents, the removal of Cr(III) ions increased. However, by using the CDCC obtained at 800°C, it was observed that all the Cr(III) in the working solutions was removed within a contact time of 5 min. Even when this CDCC was used at dosages below 2.5 g l^{-1}, the Cr(III) ions in 100 ml solution with a concentration of 100 mg l^{-1} were completely removed within 5 min. 100% removal of Cr(III) was not achieved by using pure $CaCO_3$ except in experiments in which the pure

Figure 3. Effect of contact time on the removal of Cd by pure $CaCO_3$, carbonatation cake (DCC) and CDCCs obtained at different temperatures (Conditions: initial pH, 2.00±0,05; initial concentration of solution, 100 mg-Cd l^{-1}; temperature, 25°C)



$CaCO_3$ was contacted with 100 ml Cr(III) solution (100 mg l^{-1}) for 120 min at a dosage of 10 g l^{-1}. As stated previously, the precipitation of metal hydroxides is dependent on the amount of $CaCO_3$ leading to an increase in the pH of solution by neutralising the acidity.

$$CaCO_3 + H_3O^+ \forall\ Ca^{2+} + CO_2 + H_2O \quad (1)$$

That the high temperature treated CDCCs are more effective precipitants can be attributed to their free CaO content. $CaCO_3$ in these CDCCs can partially convert into CaO which forms $Ca(OH)_2$ in aqueous solutions. As is commonly known, $Ca(OH)_2$ has a higher neutralisation capacity with respect to pure $CaCO_3$. The precipitation extent of Cr(III) ions is directly dependent on the neutralisation capacity of the agents to be used. The precipitation mechanism of Cr(III) ions is based on hydrolysis reactions, described as follows.

$$[Cr(H_2O)_6]^{3+} + H_2O\ \Delta\ [Cr(OH)(H_2O)_5]^{2+} + H_3O^+ \quad (2)$$

$$[Cr(OH)(H_2O)_5]^{2+} + H_2O\ \Delta\ [Cr(OH)_2(H_2O)_4]^+ + H_3O^+ \quad (3)$$

$$[Cr(OH)_2(H_2O)_4]^+ + H_2O\ \Delta\ [Cr(OH)_3(H_2O)_3\ ] + H_3O^+ \quad (4)$$

With the neutralisation of H_3O^+ ions by CaO and/or $CaCO_3$ the hydrolysis reaction equilibrium move to the right and Cr(III) ions are precipitated in hydroxide form. Because of the high CaO content, the Cr(III) removal efficiency of the CDCCs mentioned above is higher than that of pure CaCO3, DCC and other CDCCs obtained at lower temperatures.

In experiments using low temperature treated CDCCs and DCC samples at dosages of 5 and 10 g l^{-1}, although the pHs of solutions increased within the contact period of 15 min, after this point, the final pH values stabilised to 6.5-7.5. On the other hand, the final pHs of solutions using CDCCs produced at high temperature (700,800°C) at dosages of 5 and 10 g l^{-1} were above 10.5. This clearly shows that the neutralisation capacity of high temperature CDCCs are higher due to the presence of CaO.

The results relating to Cd removal are shown in Figure 3. In this section of the study, 100 ml of 100 mg l^{-1} Cd solutions were contacted with 0.25, 0.5 and 1.0 g of the precipitation agents at 25°C for contact times ranging from 5 to 120 min. The Cd removal yield of the CDCC obtained at 800°C was 100% for all the dosages. Cd ions could be completely removed from the solution by CDCC obtained at 700°C except for the dosage of 2.5 g l^{-1}. The removal mechanisms of Cd ions from aqueous solutions in the hydroxide form is based on the neutralisation of acidity, as described for Cr(III) removal. Although the final pHs of suspensions in which pure $CaCO_3$ were used at lower dosage (2.5 g l^{-1}) were lower than those of the CDCC produced at 700°C, the Cd removal capacity of pure $CaCO_3$ was higher. This suggests that Cd ions may precipitate in the form of carbonate. The Cd removal capacity of DCC samples were generally higher with respect to the CDCCs produced at 300, 400 and 500°C. In the experiments that DCC and the low temperature CDCCs (300-600) were used, although the Cd

removal efficiency of these agents were different from each other, there was no noticeable difference among the final pHs of the suspensions. This result shows that only the neutralisation of acidity by $CaCO_3$ and CaO present in the CDCC samples and the cake do not play a role in the precipitation of Cd ions. Precipitation of Cd ions in the form of carbonate, the existence of free CaO in the agents and partial adsorption of Cd ions on formed $CaCO_3$ affect, to a large extent, the precipitation yield of Cd ions in the hydroxide form. The presence of organic materials with functional groups such as alcohol, acid, amine and amid in precipitation agents may reduce the precipitation yield by forming complexes with metal ions (Lanouette, 1977). For these reasons, it can be stated that the removal mechanism of Cd ions by these agents is very complex.

It must be noted that all Cd and Cr(III) ions can be removed from the working solutions by using high temperature treated CDCCs within a short contact time of 5 min. However, the pHs of treated solutions were above 10 for all conditions examined, which require subsequent pH adjustment before discharge into the environment. Of course, this situation can be appreciated as a disadvantage for the precipitation process. However, the alkalinty of the treated solutions can be kept at reasonable levels by using an appropriate dosage (lower than 2.5 g l^{-1}) of the CDCCs.

Conclusion

I.carbonatation cake (DCC) used in this study contains 80 % $CaCO_3$ on dry basis and the rest mostly consists of organic materials originating from sugarbeet.The amount of organic contaminants released into water contacted with precipitation agents decreased with increasing temperature at which the DCC were calcined. The removal of Cr(III) and Cd ions from aqueous solutions at concentration of 100 mg l^{-1} by using DCC and CDCCs was studied and 100 % removal was reached when the high temperature treated CDCCs (700, 800°C) were used in the dosage of 2.5 g l^{-1} within contact time of 5 min. Cr(III) and Cd removal yield of the CDCCs obtained at lower temperatures (300-600°C) increased with contact time, however, the removal was not complete within the contact period of 30 min. It was observed that the removal capacity of high temperature CDCCs were very high with respect to pure $CaCO_3$ and DCC, hence, it can be stated that the CDCCs produced at elevated temperatures can be used instead of $CaCO_3$ and other precipitation agents such as CaO, Na_2CO_3 and NaOH. The use of carbonatation cake, which is an industrial waste, as an alternative precipitation agent to eliminate metal ions in aqueous solutions may help conservation of the natural resources.

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Un estudio sobre la remoción de metales pesados mediante la torta de carbonatación descartada en la industria azucarera

Resumen

Se investigó la remoción por precipitación de iones de cromio (III) y cadmio a partir de muestras de aguas sintéticas de deshecho utilizando torta de carbonatación descartada en la producción de azúcar. La torta de carbonatación que contiene un 75-80% de $CaCO_3$ precipita cromio (III) y cadmio neutralizando la acidez de la solución. No obstante, las substancias orgánicas en la torta causan un incremento en la demanda de oxígeno químico del agua en contacto con la torta. Se observó que las formas calcinadas obtenidas calentando la torta de carbonatación por encima de los 600°C precipitan los iones de cromio y cadmio más efectivamente sin aumentar la contaminación orgánica del agua tratada. Se concluye que las tortas de carbonatación calcinadas pueden ser usadas en la remoción de metales pesados en lugar del carbonato de calcio y/o cal en el agua de tratamiento.