Binding of Calcium and Magnesium by Modified Onion Skins

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Synopsis

The use of modified onion skins for binding of Ca^{2+} and Mg^{2+} from solutions has been investigated. The effect of time of equilibration, temperature, and pH on the sorption of the metal ions have been studied. Batch and column experiments have been performed and the adsorption isotherms have been plotted. The capacities with respect to Ca^{2+} and Mg^{2+} were found to be 4 and 16 meq, respectively, per gram of the substrate when separate column experiments were conducted using 1 L of solution containing 1000 meq of the respective metal ions at pH 6. With a solution containing 10 meq each of Ca^{2+} and Mg^{2+} together, however, the substrate seems to exhibit greater preference for Ca^{2+} than Mg^{2+}. The sorbed metal ions from the substrate can be leached into solution with a decinormal solution of HCl and the washed bed can be reused. In view of the complex organic nature of the onion skin and its considerable capacity to bind Ca^{2+} and Mg^{2+}, the possibility of its use for preventing scale formation in boilers is indicated.

INTRODUCTION

The need for effective and economic removal of Ca^{2+} and Mg^{2+} from the water to be used in the boilers for preventing scale formation resulted in the search for some unconventional methods and materials that might be useful in this field. Many agricultural by-products which are available at little or no cost have been found to be capable of binding metal ions from solutions by adsorption, chelation, or ion exchange.

The use of some of agricultural by-products have been reported, such as modified cotton by Roberts et al.;[1,2] starch xanthates by Rayford et al.,[3] Wing et al.,[4,5] Marani et al.;[6] tree barks by Masri et al.,[7] Randall et al.,[8–11] Kumar et al.;[12] peanut skins by Randall et al.;[13,14] selected agricultural products and by-products by Friedman et al.;[15] natural polymeric and agricultural waste materials by Kumar et al.;[16–18] and polymerized onion skin by Kumar et al.[19] for binding of heavy metal ions from waste waters.

While studying the variations in effectiveness of barks as scavengers for heavy metal ions, the sorption of Ca^{2+} and Mg^{2+} by a few selected barks such as Western hemlock and Coastal Redwood Bark was reported by Randall.[20] Effects of light metal ions such as Na^+, Ca^{2+}, and Mg^{2+} on the sorption of heavy metal ions by formaldehyde-treated peanut skins and some barks have also been reported by Young et al.[21]

In this article, the results obtained on the binding of Ca^{2+} and Mg^{2+} by modified onion skins are presented.

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EXPERIMENTAL

Substrate

The red onion skins were procured free of cost from the local market. They were dried and powdered in a grinding machine. The fine powder was stirred with 1% NaOH for 1 h in order to leach out the organics from the onion skins, filtered, and washed with double-distilled water until the pH of the filtrate was 7. The residue was then washed with acetone, dried at 80°C, and powdered. This substrate was used for further studies.

General Procedure

Equilibrium experiments were conducted by treating 1 g of the substrate with 25 mL of solution containing the respective metal ions of the desired concentration in stoppered bottles and agitating them for 10 min at room temperature in a shaking incubator. Then the mixture was filtered and the filtrate was analyzed for the respective metal ions. The quantity of the metal ions adsorbed was calculated by the difference in initial and final concentrations in the solution.

Column experiments were conducted using glass tubes of 20 mm internal diam packed with glass wool at the bottom. A uniform and compact column of the substrate was prepared by pouring 5 g of the substrate suspended in double-distilled water into the glass tube. Some glass wool was then placed on the top of the bed to prevent the substrate particles from floating. One liter of the metal ion solution of known concentration was slowly introduced at the top of the column and allowed to flow downward through the substrate bed. The flow rate, which could be adjusted by a stopcock at the bottom, was maintained at 5 mL per minute. The fraction of the metal ions adsorbed was determined by the difference in the initial and final concentrations of the solution. The sorbed metal ions can be eluted with 0.1 N HCl and washed with distilled water; then the bed can be reused.

Analysis

All the metal ion concentrations in solution were determined by the conventional complexometric titrations using EDTA.[22]

RESULTS AND DISCUSSION

The efficiency of binding Mg^{2+} by red onion skins pretreated by different methods is given in Table I. It can be seen that alkali-treated onion skins were very efficient in their metal binding capacity. Hence, the alkali-treated onion skin substrate was used for further investigations. This has other advantages, including simplicity of the treatment process and relative cheapness of the reagent used.

In each case 1 g substrate was equilibrated with 25 mL of the metal ion solution of the respective concentration at pH 6.

TABLE I
Relative Efficiencies of Different Onion Skin Substrates for Binding Mg^{2+} [a]

Serial no.	Feed concentration (ppm Mg^{2+})	mg Mg^{2+} adsorbed			
		A	B	C	D
1	240	5.28	5.2	5.15	0.85
2	480	9.88	8.9	8.35	1.13
3	1,200	12.15	10.2	9.3	1.8
4	1,800	12.6	10.35	9.45	2.25
5	2,400	12.8	10.35	9.9	2.44
6	12,000	21.7	12.37	9.28	9.28

[a] A, powdered onion skin treated with 1% NaOH; B, powdered onion skin treated with epichlorohydrin;[23] C, powdered onion skin xanthated after epichlorohydrin treatment;[23] D, powdered onion skin treated with $HCHO/H_2SO_4$.[8]

Equilibrium Experiments

In order to determine the minimum time of equilibration required for the maximum sorption of Ca^{2+} and Mg^{2+} by the substrate, several equilibrium experiments were conducted at different equilibration times ranging from 5 min to 24 h. In each of these experiments 1 g substrate was treated with 25 mL of 20 meq solution Ca^{2+} or Mg^{2+} at pH 6 and agitated for the desired length of time. The results showed that maximum sorption of Ca^{2+} and Mg^{2+} by the substrate occurred within 5 min. There was no change in the extent of adsorption even after an equilibration time of 24 h.

Effect of pH

The results of the investigations on the effect of pH on the uptake of Ca^{2+} and Mg^{2+} are depicted in Figure 1. In each case 1 g of the substrate at the desired pH was gently agitated for 10 min with 25 mL of 20 meq solution of Ca^{2+} or Mg^{2+}. The data show that best adsorption of the metal ions can be obtained in the pH

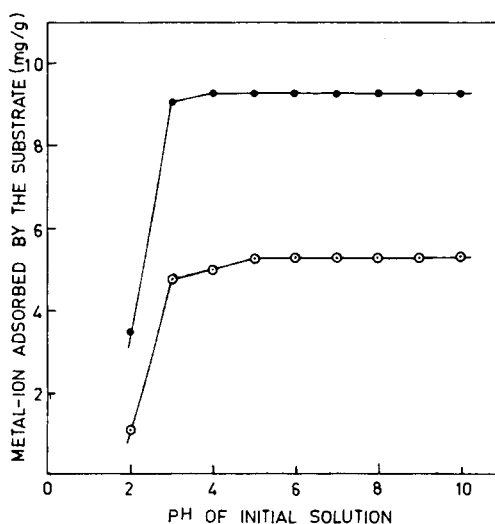Fig. 1. Effect of pH on the removal of Ca^{2+} (●) and Mg^{2+} (○).

range of 4–10 in the case of Ca^{2+} and of 5–10 in the case of Mg^{2+}. Studies at pH values beyond 10 have not been made in order to preclude the possibility of precipitation of the metal hydroxides.

Effect of Temperature

The effect of temperature on adsorption of Ca^{2+} and Mg^{2+} by the substrate was studied by carrying out equilibrium experiments at 30°C, 50°C, and 100°C. In each case 1 g of substrate was equilibrated with 25 mL of 20 meq solution of the respective metal ion at pH 6. The results indicated that the metal ion uptake remained the same at all three temperatures studied.

Effect of Concentration

The effect of initial metal ion concentration on the sorption of Ca^{2+} and Mg^{2+} was studied, and the results are shown in Tables II and III. It can be seen from the data that the metal ion uptake increases progressively with the increase in initial metal ion concentration. A typical adsorption isotherm is depicted in Figure 2.

TABLE II
Effect of Concentration on the Sorption of Ca^{2+} [a]

Serial no.	Feed Concentration (ppm Ca^{2+})	Effluent Concentration (ppm Ca^{2+})	mg Ca^{2+} adsorbed/g substrate
1	400	28	9.3
2	800	240	14.0
2	2,000	1,340	16.5
4	3,000	2,280	18.0
5	4,000	3,250	18.75
6	20,000	19,000	25.0

[a] In each case, 1 g substrate was equilibrated with 25 mL Ca^{2+} solution of the respective concentration at pH 6.

TABLE III
Effect of Concentration on the Sorption of Mg^{2+}

Serial no.	Feed Concentration (ppm Mg^{2+})	Effluent Concentration (ppm Mg^{2+})	mg Mg^{2+} adsorbed/g substrate
1	240	28.8	5.28
2	480	84.8	9.88
3	1,200	714	12.15
4	1,800	1,296	12.6
5	2,400	1,888	12.8
6	12,000	11,132	21.7

[a] In each case, 1 g substrate was equilibrated with 25 mL Mg^{2+} solution of the respective concentration at pH 6.
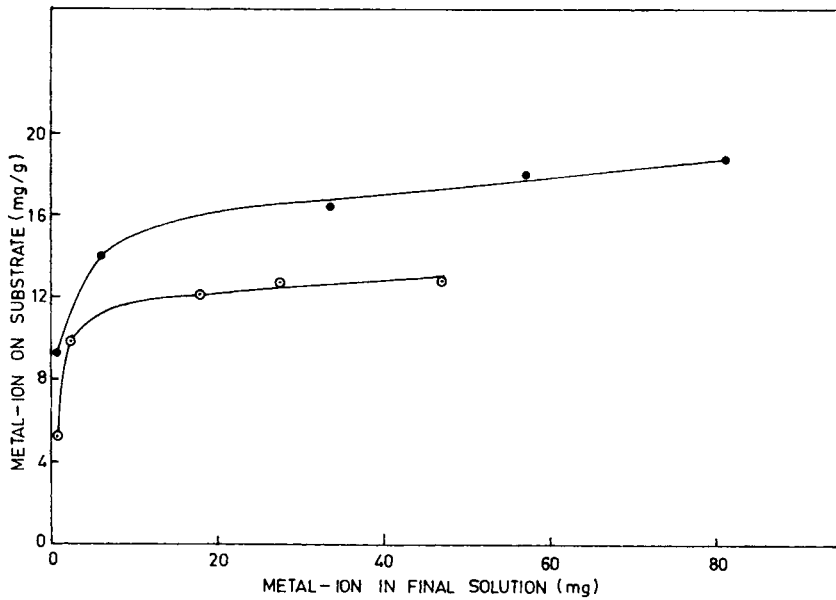
Fig. 2. Adsorption Isotherms for Ca^{2+} (●) and Mg^{2+} (○). In each case, 1 g substrate was equili-
brated with 25 mL Ca^{2+} or Mg^{2+} solution of the respective concentration at pH 6.

Column Experiments

The results on the column experiments conducted on the substrate using
different concentrations of Ca^{2+} and Mg^{2+} are given in Tables IV and V. It can
be seen that as in the case of batch experiments stated above, the absolute metal
ion uptake by the substrate increases with increase in the initial metal ion con-
centration, although the percentage of metal ions removed decreases. Further,
with lower metal ion concentrations in the feed, the effluent metal ion concen-
tration was reduced to sub-ppm levels. It can also be seen that with the highest
concentrations of the metal ions studied (i.e., 20,000 ppm for Ca^{2+} and 12,000
ppm for Mg^{2+}), the amounts of Ca^{2+} and Mg^{2+} adsorbed per gram of substrate
were 4 and 16 meq, respectively.

In the case of experiments with Ca^{2+} using lower metal ion concentrations
(<4000 ppm), the pH of the effluent was higher than the influent pH. In ex-
periments with higher metal ion concentrations, however, there was a slight

TABLE IV
Removal of Ca^{2+} from Solution on Packed Column of Substrate[a]

Serial no.	Feed Concentration (ppm Ca^{2+})	Effluent Concentration (ppm Ca^{2+})	mg Ca^{2+} adsorbed/5g substrate	meq/g substrate	pH of Effluent
1	40	0.88	39.12	0.39	7.5
2	400	308	92	0.92	7.0
3	4,000	3,840	160	1.6	6.1
4	10,000	99,800	200	2.0	5.4
5	20,000	19,600	400	4.0	5.4

[a] In each case, 1 L Ca^{2+} solution of the respective concentration at pH 6 was passed down the
column containing 5 g substrate at the rate of 5 mL/min.

TABLE V
Removal of Mg^{2+} from Solution on Packed Column of Substrate

Serial no.	Feed Concentration (ppm Mg^{2+})	Effluent Concentration (ppm Mg^{2+})	mg Mg^{2+} adsorbed/5 g substrate	meq/g substrate	pH of Effluent
1	24	0.24	23.76	0.396	6.24
2	240	182.4	57.6	0.96	6.34
3	2,400	2,136	264	4.4	6.4
4	6,000	5,400	600	10.0	6.48
5	12,000	11,040	960	16.0	6.64

ᵃ In each case, 1 L Mg^{2+} solution of the respective concentration at pH 6 was passed down the column containing 5 g substrate at the rate of 5 mL/min.

decrease in the effluent pH as compared to the initial pH of 6. In the case of experiments with Mg^{2+}, a slight increase in pH was observed as compared to an initial pH of 6 at all the metal ion concentrations studied.

Competition of Ca^{2+} and Mg^{2+} for the Substrate

In order to determine the competition of Ca^{2+} and Mg^{2+} for the substrate, when both the metal ions coexist in solution, 1 L of the solution at pH 6 containing 10 meq each of Ca^{2+} and Mg^{2+} was passed down the glass column of 20 mm internal diam packed with 2 g of substrate at the rate of 5 mL/min. The effluent was analyzed for its Ca^{2+} and Mg^{2+} contents. It was calculated that 1.4 meq of Ca^{2+} and 0.8 meq of Mg^{2+} were bound on the substrate. Thus, it appears that Ca^{2+} rather than Mg^{2+} is adsorbed on the substrate.

CONCLUSION

The present investigation clearly shows that the treated onion skin has considerable capacity to bind Ca^{2+} and Mg^{2+}. The onion skin already contains some Ca^{2+} and Mg^{2+}, which were probably taken up from the soil. But it still has further capacity to bind appreciable quantities of Ca^{2+} and Mg^{2+} from solutions. Apart from agricultural and soil chemistry applications, the present studies indicate the potential application of onion skins and similar inexpensive agricultural by-products for controlling scale formation in high-pressure boilers. The exhausted substrate can easily be expelled from the boilers during the blow-down cycle and fresh additions can be made periodically. In view of their complex organic nature, such substrates, in addition to binding residual Ca^{2+} and Mg^{2+} from the feed water may also help keep salts formed in the boiler in the form of sludge which can be expelled during blow-down operation. Further work in this direction is in progress.

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