

A Modified Miscible Displacement Technique for Investigating Adsorption-desorption Kinetics in Soils¹

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ABSTRACT

The use of miscible displacement techniques to study kinetics of ion exchange in clay minerals and soils is increasing. Although only 1 g or less of adsorbent is often used, some of the adsorbate solution will always be retained by the adsorbent. The dilution of the incoming solution by the retained solution is easily mistaken for either adsorption or desorption, resulting in an overestimation of either process. A device that ensures constant dilution volumes, regardless of adsorbent, was developed to differentiate the adsorption-desorption process from the dilution process.

Additional Index Words: dynamics of ion exchange, K and B kinetics, kinetic methodology.

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THE USE of a flow or miscible displacement technique to describe adsorption-desorption phenomena for clay minerals and soils has many advantages over traditional batch techniques. These include (i) use of narrow soil to solution ratios with adsorbate concentrations that approach field conditions, (ii) measurements at initial time steps of the reaction are possible, (iii) displaced species are removed from the vicinity of the reaction site, and (iv) the concentration of the adsorbate does not change as the reaction proceeds (Zasoski and Burau, 1978; Sparks and Rechigl, 1982). The miscible displacement technique as developed by Sparks et al. (1980) involves the introduction of an adsorbate solution of known concentration onto a thin wet layer of soil. The adsorption reaction is then followed by monitoring the increasing concentration of the leachate with time. At an apparent equilibrium, the effluent concentration equals that of the initial adsorbate solution. The desorption reaction is studied in a similar way, the reaction being followed by monitoring the decreasing concentration of the previously adsorbed ion. In either case, the reaction is followed by determining the ionic concentration in solution. This means that any process which affects a change in concentration will be interpreted as adsorption or desorption.

For the miscible displacement technique, the dilution of incoming adsorbate solution by the liquid used to load the adsorbent on to the filter, or the washing out of leftover adsorbate solution during desorption should result in concentration changes not due to adsorption or desorption. These concentration changes are potential sources of error. The effect of dilution may be particularly significant when studying soils that are known to adsorb very small quantities of ions,

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such as some of the micronutrient species. In these cases the dilution effect or washing out effect alone may account for the total amounts *adsorbed* or *desorbed*. Regardless of the adsorbent used, some solution will be held back or entrained on top of the filter. This entrained solution cannot be completely removed by suction, and the total amount will be dependent on the waterholding capacity of the adsorbent. The dependence of the amount of entrained fluid on the nature of adsorbent means that the magnitude of the dilution effect will be different for each adsorbent. The objectives of this study were to determine the magnitude of the dilution effect and to develop a method to account for it.

MATERIALS AND METHODS

Initially, the miscible displacement technique (Sparks et al., 1980) was used to assess the magnitude of error caused by the dilution or washing out of adsorbate solution. Using no adsorbent and acid-washed sand, gravimetric determinations of entrained fluid were conducted. Then determinations of boron (B) adsorption and desorption were carried out.

A new device was constructed which allows quantification of the dilution effect (Fig. 1). The basic components for the construction of this device include the barrel and plunger from a 30 mL B-D plastic syringe and a 25 mm Nuclepore Swin Lok Filter Holder. The filter holder is modified and glued to the top of the syringe barrel, and the base of the barrel is threaded to provide plunger height adjustment. The device enables one to add and to maintain a known quantity of fluid to a known amount of adsorbent regardless of the adsorbent used. The new device replaces the miscible displacement filter apparatus; the added fluid represents the entrained fluid on the miscible displacement filter. Operation of our apparatus is simple, a magnetic stirring bar is placed in the chamber above the plunger, a known amount of dry adsorbent is loaded into the reaction chamber, a 0.2 μm Gelman Metrical Membrane Filter and the top are attached, and a known volume of *entrained* fluid is added using a hypodermic syringe. A plunger is then used to displace the excess air from within the reaction chamber, thus enabling a known volume to be diluted or washed out. This volume is maintained throughout the adsorption and desorption reactions. A peristaltic pump is used to maintain a flow rate of 1 mL min⁻¹ and an LKB Ultrarac II 2070 fraction collector is used to monitor the reaction at 2 min intervals. A magnetic stirrer is used to ensure adequate mixing in the reaction chamber; stirring speed is kept to a minimum, about 100 rpm, to minimize abrasion of the adsorbent.

Standard dilution and wash-out curves were determined for the desired volume of entrained solution. These standard curves were identical and were used to quantify the dilution effect. Since this volume is then used for all adsorbents, the effect of dilution can be subtracted from the dilution-plus-adsorption curve or the dilution-plus-desorption curve for all adsorbents. The standard dilution curves were run in triplicate using no adsorbent and acid-washed sand as an inert adsorbent. Adsorption-desorption studies for B using Chester soil (Typic Hapludults) and K-Ca exchange on kaolinite were carried out.

Boron studies were conducted using a 2 μg B mL⁻¹ so-

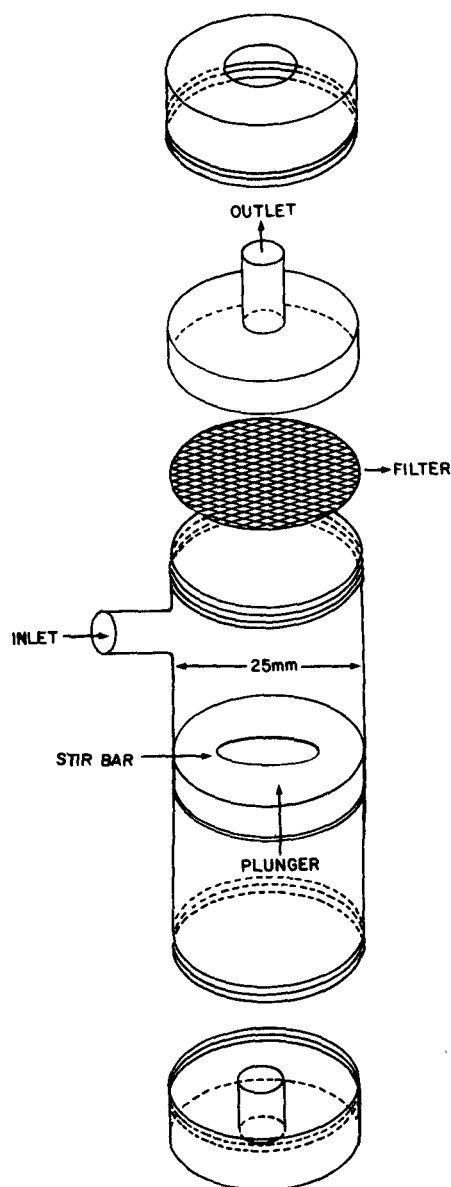


Fig. 1. Schematic diagram of modified miscible displacement reaction chamber.

lution and 1 g of soil. Boron was determined using a modified azomethine-H method (Parker and Gardner, 1981). Potassium exchange studies were conducted using a $50 \mu\text{g K mL}^{-1}$ solution and 1 g of well crystallized Washington County Georgia kaolinite obtained from the Univ. of Missouri Source Clays Depository. Potassium in solution was determined using atomic absorption spectrophotometry.

RESULTS AND DISCUSSION

The results of the initial work using the earlier miscible displacement technique (Sparks et al., 1980) with no adsorbent (Fig. 2), and with acid-washed sand were similar. For these systems where no B adsorption or desorption would be expected, the miscible displacement technique predicts both to occur. However, total amounts can be predicted quite well using the gravimetrically determined value for entrained fluid multiplied by the concentration of the initial B solution. Although such a calculation allows the total error to

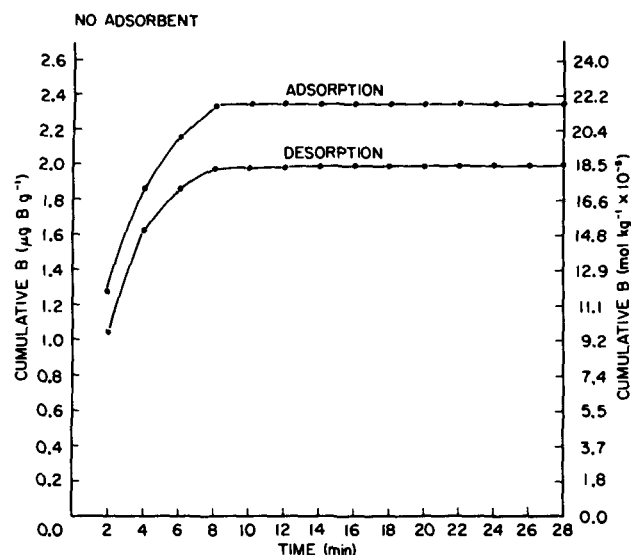


Fig. 2. Apparent adsorption and desorption of B, determined using the original miscible displacement technique (Sparks et al., 1980) with no adsorbent.

be determined, it does not provide a concentration distribution with time. Moreover, since the amounts of entrained fluid differed for the same adsorbent, the possibility of developing a standard curve to describe the error was deemed unlikely.

The standard curves developed for the new technique using no adsorbent and acid-washed sand were essentially the same. Each was conducted in triplicate; the CV values of the combined triplicate runs, at each time step, were $< 5\%$ indicating excellent reproducibility. This means that the presence of an inert material (sand) did not affect the dilution process by accelerating or inhibiting the mixing process. Therefore, one can conclude that the mixing process will not be affected by the presence of an adsorbent. Standard curves for K were also run in triplicate with similar CV values ($< 5\%$). When the K curves were scaled down to the B curves, no significant difference was seen. These findings indicate the reproducibility of the standard curve is sufficient to attempt to differentiate adsorption and desorption processes from dilution processes.

The adsorption and desorption of B on Chester soil was used to represent a low capacity adsorption system. This system had been studied previously using the miscible displacement technique (Sparks et al., 1980) and B adsorption and desorption had been predicted. However, we found by determining the amount of entrained fluid, that the predicted amount of adsorbed and desorbed B was entirely due to the dilution or wash-out error. This means that no B was adsorbed or desorbed. When this system was studied using the new technique the adsorption-desorption curves were no different from the standard curves, therefore no B adsorption or desorption would be predicted. These results for Chester soil are not surprising since the pH of the soil was equal to 4.8.

When the new device was used to study the adsorption of K on Ca-saturated kaolinite, a significant difference existed between adsorption and dilution

Table 1. Apparent adsorption and desorption rate coefficients (k'_a and k'_d , respectively), and resultant ΔG° values, for K-Ca exchange on kaolinite.

	k'_a	k'_d	ΔG° kJ mol ⁻¹
	h ⁻¹		
With dilution	2.04	8.34	3.5
Minus dilution effect	1.56	5.88	3.3

(Fig. 3). The dilution effect greatly increased the prediction of total K adsorbed. When the standard curve is subtracted from the dilution-plus-adsorption curve the amount of K removed from solution by adsorption is determined. The total K⁺ adsorbed was about 40 mg kg⁻¹ less than that predicted by the original miscible displacement technique (Sparks and Jardine, 1984). Although gravimetric determinations of entrained fluid were not originally taken, recent work would indicate that between 0.8 and 0.9 mL of entrained fluid would be expected. This would lead to an overestimation of total K⁺ adsorbed equal to 40 to 45 mg K mL⁻¹. Similarly when desorption of K by Ca was followed, the amounts desorbed were overestimated since the entrained solution at the end of the adsorption run was equal in concentration to the initial adsorbate solution (50 $\mu\text{g mL}^{-1}$). The washing out of this solution results in the overestimation of desorbed K⁺. When the standard curve for desorption is subtracted from the combined curve, the amount of desorbed K⁺ is determined. If the adsorption and desorption processes are compared several conclusions can be made. The exchange reaction is reversible although the desorption of K by Ca is faster than the reverse. The preference for Ca by kaolinite is confirmed by positive ΔG° values (Table 1) calculated using a kinetics approach (Sparks and Jardine, 1981). The presence of entrained fluid increases both k'_a and k'_d but does not greatly affect any thermodynamic conclusions i.e., k'_a/k'_d does not change markedly. This means that for this system, where only one type of reaction site is expected, the presence of entrained fluid affected the adsorption and desorption processes equally. Further work is needed to determine the effect of entrained fluid on systems having more than one type of reaction site. In such a system, dilution may affect only the initial part of the reaction, and therefore, only the kinetics determined for the first reaction site.

A final comment should be made concerning the stirring of the soil solution. Stirring may eliminate the film diffusion component of the reaction (Boyd et al., 1947). However, a kinetic comparison of the new method to the original method is confounded by the fact that both diffusion and dilution processes are present in the original technique. A kinetic study designed to compare the two procedures is presently being conducted. In the latter study we have found that the cumulative amounts of adsorbed and de-

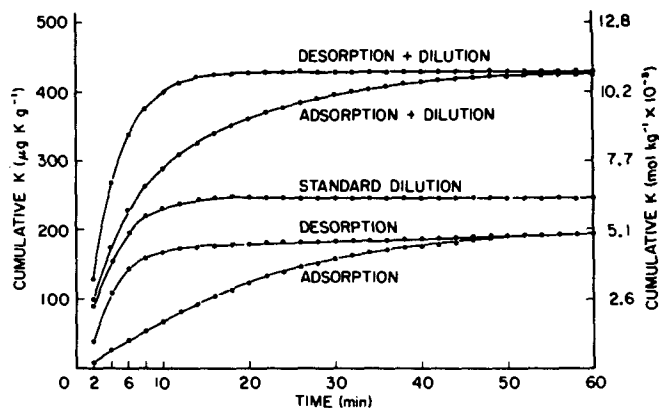


Fig. 3. Cumulative adsorption and desorption of K on kaolinite, determined using the modified miscible displacement reaction chamber.

sorbed K⁺ on kaolinite are different; however, both methods predict that (i) the reactions are reversible, (ii) the reactions conform to first-order kinetics, and (iii) Ca is preferred over K, i.e., ΔG° is positive.

CONCLUSIONS

It has been demonstrated that the fluid entrained on the filter of the miscible displacement apparatus is a significant source of error, especially for low adsorption capacity soils. The method proposed appears to account for the dilution or washing out effect. Regardless of adsorbent used, the amount of fluid *entrained* is held constant, meaning that its effect on concentration should be the same for every adsorbent. The proposed stirred-flow technique appears to refine the original miscible displacement technique in that a known source of error has been eliminated, yet the advantages of a flow technique are retained, and the kinetically based conclusions remain essentially unchanged.

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