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BASE EXCHANGE BETWEEN DYES AND SOILS

WILBUR L. HOFF[1] AND J. A. WILKINSON

Beaumont,[2] Rohland[3] and Wilkinson and Hoff[4] have shown the effect of acidity and alkalinity of solutions on the adsorption of dyes by soils. Ashley[5] found that during the adsorption of basic dyes by soils the dyes exchanged some of their positive ions for the metal ions of the soil thus fixing some of the dye by base exchange. Wilkinson and Hoff found that a methylene blue solution liberates more calcium and magnesium from a soil than does distilled water alone. Sante Mattson[6] found in the case of two soils that the methylene blue adsorbed was approximately equivalent to the monovalent and divalent bases that were set free. The purpose of this investigation is to determine quantitatively the relationship between the equivalents of dye adsorbed and the negative and metal ions liberated from several soils with two basic dyes and by comparison from this data find the fraction of the dye that is taken up by base exchange and the fraction held in some other way.

EXPERIMENTAL

The adsorption experiments were carried out by the percolation method of Lord[7] and Boyd.[8] Two basic dyes methylene blue ($C_{16} H_{18} N_3 SCl$) and neutral violet ($C_{14} H_{14} N_4 HCl$) which had been purified by several recrystallizations were used. The only metal impurity left in these was a small amount of iron in the methylene blue amounting to 0.0027 grams of iron per gram of dye. Correction was made for this in all the calculations.

The soil samples were obtained from the Department of Farm Crops and Soils of Iowa State College and were all of them Iowa Soils as follows: (1) Kansanian clay, (2) Webster clay loam from

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[1] This paper is from a portion of the work presented to the Graduate Faculty of Iowa State College in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Beaumont, Cornell Ag. Exp. Sta. Mem. 21, 494 (1914).

[3] Rohland, Glasind. 26, Nos. 19-22 (1915).

[4] Wilkinson and Hoff, Jour. Phys. Chem. 29, 808 (1925).

[5] Ashley, U. S. Bur. Standards Tech. Paper 23, 41 (1914).

[6] Sante Mattson, Jour. Am. Soc. Agron. 18, 458 (1926).

[7] Lord, Laboratory tests for determining the physical properties of subgrade soils. U. S. Bur. Public Roads.

[8] Boyd, Public Roads 6, No. 2, 34 (1925).

upland glacial soil which is usually neutral or alkaline, (3) Marion silt loam, very acid under natural conditions, (4) Carrington loam, upland glacial soil, Iowian drift, usually shows medium lime requirement, (5) Grundy silt loam, an upland loess soil, (6) Soil No. 1 was treated with an excess of calcium chloride solution so that all of the colloidal zeolitic material could undergo base exchange and all of the exchangeable bases be replaced by calcium. The soil was then washed with distilled water until the wash water gave no test for chlorides and was then dried and ground to pass a forty mesh sieve. This material is called No. 6 in the experiments.

The percolation tubes or adsorption columns were made by sealing a glass tube twelve centimeters long and one centimeter in diameter to another tube twenty centimeters long and two and a half centimeters in diameter. On the lower end of the smaller tube a piece of tubing two centimeters long was fitted by means of a ground glass joint, so that it would hold a small disk of filter paper which would keep the soil in place in the adsorption tube when this was standing upright.

The weighed sample of soil was mixed with a small amount of the standard dye solution, stirred well and after standing a little while was transferred completely by means of the standard dye solution into the percolating tube. The solution was allowed to filter slowly through the soil, a bare excess being kept present. The percolation was permitted to continue until some dye coloration appeared in the filtrate thus indicating that the soil was saturated with the dye. The volume of the clear liquid that came through was taken as a measure of the volume of standard dye adsorbed. The filtrates were analyzed for both anions and cations but the only anion found was chloride except in the case of soil No. 1 where some bicarbonate was present. As blanks, parallel with the dye solutions, similar tubes were run with distilled water of the grade of conductivity water as the percolating liquid. These filtrates were also analyzed for anions and cations and by subtracting these blanks from the values obtained from the dye solutions the amounts of ions set free by the dye could be determined.

The solutions were analyzed according to the following plan. The chloride was precipitated with an excess of silver nitrate and weighed as AgCl. The excess of silver was removed with hydrochloric acid and discarded. In the filtrate from this the R_2O_3 was precipitated with ammonium hydroxide and the calcium from this filtrate as calcium oxalate with ammonium oxalate and weighed as the oxide. In the filtrate from this the magnesium was precipitated as magnesium ammonium phosphate with secondary ammonium phosphate and weighed as the pyrophosphate. From the filtrate the excess of phosphate was removed with calcium chloride and the excess of calcium with ammonium oxalate. The sodium and potassium were determined in this filtrate as the chlorides and separated by the perchlorate method.

Although methylene blue and neutral violet are both basic dyes, they are not sufficiently dissociated in water solution to give a test for the chloride ion. However after the dye is adsorbed by the soil, chloride is found in the filtrate thus indicating that a metathetical change between the dye and the zeolite of the soil colloid has taken place. The amount of chloride in the filtrate should be equal to the amount of dye taken up by base exchange and this should also equal the amount of basic ions set free by the dye. If the dye were taken up in no other manner than by base exchange the three quantities, the chloride, the basic ions and the basic dye ion adsorbed should all be the equal.

In running the blanks with the distilled water it was found that the amounts of bases found in the solution that percolated through the soil were dependent not only upon the amounts of soil used but also upon the amount of water passed through and the time it took to percolate. In the blanks therefore an endeavor was made to have the same amount of distilled water percolate as dye solution for that soil and to have it pass through in the same time. Since the distilled water percolated through much slower than the dye solutions the rate of flow for the water was increased by applying the required amount of pressure to the solution above the soil. The dye solutions were made to contain two grams of the methylene blue or four grams of the neutral violet per liter. The data given in the following table are the averages of from three to ten results for each value given.

DISCUSSION OF RESULTS

For the sake of brevity the analytical data has all been calculated and expressed as milli-equivalents of the ions indicated in each column. In column 8 the total milli-equivalents of metal ions found in the solution after the treatment of the soil with the dye solution is given and in column 9 the same for the distilled water blanks and the differences between these or the amounts set free by the dye itself are given in column 10. The next column shows the milli-equivalents of dye adsorbed and the next the milli-

Table I — Base Exchange Between Dyes and Soils

Soil	Wg. Soil	Fe*	Ca.	Mg.	K.	Na.	Total Metals			Dye	Cl.	Metal Dye	Cl. Dye	Cl. Metal
							Dye	Water	Diff.					
CONDUCTIVITY WATER														
1	2 gm.	0.052	0.097	0.058	0.007	0.025		0.239						
2	2 gm.	0.013	0.050	0.042		0.037		0.146						
3	10 gm.	0.052	0.042	0.035	0.003	0.094		0.226						
4	5 gm.	0.022	0.087	0.032		0.018		0.159						
5	5 gm.	0.027	0.068	0.038				0.133						
6	6 gm.		0.045					0.045						
METHYLENE BLUE SOLUTION														
1	2 gm.	0.078	0.342	0.185	0.002	0.101	0.708	0.239	0.469	0.318	0.284	1.47	0.89	0.61
2	2 gm.		0.601	0.247	0.006	0.066	0.920	0.146	0.774	0.888	0.808	0.87	0.91	1.04
3	10 gm.	0.270	0.254	0.143	0.017	0.078	0.762	0.226	0.536	0.629	0.551	0.85	0.89	1.03
4	5 gm.	0.017	0.569	0.185	0.009	0.065	0.845	0.159	0.686	0.815	0.729	0.84	0.89	1.06
5	5 gm.	0.022	0.344	0.174	0.010	0.206	0.756	0.133	0.623	0.659	0.639	0.95	0.87	1.03
6	6 gm.		0.305				0.305	0.045	0.260	0.319	0.267	0.82	0.84	1.03
NEUTRAL VIOLET SOLUTION														
1	2 gm.	0.022	0.630	0.206		0.146	1.004	0.239	0.765	0.900	0.760	0.84	0.84	0.99
2	2 gm.	0.022	0.635	0.222	0.020	0.150	1.049	0.146	0.903	1.136	0.971	0.80	0.85	1.08
3	10 gm.	0.238	0.293	0.191	0.009	0.173	0.904	0.226	0.676	0.812	0.675	0.83	0.83	1.00
4	5 gm.	0.030	0.590	0.191	0.012	0.144	0.967	0.159	0.808	1.091	0.891	0.74	0.82	1.10

* All values in this table are given in milli-equivalents.

equivalents of chloride ion found in the solution from the dye. The last three columns show the different ratios between the values given in columns 10, 11 and 12. If all of the dye were replaced by base exchange only, the last three columns would all be the same and would be unity.

The last column shows that the ratio between chlorine ion and metal ions is approximately unity for most of the soils with the two dyes, thus indicating that for the metal ions set free by the dye an equivalent amount of chloride is also liberated from the dye. The only case where this ratio is not close to unity is with the first soil using methylene blue. Here the amounts of metal ions are entirely too high for the amount of chloride found and also for the amount of dye adsorbed. That this is not due to experimental error is certain since ten separate runs were made with this soil and dye and the results all showed the same relationship. The difference is accounted for by the fact that in the dye solution, which percolated through this soil, some bicarbonate ion was found. This was not analyzed for quantitatively and so its equivalent could not be added to the chloride ion. This was the only soil in which the bicarbonate ion was observed to be present. The fact that it did not appear with the same soil using neutral violet is due to the methylene blue solution being slightly acid in reaction while the neutral violet is neutral. After passing through the soils the methylene blue solution was in every case neutral while the neutral violet solution was always alkaline.

The ratios between the chloride and dye all lie between 82 and 97 percent indicating that the dye is not all adsorbed by base exchange alone but that less than 20 percent of it is held in some other manner. The ratios between the metal ions and dye also lie between the same limits with the exception of Soil No. 1 with methylene blue as explained above. The close agreement between the amounts of base ion and chloride ion is to be observed. The fact that the chloride is always the greater may be accounted for as being due to their being but one determination to be made there while with the metal ions the value is the sum of five determinations.

The ability of a soil to undergo base exchange with a dye depends upon the nature of the dye just as the base exchange of metal ion depends upon the nature of the metal ion. The data show that the neutral violet has the greater ability to replace metals from the soils used than does methylene blue. However although the equivalent weights of dye adsorbed are different the ratios of the meta ions to the dyes are about the same, the neutral violet being always the smaller.

Since this is an equilibrium phenomenon the amount of metal ion set free from any soil will depend upon the concentration of the dyes. The two dye solutions were not made of equivalent concentration but the methylene blue solution contained two grams of dye per liter and the neutral violet four grams per liter. The neutral violet was made the more concentrated because with the weaker solution it took too long for the larger amount of solution to percolate through the soils. This may account for the larger amount of neutral violet taken up.

The effect of changing all of the replaceable metals to calcium and then treating with the dye solution is shown in Soil No. 6 which was Soil No. 1 after treatment with a solution of calcium chloride. The amounts of dye adsorbed and of chloride liberated are almost the same as they were in Soil No. 1. The amount of metal ions liberated is much less than with Soil No. 1 because of the absence of the carbonate in the treated soil.

In explaining the effect of the acidity and alkalinity of the solutions on the amounts of dye adsorbed by soils Wilkinson and

Hoff attributed it to the adsorption of the positive hydrogen ion, thus cutting down the amount of the positive dye ion that could be taken up. If instead of the adsorption of the hydrogen ion the latter is used to replace the metal ions of the soil by base exchange then there will be left less metal ions to be replaced by the dye and therefore less dye will be taken up. This is also aided by the repression of the ionization of the weakly dissociated dye molecule by the chloride ion of the highly dissociated hydrochloric acid.

The fact that the solutions of the dyes are less acid after percolation through the soils would tend to show that some of the acid had been taken up but there is found no equivalent anion in the solution that comes through. If this has been taken up by the soil by base exchange in preference to the dye ion the amount of dye taken up is less than it should be and yet the data shows that more dye has been taken up than is equivalent to the metal ions set free. Which tends further to show that some of the dye is held other than by base exchange.

The assumption that the volume of liquid that filtered through clear is equal to the volume of the dye solution required to saturate the soil is in error by an amount equal to the water required to wet the soil. This is about from one to one and a half cubic centimeter per gram of soil. No correction was made for this in the data given in the table. If this is done the equivalent of dye would be still larger than it is calculated to be indicating that even more than 20 percent in some samples is held other than by base exchange.

CONCLUSIONS

1. The larger portion, from eighty to ninety-seven percent, of the dye taken up by soils is taken up by the process of base exchange with the metals of the soil.
2. The equivalent weights of the metal ions from the soil and the chloride ion from the dye are very closely equal.
3. The amounts of metal ions displaced from a soil by the percolation of distilled water are dependent upon the amount of water allowed to percolate and also the time required for this process to take place.
4. Different dyes have different replacing power for the metal ions from any soil but the ration of dye adsorbed to the base exchange is very nearly the same regardless of the dye used.