RESEARCH PAPER

Kinetics of sulphate release in soils of Jharkhand

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Abstract : Ten selected soils from Alfisols and Ultisols soil orders of Jharkhand having varied physico- chemical properties were extracted with 0.15% $CaCl_2$ (1: 5 soil solution ratio) at selected time intervals (15, 30, 45, 60, 120, 300, 600 and 1200 minutes). The results indicated that each soil has differential variable with respect to sulphate desorption. The amount of sulphate S desorbed by 0.15 % $CaCl_2$ at different time intervals varied from 11.60 in Alfisol of Dhanbad after 15 minutes of extraction to 63.13 mg kg^{-1} after 1200 minutes. The mean amount of sulphate desorbed at different time intervals varied from 19.84 to 43.86 mg kg^{-1}. The per cent of sulphate S desorbed was more in Alfisols as compared to Ultisols. The amount of sulphate S desorbed varied with soil type as the rate of desorption reaction is controlled by the diffusion of sulphate ions through soil particles or aggregates. The amounts of sulphate S desorbed at different time interval were fitted into different kinetic models wherein it was found that the desorption of sulphate in the soils of Jharkhand was satisfactorily described by the first estimate equation.

Key Words : Kinetics, Sulphate, Soils, Alfisols, Ultisols

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INTRODUCTION

Kinetics of soil chemical process is one of the most controversial, challenging and exciting areas in soil and environmental chemistry (Aylmore *et al.*, 1967). Even though the equilibrium studies are often not applicable in the field conditions (because the soils are nearly always at disequilibrium with respect to ion transport and organic molecule interaction), the results of these studies have proven enlightening and beneficial. Soils, which have been exposed to high sulphur loading, and have a relatively small sulphate retention capacity may show, more release than adsorption.

Sulphate adsorption on kaolinite (Aylmore *et al.*, 1967), is mostly reversible (> 50%) but sulphate adsorbed on to Fe and Al oxides is essentially irreversible (50%). The mechanism of retention and release of S from soil is an important factor in S nutrition The salient reasons for studying the rate of soil chemical processes are: to predict how quickly reactions approach equilibrium or quasi - equilibrium and to investigate the reaction mechanisms. Various adsorption studies suggest that sulphate might be held in various soil fractions each having unique retention sites and energy of each retention site will add in predicting the desorption and release of soil S and in describing chemical and physical procedures to just enhance the sulphate removal.

The aim of the present study was to study kinetics of sulphate desorbed, to compute the order of reaction followed when adsorbed SO_4^{2-} is desorbed at different time intervals and to test a suitable kinetic model for desorption of sulphate for soils of Jharkhand.

MATERIALS AND METHODS

Surface soil samples (0-15 cm) were collected in bulk from twenty different sites from plateau region of Jharkhand comprising the districts of Dhanbad, Giridih, Hazaribagh and

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Ranchi. The collected samples were air-dried after mixing them thoroughly. The air-dried samples were passed through 2 mm sieve and processed for characterizing various soil physico-chemical properties. Ten soils which varied widely in their physico-chemical properties and sulphate concentration were selected for desorption studies. The selected soils were extracted with 0.15% CaCl$_2$ (1: 5 soil solution ratio) at certain time intervals (15, 30, 45, 60, 120, 300, 600 and 1200 minutes). Two hundred fifty gram of each of the air-dried soil sample was saturated overnight with 500ml of 100µg S ml^{-1} solution of K$_2$SO$_4$. Then the soil suspension was washed with ethanol until excess SO$_4$ is leached out, the filtrate was collected and made up to 1000 ml. Then 10 g of soil sample was transferred to a series of 100 ml plastic bottles containing 50 ml of 0.15 % CaCl$_2$ solution. After shaking upto the specified time interval proposed under the study, the suspensions were centrifuged and sulphate content in these solutions and in the filtrates collected earlier were determined by turbidimetric method (Chesnin and Yien, 1951). The data was fitted into different orders of reactions and their kinetic parameters were computed. Various equations employed for the computation of kinetic parameters are given below:

– First estimate: $$\frac{1}{Ct} = \frac{1}{Co} + \frac{b}{t} \quad\quad \text{..... (1)}$$

– Second approximation: $$In\,(Co-Ct) = In\,Co - Kt \quad\quad \text{.....(2)}$$

– First order: $$In\,Ct = In\,Co - Kt \quad\quad \text{.....(3)}$$

– Second order: $$\frac{1}{Ct} = \frac{1}{Co} + Kt \quad\quad \text{......(4)}$$

– Third order: $$\frac{1}{Ct^2} = \frac{1}{C^2o} + Kt \quad\quad \text{......(5)}$$

– Parabolic diffusion: $$Ct = Co - Kt\frac{1}{2} \quad\quad \text{......(6)}$$

– Elovich equation: $$Ct = \frac{1}{b}In\,(ab) + \frac{1}{b}In\,t \quad\quad \text{......(7)}$$

where,

Co = initial SO$_4^{2-}$ concentration added to soil (ppm)
Ct = Concentration of SO$_4^{2-}$ after time t (ppm)
t = Time (minute)
K, m, b, a are rate constants.

RESULTS AND DISCUSSION

The amount of sulphate desorbed at various time intervals are presented in Table 1. The data indicated that each soil has differential variable with respect to sulphate desorption. Regardless of soil order, the mean amount of sulphate desorbed at different time intervals varied from 19.84 to 43.86 mg kg^{-1} (Table 1). In the Alfisol from Dhanbad the amount of sulphate S desorbed by 0.15 % CaCl$_2$ at different time intervals varied from 11.60 after 15 minutes of extraction to 63.13 mg kg^{-1} after 1200 minutes. The highest amount of sulphate desorbed was in the case of Alfisol from Kaludih

Table 1 : Showing amount of sulphate desorbed at different time interval

Soil no.	0 min	15min	30min	45min	60min	120min	300min	600min	1200min
1	204.85	29.9	35.95	25.9	18.65	24.8	11.6	39	36.8
2	234.2	29.8	38.85	30.1	31.05	43.1	20.6	38.4	30.8
3	183.95	28.3	26.3	35.15	40.85	37.85	23.9	36.85	26.8
4	197.1	26.85	32.05	32.6	50.35	44.65	31.55	45.25	18.5
5	184.3	24.25	26.35	28.5	53.5	24.3	21.5	37.5	27
9	191	15.4	28.25	20.3	27.25	37.8	13.2	36.5	26.9
10	180.85	25.5	20.45	30.35	43.75	16.25	17.65	42.1	26.75
12	199.15	19.25	22.8	23.3	35.9	22.2	35.65	43	27
18	204.88	25.55	38.85	23.75	26.55	34.7	27.95	38.5	37
19	193.6	25.93	28.95	32	35	27.1	25.45	36.8	24.85

Table 2: Showing percentage of sulphate desorbed at different time interval

Soil no	15min	30min	45min	60min	120min	300min	600min	1200min
1	24.50	43.75	62.25	60.25	63.13	30.13	34.13	30.63
2	20.75	40.25	73.75	52.13	57.25	38.50	38.50	39.00
3	26.75	47.00	65.75	55.50	55.00	33.13	31.25	27.88
4	16.38	37.63	69.00	60.13	58.38	25.63	25.75	30.50
5	24.13	43.38	62.75	55.25	58.50	25.25	31.00	40.25
9	13.25	42.00	78.00	53.13	54.50	30.50	35.00	39.75
10	25.63	49.25	73.63	61.50	55.25	34.50	32.13	31.88
12	23.88	55.25	74.58	67.63	58.38	42.00	31.63	32.88
18	26.20	50.08	71.00	62.83	64.45	38.08	35.08	43.95
19	28.13	49.88	65.02	66.00	58.75	41.75	41.13	40.63

(Dhanbad), where it varied from 23.90 to 63.13 mg kg^{-1} at different intervals of time (Table 1).The percentage of sulphate desorbed from the soils at different time intervals is given in Table 2. The mean desorption percentage varied from 9.72 (at 15 minutes) to 21.49 (at 1200 minutes).

On an average, about 21 per cent of sulphate S was desorbed after shaking of 1200 minutes. However, Courchesne and Hendershot (1990), found that about 50 per cent of sulphur was desorbed within five minutes and thereafter the desorption process slowed down, though it continued up to four days. This implies that further release of sulphate S after 300 minutes was due to a slow reaction as a result of diffusion controlled ion exchange (Hodges and Johnson, 1987).

The amount of sulphate S desorbed was almost stabilized after 300 minutes of extraction. The remaining portion of sulphate got fixed in the soil particle or the adsorbate. These results are in close agreement with the findings of Barrow and Shaw (1977) and Singh (1984). The per cent of sulphate S desorbed was found more in Alfisols as compared to Ultisols. The rate of desorption reaction is controlled by the diffusion of sulphate ions through soil particles or aggregates (Hodges

and Johnson, 1987). Perhaps this is the reason why the amount of sulphate S desorbed varied with the soil type. The differential behaviour of soils with respect to sulphur desorption has also been observed by Dolui and Nandi (1989), while studying the desorption of adsorbed sulphate S in the soils of West Bengal. According to them, the adsorbed sulphate S was desorbed partially in some soils, while in other soils, sulphate was desorbed in larger amounts indicating a release of native sulphur. Least amount of sulphate S was recovered from soil no. 9 (Ultisol), while maximum percentage of sulphate S was desorbed in case of soil no. 3 (Alfisol). It was observed that after a certain period of time (300 min), the relationship between per cent sulphate desorption and time was approximately linear with little slope in almost all the soils indicating that the faster reactions occurred within 300 minutes and that the further desorption of sulphate was due to some slow reactions as a result of diffusion controlled ion exchange.

The amounts of sulphate S desorbed at different time interval were fitted into different kinetic models, namely first estimate equation, second estimate, first order kinetics, second order kinetics, third order kinetics, parabolic diffusion and

Table 3: First estimate kinetic model used for describing desorption of native sulphur

Type of reaction / soil type	Observed equation	S.E.	R^2
First estimate equation ($1/C_t = 1/C_0 + b/t$			
1	y = 0.013 - 0.002 x	0.018000	0.65**
2	y = 0.123 + 0.0054 x	0.017913	0.72**
3	y = 0.012791 - 0.00463 x	0.015623	0.81**
4	y = 0.013591 + 0.001177 x	0.018338	0.70**
5	y = 0.01538 – 0.00106 x	0.035700	0.88 **
9	y = 0.012631 + 0.000392 x	0.014136	0.80**
10	y = 0.012761 + 0.000203 x	0.017282	0.87**
12	y = 0.021552 - 0.03938 x	0.081190	0.73 **
18	y = 0.011141 - 0.00096 x	0.015170	0.82**
19	y = 0.010913 + 0.000337 x	0.013309	0.81**

* and ** Indicate significance of value at P=0.05 and 0.01, respectively

Table 4: First order model used for describing desorption of native sulphur

Type of reaction / soil type	Observed equation	S.E.	R^2
First order ($\ln C_t = \ln C_0 - kt$)			
1	y = 4.512915 - 0.00037 x	0.000363	0.38
2	y = 4.44273 - 0.00064 x	0.000332	0.60**
3	y = 4.56927 - 0.00046 x	0.000300	0.52*
4	y = 4.45616 - 0.00033 x	0.000365	0.63**
5	y = 4.337265 - 0.000056 x	0.000525	0.70**
9	y = 4.452237 - 0.00014 x	0.000295	0.61**
10	y = 4.538618 - 0.00038 x	0.000356	0.40
12	y = 4.543112 - 0.00083 x	0.000680	0.44
18	y = 4.612914 - 0.00022 x	0.000318	0.62**
19	y = 4.628601 - 0.00022 x	0.000303	0.72**

* and ** Indicate significance of value at P=0.05 and 0.01, respectively

Elovich equation as used by different workers (Cooke, 1966; Kuo and Lotse, 1973; Evans and Jurinak, 1976). The various kinetic equations are presented in Table 3 to 9 alongwith observed equation, standard error and R^2 value (as computed

from the experimental desorption data). The desorption data for all the ten soils were best fitted into the first estimate equation as evident from the highly significant R^2 values and lower standard error. Among the ten soils, the highest R^2 value

Table 5: Second order model used for describing desorption of native sulphur

Type of reaction / soil type	Observed equation	S.E.	R^2
Second order $(1/C_t = 1/C_0 + kt)$			
1	y = 0.011973 + 0.00039	0.000488	0.43
2	y = 0.012785 - 0.00037	0.000494	0.34
3	y = 0.01089 - 0.00055	0.000367	0.32
4	y = 0.012622 + 0.000349	0.000482	0.42
5	y = 0.016042 + 0.000024	0.000097	0.41
9	y = 0.012343 + 0.000015	0.000038	0.44
10	y = 0.011603 + 0.0000395	0.000044	0.53*
12	y = 0.013519 + 0.0000196	0.000021	0.63**
18	y = 0.010608 + 0.0000172	0.000036	0.71**
19	y = 0.010426 - 0.0000171	0.000035	0.49

* and ** Indicate significance of value at P=0.05 and 0.01, respectively

Table 6: Third order model used for describing desorption of native sulphur

Type of reaction / soil type	Observed equation	S.E.	R^2
Third order $(1/C_t^2 = 1/C_0^2 + kt)$			
1	y = 0.000174 + 0.0000759	0.000014	0.42
2	y = 0.000197 + 0.000048	0.000016	0.41
3	y = 0.000132 + 0.000014	0.000097	0.50
4	y = 0.000188 + 0.0000709	0.000013	0.4 0
5	y = 0.000386 - 0.000022	0.000044	0.51*
9	y = 0.000171 + 0.0000783	0.000010	0.50*
10	y = 0.00016 + 0.000788	0.000012	0.62**
12	y = 0.000405 + 0.0000147	0.000018	0.43
18	y = 0.000129+ 0.0000224	0.000089	0.51*
19	y = 0.000126 + 0.0000191	0.000091	0.58*

* and ** Indicate significance of value at P=0.05 and 0.01, respectively

Table 7: Parabolic diffusion model used for describing desorption of native sulphur

Type of reaction / soil type	Observed equation	S.E.	R^2
Parabolic diffusion $(C_t = C_o - Kt^{1/2})$			
1	y = 105.3701 - 1.27645 x	1.175700	0.60**
2	y = 91.64863 - 0.30741 x	0.980815	0.61**
3	y = 109.6015 - 1.45494 x	1.069505	0.69**
4	y = 100.2736 - 1.17735 x	1.166155	0.68**
5	y = 92.65047 - 0.62675 x	1.374017	0.71**
9	y = 94.26612 - 0.60809 x	0.935818	0.82**
10	y = 109.237 - 1.3995 x	1.261385	0.74**
12	y = 119.5194 - 2.185 x	1.429526	0.52*
18	y = 113.0045 - 0.98355 x	1.160987	0.63**
19	y = 113.3361 - 0.94222 x	1.104397	0.73**

* and ** Indicate significance of value at P=0.05 and 0.01, respectively

(0.88**) was observed in the Alfisol from Dhanbad (soil no. 5).

The second estimate equation did not describe the process of desorption satisfactorily, since R^2 value was significant for four soils (two Alfisols and two Ultisols).

From the first order equation, the desorption rate co-efficient (Kd) was calculated by the formula log $(C_t/C_o) = -Kd$ t / 2.303 as proposed by Sivasubramanium and Talibuddin (1972), based on the assumption that the rate of desorption is proportional to the amount of potentially desorbed ions. The desorption rate co-efficients were found to be 3.7 x 10^{-5}, 6.4 x 10^{-5}, 4.6 x 10^{-4}, 3.3 x 10^{-4}, 5.6 x 10^{-5}, 1.4 x 10^{-4}, 3.8 x 10^{-4}, 8.3 x 10^{-4}, 2.2 x 10^{-4} and 2.2 x 10^{-4} min^{-1} for the soils no. 1, 2, 3, 4, 5, 9, 10, 12, 18 and 19, respectively. The R^2 values for this kinetic equation were found to be significant in most of the soils. On fitting the desorption data in the first order equation, a curvature is obtained. Incorrect assumption of reaction order probably is one of the reasons for getting such curvature. For example, if the first order kinetics is assumed but in reality the reaction is second order, there is possibility of obtaining downward curvature in such cases (Bunnet, 1986). The plots for all the ten soils under investigation definitely show a downward curvature on assuming first order kinetics, which may probably be due to incorrect assumption of reaction order.

The second order and third order kinetic equations did not describe the process of desorption satisfactorily, since most of the soils failed to indicate appreciable R^2 values, though the standard error was less in all the soils.

The desorption process was found to be described satisfactorily by parabolic diffusion equation as all the soils indicate highly significant R^2 values. However, the standard error values were high making it difficult to conclude that parabolic diffusion adequately described the desorption process. According to Bolan et al. (1993), the parabolic diffusion equation would only be applicable if the sulphur concentration is constant over the course of experiment. On the contrary, the S content in solution increased with time in the present study in all the soils. Since, soils under study follow parabolic diffusion equation, it may be assumed that the reaction rate is controlled by the diffusion of ions to the

Table 8: Elovich equation model used for describing desorption of native sulphur

Type of reaction / soil type	Observed equation	S.E.	R^2
Elovich equation $(C_t = a + b \ln t$			
1	y = 114.9025- 5.74437 x	8.806416	0.82**
2	y = 84.01463 + 0.707659 x	7.000870	0.83**
3	y = 124.7814 - 7.55624 x	8.116978	0.73**
4	y = 111.0019 - 5.70607 x	8.628982	0.72**
5	y = 92.61634 - 1.82768 x	9.875670	0.83**
9	y = 97.80234 - 2.52434 x	6.782796	0.79**
10	y = 122.3771 - 6.68436 x	9.403803	0.75**
12	y = 148.8303 - 12.5695 x	10.78124	0.84**
18	y = 120.6105 - 4.48119 x	8.510615	0.82**
19	y = 117.7582 - 3.68969 x	8.148589	0.71**

* and ** Indicate significance of value at P=0.05 and 0.01, respectively

Table 9: Second estimate model used for describing desorption of native sulphur

Type of reaction / soil type	Observed equation	S.E.	R^2
Second estimate $(C_0 - C_t) = \ln C_0 - kt$			
1	y = 4.5742 + 0.000351 x	0.000286	0.44
2	y = 4.65 + 0.000136 x	0.000226	0.23
3	y = 4.654063 + 0.000392 x	0.000295	0.47
4	y = 4.62323 + 0.000307 x	0.000283	0.40
5	y = 4.6456 + 0.000205 x	0.000322	0.55*
9	y = 4.6654 + 0.000166 x	0.000222	0.52*
10	y = 4.627204 + 0.0002 x	0.000452	0.61**
12	y = 4.3856 + 0.001274 x	0.000719	0.62**
18	y = 4.46746 + 0.000312 x	0.000329	0.36
19	y = 4.46122 + 0.00032 x	0.000306	0.39

* and ** Indicate significance of value at P=0.05 and 0.01, respectively

reactive sites, either through stagnant water films surrounding the soil particles or through particles itself .

The Elovich model was also found to describe adequately the sulphate desorption process. All the ten soils gave the significant R^2 values ranging from 0.71** (Ultisol from Hazaribagh) to 0.84** (Alfisol from Ranchi) but comparatively higher standard error values. Therefore, conclusion is as same as parabolic diffusion equation. Since, true rate constants could not be calculated from the simplified Elovich equation, the slope of the linear regression equation (apparent rate co-efficient) was used to evaluate the dependence of sulphate desorption on soil properties. The rate constants 'a' varied from 84.0146 (Alfisol from Dhanbad) to 148.8303 (Alfisol from Ranchi). The rate constant 'b' varied from –12.5695 (Alfisol from Ranchi) to 0.7076 (Alfisol from Dhanbad). The significance of 'a' and 'b' values is that they can be used to compare the real rates of sulphate released in different soils. The decrease in the value of 'b' and an increase in the value of 'a' should enhance the reaction rate.

The Elovich equation is a useful tool to investigate any change of surface reactivity in the absorbent (soil) during whole course of reaction (Chien and Clayton, 1980) and described the number of processes including bulk and surface diffusion as well as activation and inactivation of catalytic surfaces. However, recent theoretical studies on adsorption / desorption phenomenon in oxides / aqueous solution systems illustrate that the applicability and methods of fitting kinetic data require accurate data at short reaction times (Aharoni and Ungarish, 1976). Prediction is still marginal at very low and very high surface coverage (Ungarish and Aharoni, 1981). These type of situations could well establish in soil or on soil constituents system. This equation has been used to describe kinetics of sulphur sorption / desorption in soils by Hodges and Johnson (1987), who claimed it to be superior to other kinetic equations based on high R^2 and low standard error values.

Conclusion :

Therefore, it may be concluded that sulphate S desorbed more in Alfisols of Jharlhand and the desorption of sulphate in the soils is satisfactorily described by the first estimate equation, which is basically a hyperbolic equation.

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