Leaching Kinetics of Sulphates in Acidic Soil

Anuj Kumar Garg[1*], A. K. Gupta[1] and Ashu Rani[2]

[1]*Department of Chemistry, S.S.V. P.G. College, Hapur, U.P, India.*
[2]*Department of Pure and Applied Chemistry, University of Kota, Kota, Rajasthan, India.*

Authors' contributions

This work was carried out in collaboration between three authors. Author A. K. Garg designed the study, conduct the experimental work, collected the soil samples, wrote the protocol, wrote the first draft of the manuscript and the literature searches. Authors A. K. Gupta and AR managed the analyses of the study and the interpretation of results. All authors read and approved the final manuscript.

Original Research Article

ABSTRACT

Aims: Present study is concerned about the leaching kinetics of sulphate anions in soil using glass column method.
Study Design: We have focused our attention on the mechanism of solute transport via leaching.
Place of Study: Soil samples were collected from the barren field located in the industrial area near Hapur district.
Methodology: The leaching study of sulphate is carried out in the laboratory by using the glass column. During the entire course of study the flow rate of deionised water or salts solution from glass column was maintained at 10 ± 0.2 mL/10 min. Three salts of sulphates Na_2SO_4, $MgSO_4$ and $Al_2(SO_4)_3$ were used to study the leaching kinetics of sulphates in soil.
Results: Initial leaching rate profiles are determined for each salt. On increasing $[SO_4^{2-}]_i$, LR_{obs} values are seen to increase for all sulphate salts. The log-log plots of $[SO_4^{2-}]_i$ and LR_{obs} indicated to be the fractional order in $[SO_4^{2-}]_i$. The effect of temperature on sulphate leaching was studied in the range 20-50°C. It is clear that total initially leach able content i.e. $[SO_4^{2-}]_i$ increases with the increase in temperature, probably due to the mobilization and leaching of some insoluble sulphate. LR_{obs}

Corresponding author: E-mail: anujkgarg02@gmail.com;

values increases with the size of cation. The results can be explained on the basis of covalent character and radii of the hydrated ions. Initial water content or water filled porosity (θ) of the soil column was varied from .33 to .51 $cm^3 cm^{-3}$. LR_{obs} calculated values were found to increase only slightly on increasing initial water content of the soil column. Leached concentration were found time dependent and varied with time as the pore volume of effluent increased with time. The first order kinetics and Elovich model has been found to have excellent correlation for the desorption/Leaching of the sulphate confirmed by SEE and high r^2 values. However there is little correlation for the zero order and parabolic profiles.

Conclusion: Present study proves that leaching of sulphate salts can be studied by initial rate method, which can also be applied for monitoring the fate of applied sulphate in agricultural fields and its diffusion into soil solution for plants uptake as well as in calculating the downward transportation of sulphate from polluted site to the underground water.

1. INTRODUCTION

Atmospheric constituents containing sulphates can significantly affect humans and environment. The wet and dry deposition of SO_4^{2-} has received considerable attention throughout the world. Sulphate is a relatively mobile anion. Sulphate desorption can enhance leaching of acid cations (H^+ and Al^{3+}) and base cations such as sodium (Na^+) potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}). The leaching of base cations from the soil due to the deposition of SO_4^{2-} anions can therefore results in both acidification and loss of fertility of the soil [1-3]. The pH lowering in stream and lake waters is due to the mobility of suphate in the soil which lowers the pH of percolating and run off waters [4,5]. Substantial leaching loss via leaching can occur in soils with low retention capacity observed in New Zealand [6].

The wet and dry depositions of sulphate have changed the soil characteristics in many polluted areas, where acid precipitation and sulphate deposition is a common phenomenon. The tendency of SO_4^{2-} to be removed from soils varies widely and the extent of leaching depends upon the soil properties and fertilization practices. Sulphate is retained to certain extent by most soils [2,3].

To understand the behaviour of sulphate leaching, especially during short period of soil water interaction and at a wide range of water soil ratios, studies on sulphate desorption during continuous flow as well as restricted flow are needed. Literature survey revealed that soil's capacity to adsorb sulfate depends on numerous soil properties, including the concentrations of Al and Fe-hydrous oxides, clay mineralogy, soil pH [6,7] organic matter content and soil temperature [8,9]. Leaching studies of sulphate through soil have significance in environmental as well as in agronomy and agricultural sciences.

The forces involve in SO_4^{2-} adsorption can range from weak, physical, vanderwaals forces and electrostatic outer sphere complexes and chemical interaction. The chemical interactions include the inner sphere complexation which involve ligand exchange mechanism, covalent bonding or there can be precipitation of basic Al sulphate. The ligand exchange mechanism found to be applicable on a time scale of weeks for sulphate adsorption studies [10]. Rajan [11] studied the sorption of sulphate on hydrous alumina and found that the reaction was 90% complete within 10 min and 95% within 60 min. He suggested the formation of inner sphere complexes responsible for sorption. Sulphate ions were found to form bridge between two aluminium ions to form 6 membered rings. Sparks [12] and Jung K, et al. [9] also studied the kinetics of sulphate adsorption and desorption on soil and soil constituents.

Most of the studies consider only the sulphate adsorption kinetics rather than desorption and leaching kinetics. The desorption process is also very important for the release of ions which can increase the nutrients available to plants but also allows them to leach and contaminate the ground water. Advanced techniques like miscible displacement [13], stirred batch procedures [25] pressure jump relaxation [14] etc. have been used by several workers for studying adsorption and desorption of sulphates on soil materials and on rocks and minerals. However, they noted that the lack of suitable techniques to measure the rate of sulphate adsorption and desorption is the major obstacle in understanding the mechanism of sulphate retention and transport in the soil system.

Preliminary investigations on movement of sulphates in Indian soils have been conducted by Malik et al. [15] on soil columns and found that higher amounts of calcium carbonates, phosphates and higher soil pH result in increased sulphate leaching. Although, several studies have been conducted on sulphate adsorption and desorption from soils, but the mechanism of ionic adsorption and desorption is still not well understood. As far as Indian studies are concerned, only very little information is available on the kinetics of sulphate desorption from Indian soils under field and laboratory conditions.

Present work describes the results of investigations carried out on the leaching behavior and kinetics of the sulphate ion in acidic soil of Indian origin. The water soluble salts of sulphates viz. Na_2SO_4, $MgSO_4$ and $Al_2(SO_4)_3$ have been chosen for the present study.

2. MATERIALS AND METHODS

A glass column of 50 cm length and 2.5 cm diameter, For leaching kinetic studies, in which 60 g fine textured soil was filled. The temperature of the column, the flow rate of extractant was found constant in columns of similar sizes. A fixed volume of aqueous salt solutions (slug) with desired anion concentration was added on the top of the soil column in each experiment. Salt solution was allowed to get adsorbed uniformly in the column for 24 h, after which the column was continuously leached with deionised water or with other extractants as per the requirement of the study. The leaching was carried out till the soluble anions were completely removed.

For calculating initial leaching rates, the concentrations of anions were determined in leachates collected periodically at an interval of 10 min. Sulphate ions leached were determined by measuring the degree of turbidity by Systronics (106) UV-VIS spectrophotometer at 440 nm. In order to determine the SO_4^{2-} ions, the buffer solution is added to the suitable volume of sample in 250 mL flask and mix in stirring apparatus. While stirring, a spoonful $BaCl_2$ crystals were added and diluted up to the desired volume and the turbidity was determined [26]. The flow rate was quite slow with only 10 ± 0.2 mL leachate per 10 min. The total leached concentration was taken equal to the total leachable content present at t = 0. After completely removing the soluble ions from column, the soil of columns was transferred into a beaker and suspension was obtained in a known volume of extractant solution or deionised water. This soil suspension was stirred for 2 h. The ion concentration were further determined in the filtrate of the soil suspension to ensure the complete removal of soluble ions from the soil in the column.

The effect of variation of temperature was studied by maintaining the temperature of the column in the range 20°C to 50°C.The analysis of soil has been carried out by using standard methods [27] and given in Table 1.

Table 1. Physico-chemical characteristics of the column soil

Properties	Values
pH	**6.4**
E C (dsm^{-1})	0.87
Bulk Density (mgm^{-3})	1.44
Colour	Greyish black
Sp. Gravity	2.47
Textural class	Sandy-clay loam
Sand %	48%
Silt %	25%
Clay %	27%
C.E.C.	16.54 cmol kg^{-1}
O.C.%	0.60
Exchangeable cations (mg / 100g)	
Ca^{+2}	20.5
Mg^{+2}	10.4
Na^{+}	4.2
K^{+}	1.9

3. RESULTS AND DISCUSSION

3.1 Data Interpretation

The abbreviations used for the presentation of data are:

$[SO_4^{2-}]_s$ = leachable sulphate present in column soil, 13.6 mg/kg

$[SO_4^{2-}]_{add}$ = SO_4^{2-} concentration introduced in the soil column

$[SO_4^{2-}]_i$ = total leachable content present initially

$[SO_4^{2-}]_t$ = leached concentration at time t

$[SO_4^{2-}]_1$ = $[SO_4^{2-}]_i$ - $[SO_4^{2-}]_t$

= leachable concentration remaining at time t

3.2 Total Leachable Sulphate, $[SO_4^{2-}]_i$

The values of total leachable concentrations of $[SO_4^{2-}]_i$ ions for Na_2SO_4, $MgSO_4$ and $Al_2(SO_4)_3$ are given in Table 2,3,4. It is clear that $[SO_4^{2-}]_i$ increases with the $[SO_4^{2-}]_{add}$. The soil has itself has leachable SO_4^{2-} present in it i.e. $[SO_4^{2-}]_s$. If we add the salt of sulfate from outside in the soil column, the concentration of leachable SO_4^{2-} increases. In the absence of added SO_4^{2-}, the total leachable contents are equal to the water soluble sulphate presents naturally in soil itself. Similar results have been noted by Rajan [11]. He observed an increase in percentage desorption of SO_4^{2-} from soil when added SO_4^{2-} concentration was increased. He suggested that desorption of sulphate may be related with the surface charges on clay and found that the sulphate quantity left on the surface after desorption is about the same even on increasing the initial SO_4^{2-} concentration.

3.3 Leaching Rate Profiles

Initial rates for leaching, LR_{obs}, (observed leaching rate) represents the rate of change in leachable concentration $[SO_4^{2-}]_1$ with time. LR_{obs} value were obtained from the slope of the plot between $[SO_4^{2-}]_1$ and time as shown in Figs. 1, 2 and 3 .

3.3.1 Leaching of Na_2SO_4

Leaching of SO_4^{2-} ions was studied at different added concentrations of Na_2SO_4 on soil in columns. Amount of $[SO_4^{2-}]_{add}$ was varied from 0-30 mg/kg. The flow rate of percolating water was 10±0.2 ml/10 min. Low width of the column was found advantageous in minimizing the flow rate of percolation of water and maximize the soil water interaction period. The detailed results of Na_2SO_4 leaching for varying $[SO_4^{2-}]_i$ are given in Table 2. Initial rate profiles for Na_2SO_4 leaching at different $[SO_4^{2-}]_i$ are shown in Fig. 1. This figure show that initially leaching is in general relatively fast at almost all the $[SO_4^{2-}]_i$ concentrations.

3.3.2 Leaching of $MgSO_4$

Reaction profiles of SO_4^{2-} leaching in case of $MgSO_4$ are presented in Fig. 2. Detailed results and LR_{obs} Value are given in Table 3.

3.3.3 Leaching of $Al_2(SO_4)_3$

Leaching rate profiles for $Al_2(SO_4)_3$ are given in Fig. 3 and detailed results are given in Table 4.

Table 2. Variation in $[SO_4^{..-}]_1$ and $[SO_4^{..-}]_t$ with time at different $[SO_4^{..-}]_{add}$ and $[SO_4^{..-}]_i$ concentrations for Na_2SO_4 leaching at 30°C

$[SO_4^{2-}]_{add}$-->	0		10		20		30	
time, s	$[SO_4^{..-}]_t$	$[SO_4^{..-}]_1$	$[SO_4^{..-}]_t$	$[SO_4^{..-}]_1$	$[SO_4^{..-}]_t$	$[SO_4^{..-}]_1$	$[SO_4^{..-}]_t$	$[SO_4^{..-}]_1$
0	0	13.6	0	23.8	0	32.9	0	30.3
600	3.1	10.5	4.3	19.5	6.0	26.9	4.3	26.0
1200	6.0	7.6	8.4	15.4	12.7	20.2	8.5	21.8
1800	8.0	5.6	10.8	13.0	16.6	16.3	12.4	17.9
2400	10.1	3.5	12.2	11.6	19.5	13.4	15.2	15.1
3000	11.6	2.0	13.8	10.0	22.6	10.3	17.9	12.4
3600	12.6	1.0	15.7	8.1	25.2	7.7	20.9	9.6
$[SO_4^{..-}]_i$	13.6		23.8		32.9		30.3	
LR_{obs} mgkg^{-1}s^{-1}	0.048		0.099		0.227		0.172	

$[SO_4^{..-}]_1$, $[SO_4^{..-}]_{add}$, $[SO_4^{..-}]_t$ and $[SO_4^{..-}]_i$ are in mg/kg
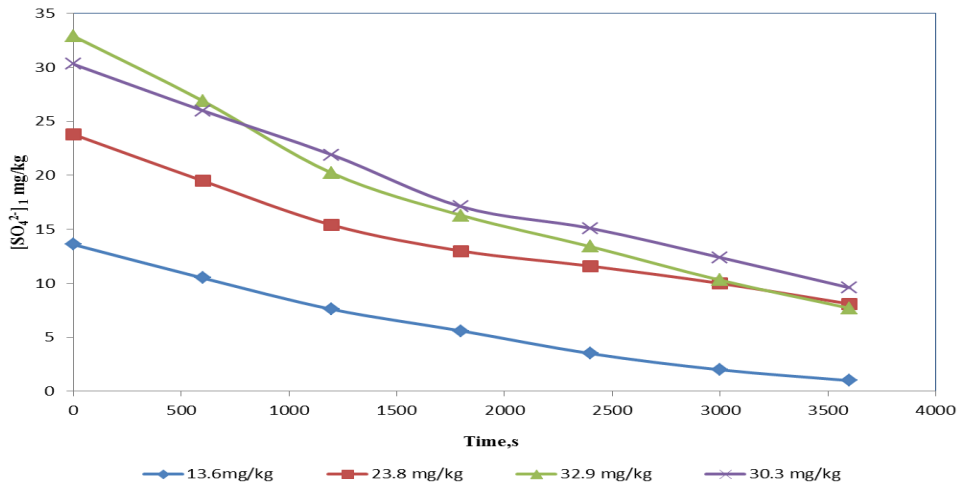
Fig. 1. Initial leaching rate profiles for Na$_2$SO$_4$ leaching at different concentration of [SO$_4^{2-}$]$_i$ at 30°C

Table 3. Variation in [SO$_4^{--}$]$_1$ and [SO$_4^{--}$]$_t$ with time at different [SO$_4^{--}$]$_{add}$ and [SO$_4^{--}$]$_i$ concentrations for MgSO$_4$ leaching at 30°C

[SO$_4^{2-}$]$_{add}$-->	0		10		20		30	
time, s	[SO$_4^{--}$]$_t$	[SO$_4^{--}$]$_1$	[SO$_4^{--}$]$_t$	[SO$_4^{--}$]$_1$	[SO$_4^{--}$]$_t$	[SO$_4^{--}$]$_1$	[SO$_4^{--}$]$_t$	[SO$_4^{--}$]$_1$
0	0	13.6	0	35.9	0	41.8	0	54.7
600	3.1	10.5	5.8	30.1	4.5	37.3	6.1	48.6
1200	6.0	7.6	11.4	24.5	8.6	33.2	11.8	42.9
1800	8.0	5.6	15.3	20.6	12.3	29.5	18.2	36.5
2400	10.1	3.5	19.1	16.8	16.3	25.5	23.9	30.8
3000	11.6	2.0	22.2	13.7	20.3	21.5	29.8	24.9
3600	12.6	1.0	24.6	11.3	23.6	18.2	36.1	18.6
[SO$_4^{--}$]$_i$	13.6		35.9		41.8		54.7	
LR$_{obs}$ mgkg^{-1}s^{-1}	0.048		0.244		0.275		0.492	

[SO$_4^{--}$]$_1$, [SO$_4^{--}$]$_{add}$, [SO$_4^{--}$]$_t$ and [SO$_4^{--}$]$_i$ are expressed in mg/kg
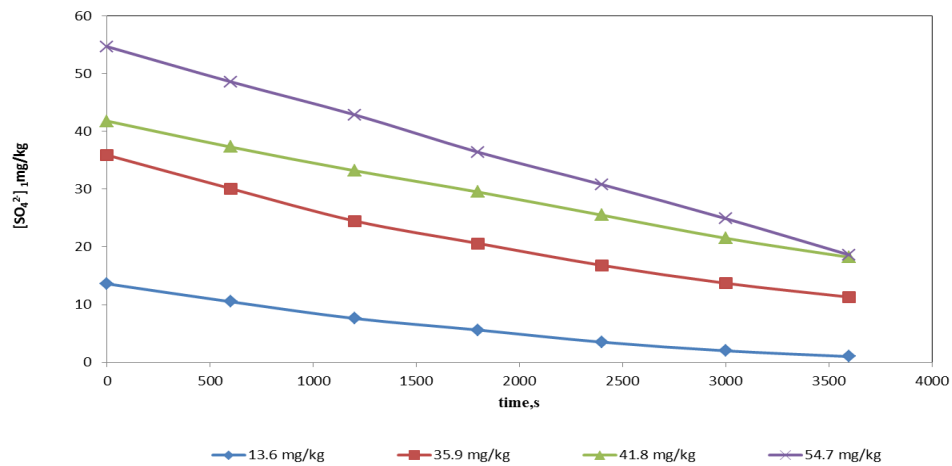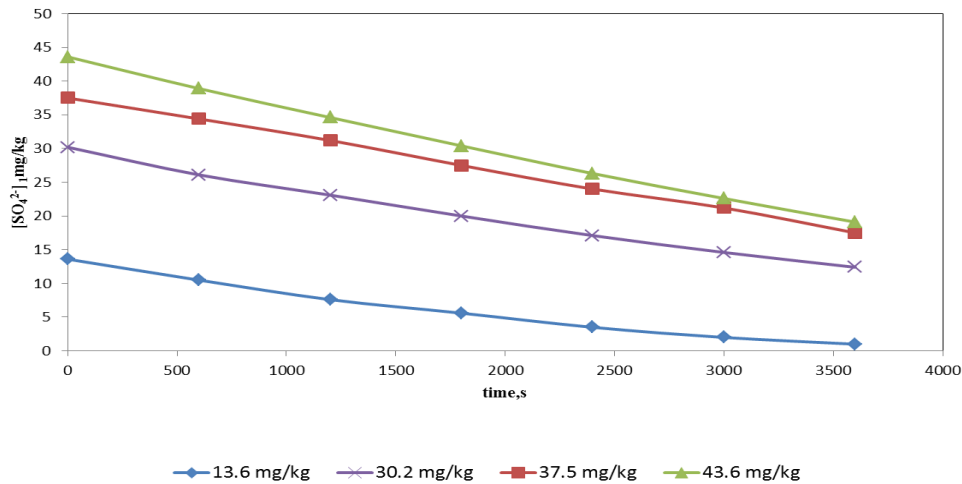

Fig. 2. Initial leaching rate profiles for MgSO$_4$ leaching at different concentration of [SO$_4^{2-}$]$_i$ at 30°C

Table 4. Variation in $[SO_4^{--}]_1$ and $[SO_4^{--}]_t$ with time at different $[SO_4^{--}]_{add}$ and $[SO_4^{--}]_i$ concentrations for $Al_2(SO_4)_3$ leaching at 30°C

$[SO_4^{2-}]_{ad}$-->	0		10		20		30	
time, s	$[SO_4^{--}]_t$	$[SO_4^{--}]_1$	$[SO_4^{--}]_t$	$[SO_4^{--}]_1$	$[SO_4^{--}]_t$	$[SO_4^{--}]_1$	$[SO_4^{--}]_t$	$[SO_4^{--}]_1$
0	0	13.6	0	30.2	0	37.5	0	43.6
600	3.1	10.5	4.1	26.1	3.1	34.4	4.7	38.9
1200	6.0	7.6	7.1	23.1	6.3	31.2	9.0	34.6
1800	8.0	5.6	10.2	20.0	10.0	27.5	13.2	30.4
2400	10.1	3.5	13.0	17.2	13.5	24.0	17.3	26.3
3000	11.6	2.0	15.6	14.6	16.3	21.2	21.0	22.6
3600	12.6	1.0	17.8	12.4	20.0	17.5	24.5	19.1
$[SO_4^{--}]_i$	13.6		30.2		37.5		43.6	
LR_{obs} mgkg^{-1}s^{-1}	0.048		0.147		0.210		0.296	

$[SO_4^{--}]_1$, $[SO_4^{--}]_t$, $[SO_4^{--}]_{add}$ and $[SO_4^{--}]_i$ are expressed in mg/kg

Fig. 3. Initial leaching rate profiles for $Al_2(SO_4)_3$ leaching at different concentration $[SO_4^{2-}]_i$ at 30°C

3.4 Dependence of LR_{obs} on $[SO_4^{2-}]_i$

In general, the leaching profiles for different salts studied are of the same type. On increasing $[SO_4^{2-}]_i$, LR_{obs} values are seen to increase for all sulphate salts. The log-log plots of $[SO_4^{2-}]_i$ and LR_{obs} indicated to be the fractional order in $[SO_4^{2-}]_i$. The leaching rates fitted the rate laws 1 to 3 for different salts.

(i) Na_2SO_4

$$LR_{obs} = k_1 [SO_4^{2-}]_i^n \qquad (1)$$

(i) $MgSO_4$

$$LR_{obs} = k_2 [SO_4^{2-}]_i^n \qquad (2)$$

(i) $Al_2(SO_4)_3$

$$LR_{obs} = k_3 [SO_4^{2-}]_i^n \qquad (3)$$

From the linear plot of LR_{obs} vs $[SO_4^{2-}]_i^n$ as defined by rate laws 1 to 3, the values of k and n for all three salts are given in Table 5.

Table 5. The values of rate constant (k), order (n) and correlation parameters for different salts of sulphates

Parameters	Na_2SO_4	$MgSO_4$	$Al_2(SO_4)_3$
k×10^7	0.36	0.44	1.00
n	1.66	1.63	1.51
r^2	0.971	0.996	0.993
SEE	0.138	0.076	0.079

Units of k is mg^{1-n}kg^{n-1}s^{-1}

A comparison of n values shows these to be almost same for Na_2SO_4, $MgSO_4$ but slightly less

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for $Al_2(SO_4)_3$. The comparison of LR_{obs} values show these to be in order $Na_2SO_4 > MgSO_4 > Al_2(SO4)_3$. The linear power form equation (1-3) which express the sulphate leaching rates are similar to the equation, proposed by Sharply [16] for desorption of sulphate.

$$S_d = KS_e t^\alpha W^\beta$$

Where

- S_d = amount of sulphate desorbed in time t at a water/ soil ratio W
- S_e = Initial amount of extractable SO_4 present in the soil.
- α, β and K are constant for given soil

3.5 Effect of Temperature on $[SO_4^{2-}]_i$

The effect of temperature on sulphate leaching was studied in the range 20-50°C. Fig. 4 clearly indicate that total initially leachable content i.e. $[SO_4^{2-}]_i$ concentration increases with the increase in temperature, probably due to the mobilization and leaching of some insoluble sulphates with increase in temperature.

3.6 Effect of Temperature on LR_{obs}

The effect of temperature on LR_{obs} at $[SO_4^{--}]_{add}$ =20 mg/kg is shown in Fig. 5, which show that the temperature has only a small effect on LR_{obs}, although there is only a sizeable effect on $[SO_4^{--}]_i$ at fixed $[SO_4^{--}]_{add}$ concentration.

From the intercept of log LR_{obs} vs log $[SO_4^{--}]_i$ curve, the value of log k were determined at different temperatures. The Values of the rate constant are found out to be different at all temperatures.

Earlier the effect of temperature on sulphate desorption in cecil soil has been studied by Hodge and Johnson [13]. The first order desorption plots show an initial increase with increase in the temperature range 4-20°C however first order rate constant varied directly with the percentage of sulphate desorbed. Since the temperature changes with the change in climatic condition, soil depth and crop growth. A study of temperature dependence on the rate of leaching is important to understand the effect of climatic factors on leaching.

3.7 Effects of Attached Cation Size on LR_{obs}

The sulphate salts used in this study have the different cations. The role of attached cation on the leaching of sulphate is also very important and has not been studied in the earlier works. In the present study, the effect of attached cation on the sulphate leaching appears to be related to the size of cation. Fig. 6 depicts the plot between LR_{obs} vs radii of the cations. It can be seen clearly from Fig. 6 that LR_{obs} values increases with the size of cation. The results can be explained on the basis of covalent character and radii of the hydrated ions. Smaller the size of cation, larger will be the radius of the hydrated ion and lesser will be its mobility. The ionic size, ionic character, radii of hydrated ions, mobility of ions and LR_{obs} values for different ions are in following order.

Cations size	$Na^+ > Mg^{2+} > Al^{3+}$
Radii of hydrated ion	$Al^{3+} > Mg^{2+} > Na^+$
Mobility of ion	$Na^+ > Mg^{2+} > Al^{3+}$
Ionic character	
	$Na_2SO_4 > MgSO_4 > Al_2(SO4)_3$
LR_{obs}	
	$Na_2SO_4 > MgSO_4 > Al_2(SO4)_3$

3.8 Effect of Water Filled Porosity

Initial water content or water filled porosity (θ) of the soil column was varied from .33 to .51 $cm^3 cm^{-3}$. LR_{obs} calculated values were found to increase only slightly on increasing initial water content of the soil column.

3.9 Application of the Kinetics Models

The data for the leaching of sulphate in acidic Indian soils were used to find the best fit model describing the kinetics of leaching of water soluble sulphates in soil. It appears from the leaching profiles that the rate of leaching in the first few hours is relatively fast becoming quite slow in the later stage. A similar behavior has been noted earlier in the sulphate desorption [17]. While applying the various integrated equations of different kinetics models, the concentration of leachable sulphates was assumed to be the maximum initially, i.e. at t=0 for $[SO_4^{--}]_i$. The concentration terms used in different equations are defined as

$[SO_4^{..-}]_i = C_0$ $[SO_4^{..-}]_t = C_t$ $[SO_4^{..-}]_1 = [SO_4^{..-}]_i - [SO_4^{..-}]_t = C_0 - C_t$

Zero Order Kinetics Model $C_0 - C_t = a - bt$
First Order Kinetics Model $\ln[C_0 - C_t] = a - bt$
Elovich Equation $C_t = a + b\ln t$
Parabolic diffusion $C_t = a + b\,t^{1/2}$

These equations were tested by using the statistical analysis on the excel software. The first order kinetics and Elovich model has been found to have excellent correlation for the desorption/Leaching of the sulphate attested by SEE and high r^2 values. However there is little correlation for the zero order and parabolic profiles.
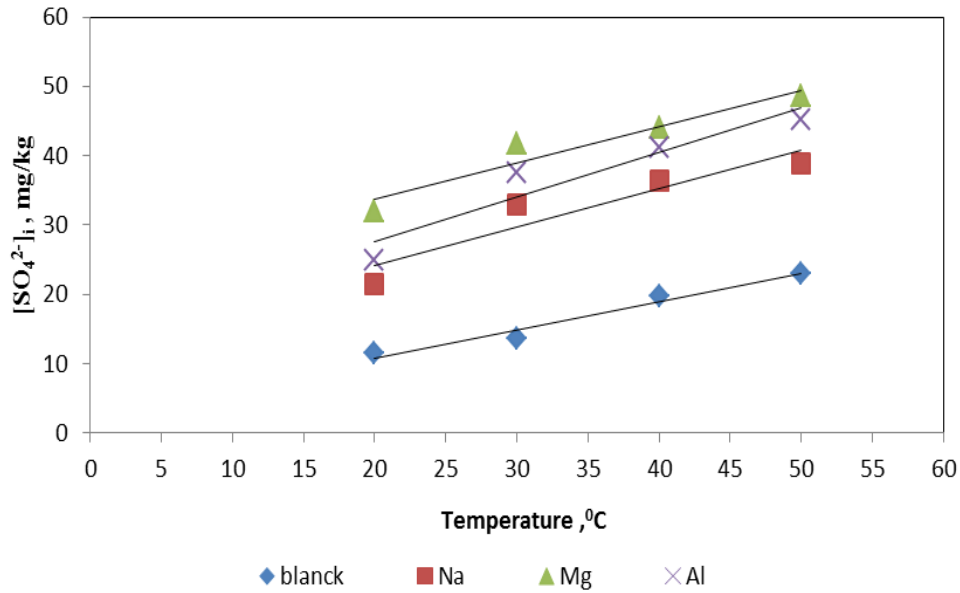

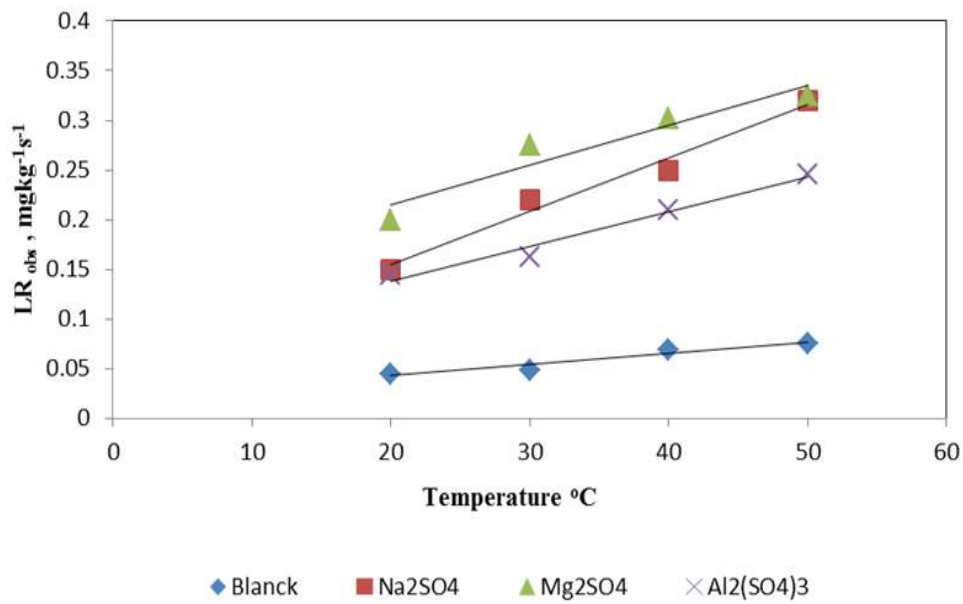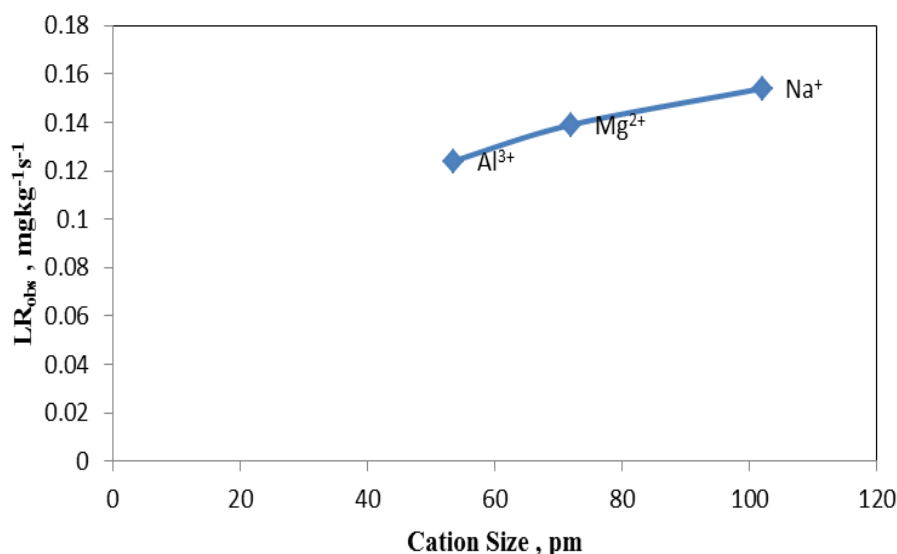**Fig. 4. Variation of $[SO_4^{2-}]_i$ with temperature for leaching of different sulphate salts**

Fig. 5. Variation of LR_{obs} with temperature for the leaching of sulphate salts, $[SO_4^{2-}]_{add} = 20$ mg/kg

Fig. 6. Change in LR$_{obs}$ with size of cation for different sulphate salts at fixed [SO$_4^{2-}$]$_i$=20 mg/kg at 30°C

4. CONCLUSION

Investigations have been carried out to study the leaching behavior and kinetics of three different sulphate salts viz. Na$_2$SO$_4$, MgSO$_4$ and Al$_2$(SO$_4$)$_3$ in Indian soil environment. In this work the initial rate method has been applied for the first time for the study of sulphate leaching using glass column method. The importance of this study is underlined by the preliminary reports of earlier workers that the sulphate desorption is time dependent. Almost all the sulphate desorption studies carried out so far explained that maximum desorption (75% to 100%) has been achieved during the initial period of 30 min [11]. We have also arrived to a similar conclusion in the present study.

The results of the present study show that the sulphate leaching rate is least for Al$_2$ (SO$_4$)$_3$ which can be explained as follows-

(i) Al$_2$ (SO$_4$)$_3$ in the soil systems is reported to [19] make a complex with hydroxyl ions e.g. Zurbanite Al(OH)SO$_4$, basaluminite [Al(OH)$_{10}$SO$_4$] and alunite [KAl$_3$(OH)$_6$(SO$_4$)$_2$]. There is always a possibility of formation of such complexes in the present study too, which may result in the hindrance in leaching, thus resulting in lower leaching rates for Al$_2$ (SO$_4$)$_3$.

(ii) In soil, sulphate is reported [20] to form a binuclear bridge complex with aluminium which may also hinder the mobility of Al$_2$(SO$_4$)$_3$ in soil.

(iii) So far as, the diffusion of salts in heterogeneous soil is concerned, in order to maintain electrical neutrality during diffusion of an ionic species, inter diffusion of the ions of opposite charge occur in the same direction [21]. It is studied [22] that an anion species while leaching may slowly change the partners with invading cations and become more inhabitant anion. If the salt concentration is high, this change of partners will have insignificant effect on anion diffusion. But, this earlier fact could not explain our results of change in leaching rates of sulphate with change in cation partners. In the present case, increase in LR$_{obs}$ with increase in size of the attached cation can be explained on the basis of the covalent character and radii of the hydrated cation.

As the ionic size increases, the ionic character decreases, but covalent character increases. Moreover, smaller is the size of cation, larger will be the radii of the hydrated ion. Thus the mobility of the ion will decrease with the increase in the size of hydrated ion [22]. Our results support this explanation as maximum leaching rate is observed with Na$_2$SO$_4$ while minimum for Al$_2$(SO$_4$)$_3$.

The raise in [SO$_4^{2-}$]$_i$ at constant [SO$_4^{2-}$]$_{add}$ value with increase in temperature, in the range 20-50°C seems to be due to increase in solubility of salt. It was observed that at fixed [SO$_4^{2-}$]$_{add}$, LR$_{obs}$

varied with temperature due to increase in $[SO_4^{2-}]_i$. Temperature variation at fixed $[SO_4^{2-}]_i$ was not possible in our study as soil columns were not saturated with salt solutions prior to leaching.

The present study shows, beyond doubt that first order and Elovich equation are the best fit models for representing sulphate leaching with water in acidic soil. Hodge and Johnson while studying desorption of sulphate with KCl solution found parabolic diffusion to be the best fit, while other studies [18,23,24] support applicability of Elovich and first order equations.

This study suggests that for development of salt transport models in soils, influence of porosity, attached cations and temperature should also be taken into consideration along with other physico-chemical characteristics of the soil [25].

Thus, the present study proves that leaching of sulphate salts can be studied by initial rate method, which can also be applied for monitoring the fate of applied sulphate in agricultural fields and its diffusion into soil solution for plant up take as well as in calculating the downward transportation of sulphate from polluted site to the underground water.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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