Controlling the Release of Active Iron and Manganese Ions from Styrene-Butadiene Rubber-Binding Matrix Containing Chloride Salts of Them

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ABSTRACT: Slow release technique is a new trial to control the release of manganese and iron ions from styrene-butadiene rubber (SBR) formulations containing manganese and iron chlorides. The SBR compounded was mixed and vulcanized according to the general equipment of rubber. Discs of surface area about 16 cm^2 for each one were prepared and subjected to leaching rate test in aqueous media. The release rate of manganese and iron ions was prolonged for up to 5 months. The profile behavior of the release for the two investigated ions are similar, the difference between them is in the amount of release dispersed ions in water. The concentration of active ingredients; manganese and iron chlorides; and environmental water temperature were affected on the amount of release rate. According to the higher solubility of manganese chloride on aqueous media, the release of manganese was greater than iron. The diffusions coefficient of the released manganese and iron ions in aqueous media were 7.9×10^{-7} and 4.9×10^{-7}, respectively, according to Higuch's equation. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 811–817, 2009

Key words: controlled release; release of manganese and iron; micronutrients; styrene-butadiene rubber (SBR)

INTRODUCTION

Slow and controlled release fertilizers are fertilizers containing a plant nutrient in a form which delays its availability for plant uptake and use after application.[1]

The massive use of commercial fertilizers in agriculture, as well as the concentration of life-stock production by conventional methods, result in greater risks of polluting surface and underground water.[2]

The controlled release techniques can be used as a new means of applying fertilizers to reduce the draw backs resulted from using conventional methods, as losses of fertilizers from agricultural lands and increase the efficiency of uptake by plant. The seven micronutrients elements, including born, copper, chlorine, iron, manganese, molybdenum, and zinc, are no less important to plant growth that are the macronutrients in the soils. Micronutrients are required in a very small quantities; only few mg/kg; in plant tissues being one or more orders of magnitude lower than for the macronutrients. The main symptoms of iron and manganese deficiency are chlorosis or yellowing between the veins of new leaves. The functions of manganese and iron are activating number of important enzymes, important for photosynthesis and nitrogen metabolism.[3]

The slow release technique depends on regulating the release of the active material from polymeric matrices and releasing it in minute amounts over long periods[4] of time. The main advantages of this technique are to increase the efficiencies of uptake by plants as well as reducing application cost. Several polymeric materials have been developed for controlled release formulations.[5]

Rubber is suitable to be used as binding matrix for bioactive ingredients and releasing them through diffusion dissolution mechanism.[4] Rubber compounds have been used as vulcanizates which is prepared by using the conventional mixing equipment[6,7] for rubber.

This work aims to prepare styrene-butadiene rubber (SBR) formulations containing manganese and iron chlorides as micronutrient elements for plant also for studying the parameters affecting the performance of releasing these ions in water.

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MATERIALS AND EXPERIMENTAL TECHNIQUES

Materials

1. Styrene-butadiene rubber (SBR 1502, was a product from Bayer AG (Germany).

TABLE I
SBR Formulation Containing Different Concentrations of $MnCl_2$ and $FeCl_2$

Ingredients (phr)	Formula no.														
	M1	M2	M3	M4	M5	M6	M7	M8	F1	F2	F3	F4	F5	F6	F7
SBR	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Stearic acid	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
ZnO	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
MBT	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
S	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
PBN	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Silica	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20
$MnCl_2$	10	20	30	40	50	60	70	80	0	0	0	0	0	0	0
$FeCl_2$	0	0	0	0	0	0	0	0	10	20	30	40	50	60	70

2. Strearic acid with specific gravity at 15°C = 0.9–0.97, with white flakes was supplied by Aldrich Company, Germany.
3. Zinc oxide (ZnO) with specific gravity = 5.55–5.61, was supplied by Aldrich Company, Germany.
4. 2-mercaptobenzothiazole (MBT) with specific gravity = 1.47–1.53, was supplied by Aldrich Company, Germany.
5. Elemental sulfur (S) with fine pole yellow powder and specific gravity = 2.04–2.06 was supplied by Aldrich company, Germany.
6. Phenyl β naphthyl amine (PBN) with specific gravity = 1.16–1.18, was supplied by Aldrich Company, Germany.
7. Silica light reinforcing 82% precipitated silicon dioxide with specific gravity 1.95, pH 6.2 ± 0.8 were used as filler supplied from the Degussa, Germany.
8. Manganese chloride ($MnCl_2$) as a source of manganese (Mn), particle size 40 μm was a product from Sisco Research Laboratories, India.
9. Iron chloride ($FeCl_2$) as a source of iron (Fe), particle size 50 μm was a product from BDH Laboratory England.

Experimental techniques

The typical investigated formulations of rubber compounds are shown in Table I. These mixings were carried out on a laboratory two-roll mill (470 mm diameter and 300 mm working distance). The speed of the slow roll is 24 rev/min with a gear ratio of 1 : 1.4.

An oscillating disc rheometer model 100 from Monsanto, USA was used for measuring the curing characteristics of the rubber compounds according to ISO 289-1994.

The compounded rubber was vulcanized in a hydraulic press under a pressure of about 4 MPa and temperature of (152 ± 1)°C for their optimum cure time (T_{c90}).

Leaching rate

The leaching rate technique used was similar to that described by Marson.[8] The rubber formulations were used as rectangular discs 2 cm in length, 1 cm thickness, and total surface area is about 16 cm^2. The discs were immersed in 500 mL of water at different temperatures (15, 25, 30, and 50°C) and the water was changed daily during the period of study. The amount of released manganese and iron were determined spectrophotometrically[9] at wave length 415 nm for both manganese and iron chloride. The spectrophotometer used type was UV-240 1PC Visible VIS. A calibration standard was shown in Figures 1 and 2.

Water uptake

A disc of 1 g weight was suspended in 50 mL of distilled water. The sample was blotted between two filter papers and weighed the swollen disc. This

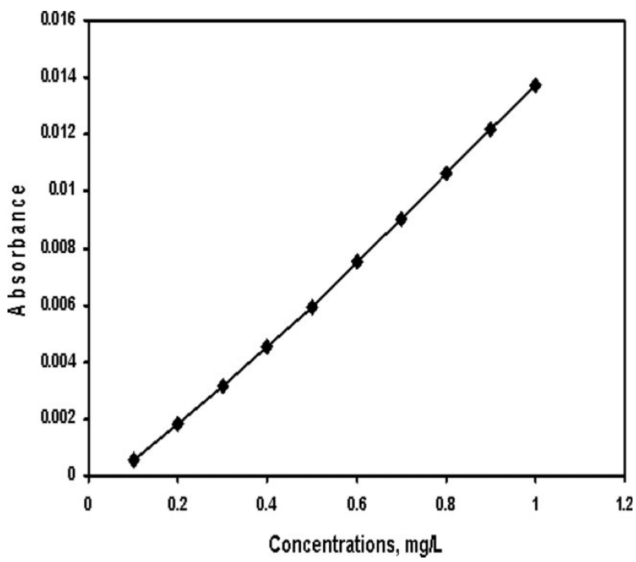

Figure 1 Calibration curve for manganese chloride ($MnCl_2$).

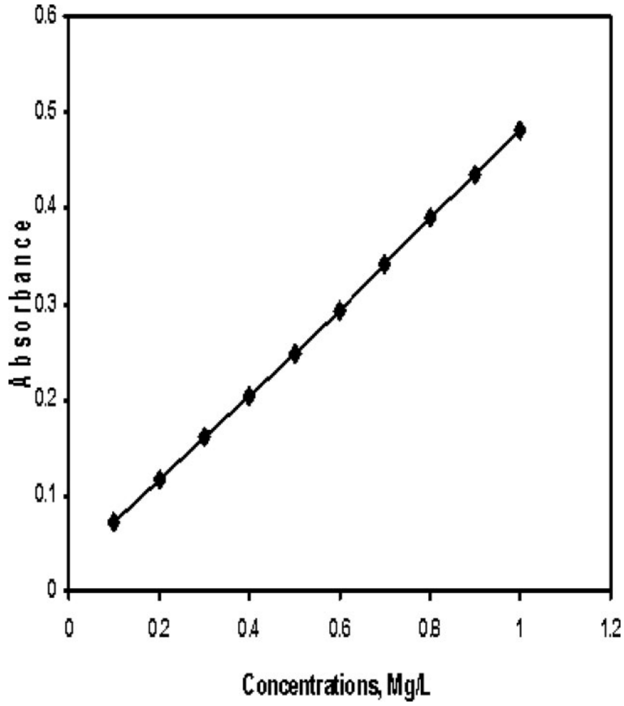

Figure 2 Calibration curve for iron chloride ($FeCl_2$).

process was repeated until the equilibrium swelling. This constant weight of the swollen disc of the water uptake was determined according to the following equation:

$$\text{Water uptake } \% = (w - w_0/w_0) \times 100$$

where, w_o and w are the weight before and after immersion, respectively.

RESULTS AND DISCUSSIONS

Rheological characteristics

A Monsanto oscillating disc rheometer was used to characterize the rubber mixes and the various measures are given in Table II. It can be seen that the minimum torque decreased as the loading of manganese and iron chlorides increased for all rubber formulations.

The maximum torque increased and the time of 90% cure decreased as the loading of manganese and iron chlorides increased for all rubber formulations. These results for cure time were reflected in the cure rate index.

The formulated discs were vulcanized at the optimum cure time given from Table II.

Evaluation of the release of iron and manganese ions from the investigated formulated discs

This work deals to investigate the release rate of manganese and iron ions from controlled release formulations containing manganese and iron chlorides, physically bonded with SBR and evaluate their availability for sustained release over long periods. Disc of surface area 16 cm^2 each where subjected to leaching rate test. Figure 3 represents the leaching rate of manganese and iron ions released from formulations No (M5) and (F5). The leaching rate was expressed as (mg cm^{-2} day^{-1}). The results had shown that, both of the formulations (M5) and (F5). In the first few days the release of manganese and iron ions were leached at higher rate, then this rate of release was decreased and after twenty days we observed that this release is in steady state and was extended up to five months. The results indicate that, the formulation which is containing the manganese is higher leaching rate than the formulation which is containing iron. This may be attributed to the structural formula of manganese, shows lower particle size which helps in making micropores in rubber that leads to increase the release.[10]

Effect of manganese and iron chloride loading on the release rate

Figures 4 and 5 were represented the release rate of manganese and iron ions in aqueous media from all different formulations in Table I which are containing different loading of the active ingredients (manganese and iron chlorides). From all these figures, we can be

TABLE II
Rheometric Characteristics of SBR Containing Different Concentrations of $MnCl_2$ and $FeCl_2$

	Formula no.														
	M1	M2	M3	M4	M5	M6	M7	M8	F1	F2	F3	F4	F5	F6	F7
Rheometric characteristics at (152 ± 1)°C															
ML (dN m)	12	11.5	7.5	7	6	5.5	5	5	12	11	9.5	8.5	8	8	7.5
MH (dN m)	61	70	71	74	75	78	79	80	55	57	61	63	65	68	70
T_{c90} (min)	23.5	21	21	18	17	16	16	15	26	24	23	21	21	20	20
T_{s2} (min)	5.5	5	4.5	3.5	3	3	3	2.5	6	4	4	3.5	3.5	2.5	2.5
cRI (min^{-1})	5.5	5.88	6.06	7	7.4	7.69	7.69	8	5	5	5.26	5.71	5.71	5.71	5.71

ML, minimum torque; MH, maximum torque, T_{c90}, optimum cure time; T_{s2}, scorch time; cRI, cure rate index.

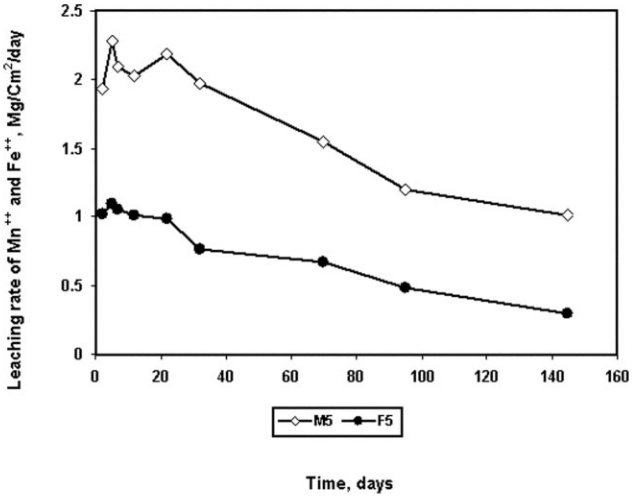

Figure 3 The release rate of manganese and iron ions from SBR vulcanizates.

seen that, the behavior of release profiles of the investigated ions are nearly similar to each other, the difference between them is in the amount of released ions which depends on manganese and iron chlorides loading in the formulations. So, we can see that when the loading ions are high give higher release and also when the loading ions are small give smaller release. The release was observed through diffusion-dissolution mechanism, diffusion of water inside formulation, and dissolution out side upon exposure to water, due to presence manganese and iron molecules near the rubber surface readily migrate into solution. As the surface layers of the discs depleted, the pore structures were formed also they provided the manganese and iron release to be sufficiently rapid, these leads to the penetration of water to the pore structures.

The process continues, although the rate of lose usually varies with the tortoises of the growing pore structure and other factors.[11]

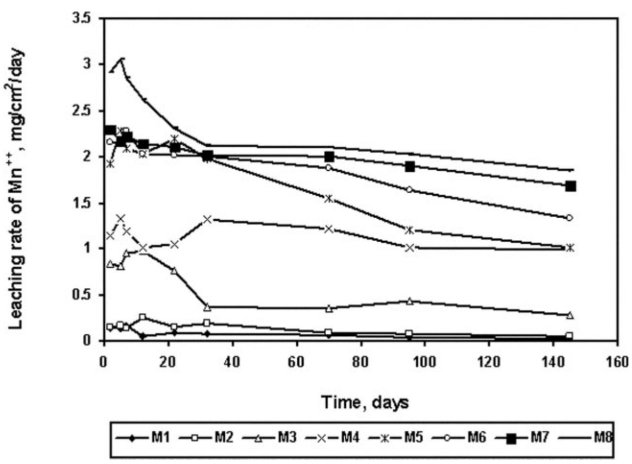

Figure 4 The leaching rate of manganese ions from SBR formulations at 25°C.

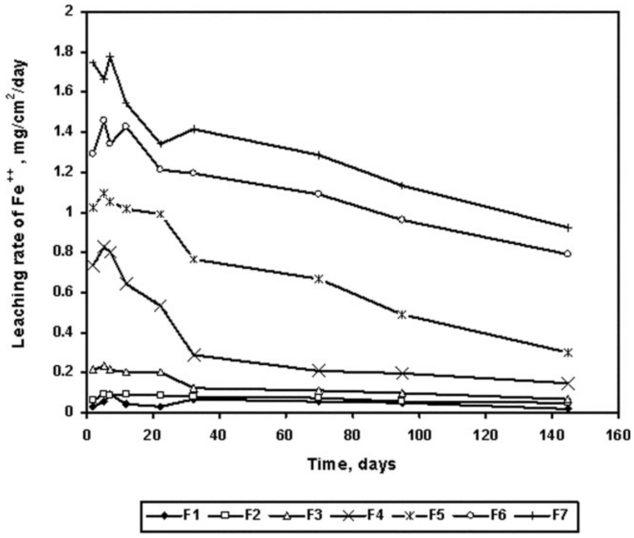

Figure 5 The leaching rate of iron ions from SBR formulations at 25°C.

Also it was found that, the diffusions coefficient of the released manganese and iron were 7.9×10^{-7} and 4.9×10^{-7}, respectively, according to Higuch's equation[12]

$$M_t = A(2DTC_sC_0)^{1/2}$$

where, M_t, Accumulated amount of release manganese and iron at time T; A, the surface area; D, Diffusion coefficient; C_s, solubility[13] of manganese chloride and iron chloride (143 parts and 98 parts/100 part of water by weight, respectively); C_o, initial drug; T, the time.

Effect of pH of the aqueous media on the release rate of manganese and iron ions

Figures 6 and 7 show the release pattern of manganese and iron in aqueous media having different pH values at room temperature for different time periods up to 12 days, using formulation No (M8) for manganese and formulation No (F7) for iron. It is clear that, the amount of manganese and iron released depend on the pH value of aqueous media. The lowest release was observed in tap water pH 7.3, whereas at the acid media pH 2 the release of manganese and iron are greater than in the basic media pH 11. The effect of pH on the release of manganese and iron ions may be due to the presence of hydrogen (H^+) and hydroxyl (OH^-) ions in the acidic and alkaline media, also the leaching rate of manganese ions was more than iron ions and that results confirmed the results of the leaching rate at room temperature.

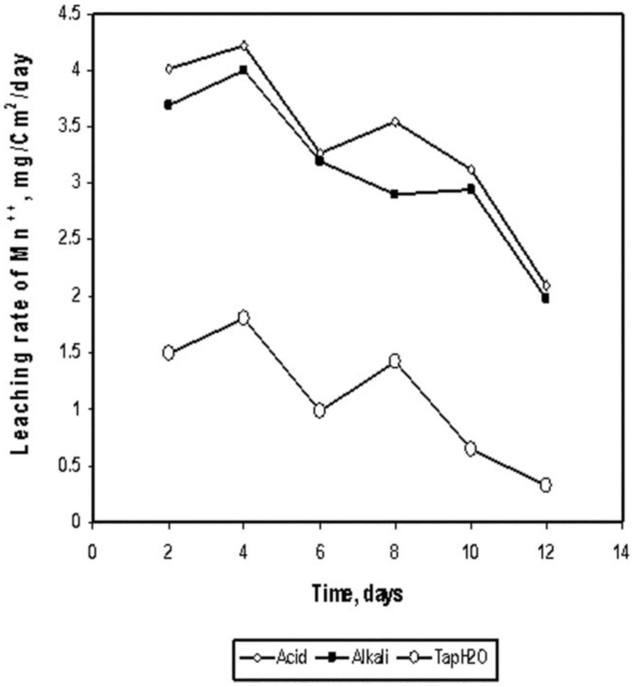

Figure 6 Effect of pH of the aqueous medium on the leaching rate of Mn^{++}.

Effect of temperature on the leaching rate

The effect of environmental temperature on the leaching rate of manganese and iron from the formulation No (M8 and F7), respectively, were studied at temperature range of 15, 25, 40, and 60°C for 7 days. The results obtained represented in the Figure 8, which is shown that, the leaching rate increases as the temperature increases. So, higher release was observed at

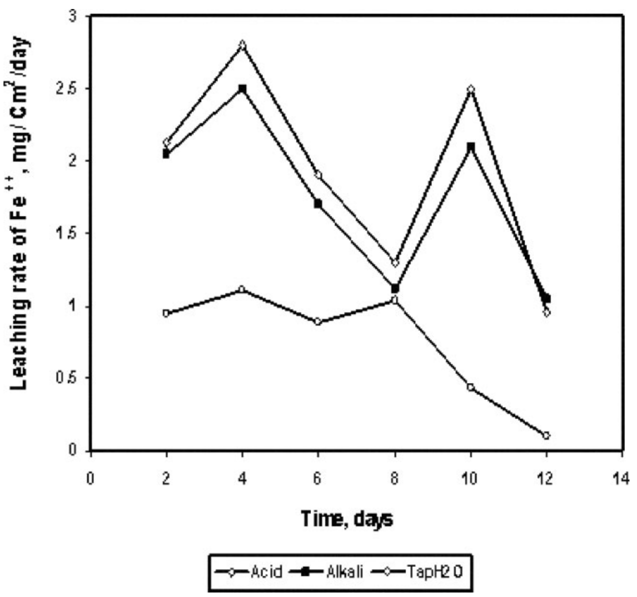

Figure 7 Effect of pH of the aqueous medium on the leaching rate of Fe^{++}.

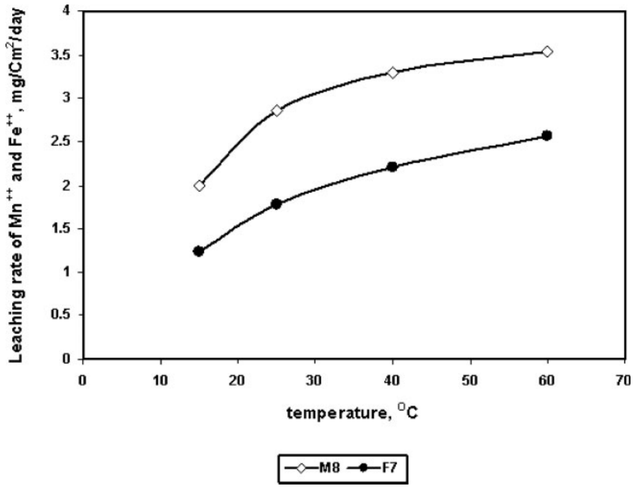

Figure 8 Effect of temperature on the leaching rate of Mn^{2+} and Fe^{++}.

60°C, whereas the lowest release took place at 15°C, also moderate release was obtained at 25 and 40°C. This may be due to the greater space between the molecular chain of the investigated formulation which affected by high temperature.

Effect of manganese and iron chlorides loading on the water uptake of SBR formulations

The water uptake of the investigated SBR formulations, which was loaded with different concentrations of manganese and iron chlorides, were evaluated for along time to investigate the impact loading of manganese and iron chlorides on the water uptake of the SBR formulations as shown in Figures 9 and 10. It can be observed that, the water uptake was greatly increased with increasing the

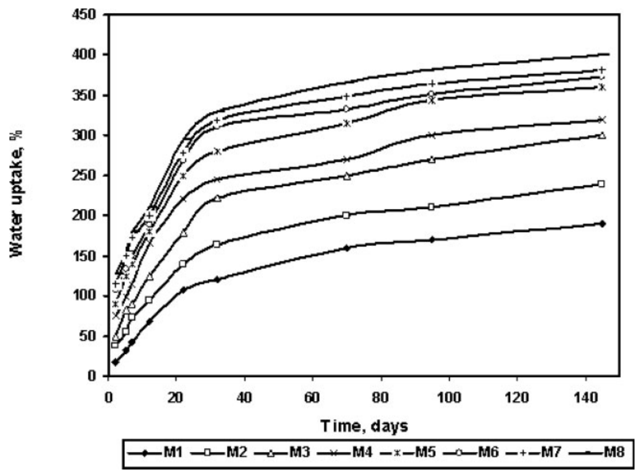

Figure 9 Effect of concentrations of manganese chloride on the water uptake for SBR/$MnCl_2$ at 25°C.

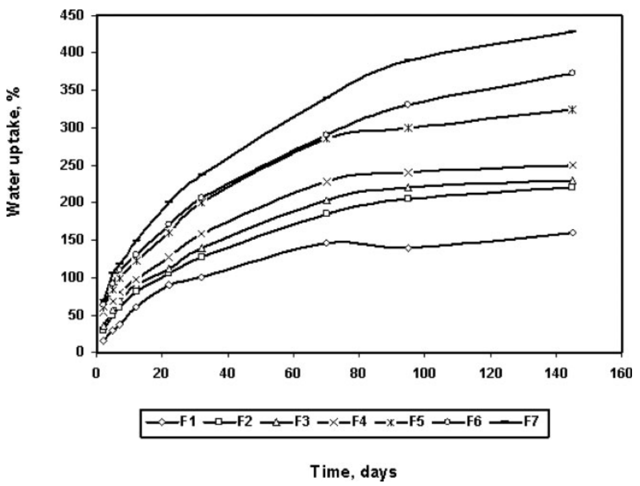

Figure 10 Effect of concentrations of iron chloride on the water uptake for SBR/$FeCl_2$ at 25°C.

amount of manganese and iron chlorides and reached the maximum at 80 phr for manganese and 70 phr for iron; this can be attributed to the presence of the pores inside the formulation formed due to dispersion of water. The water uptake of the formulation containing manganese chloride was more than that water uptake of the formulation containing iron chloride, this is may be due to that the manganese chloride dissolved in water greater than iron chloride,[13] i.e., higher solubility in water enhances its diffusion from the matrix and consequently the released amount of active agent increased.

The kinetics release of formulation containing manganese and iron chlorides

It is interesting to calculate the release kinetics to show the behavior of the release. The release data from the formulations containing 80 phr and 70 phr for manganese and iron chlorides, respectively, at 70°C for different time ranged from 1 to 6 h were followed by the following equation:

$$Q = Ktn$$

where, Q is the fractional amount released at time t, K is the kinetic constant, n is the release exponent indicate Fickian diffusion,[14] values of $n \sim 0.5$.

Figure 11 indicates the release kinetics of manganese and iron chlorides. In case of, that the kinetic constant (K) decrease as the time increased and consequently the release increased.

Permeation of Mn^{2+} and Fe^{2+} from SBR formulations containing manganese and iron chlorides

To characterize the system, Mn^{2+}/water and Fe^{2+}/water partition coefficient, two formulations were

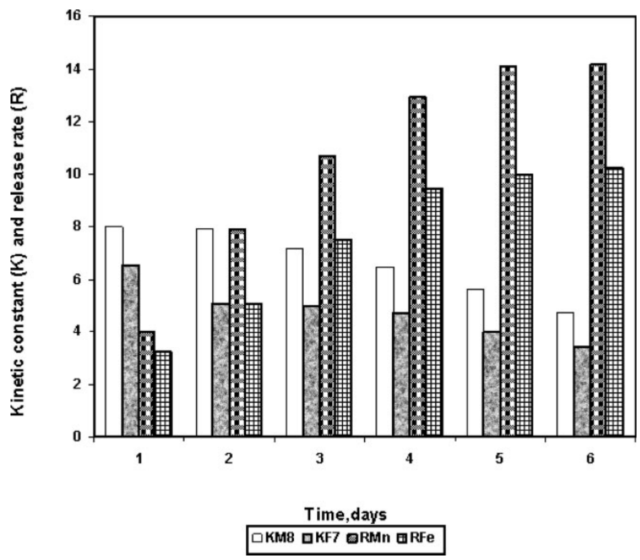

Figure 11 The kinetic constant (k) and accumulated release of Mn^{++} and Fe^{++} from SBR vulcanizates at 70°C.

used (20 and 80 phr) and (20 and 70 phr) for manganese and iron chlorides, respectively. The permeation coefficient (P) was calculated using the following relationship.[15]

$$J = PC_d$$

where, J is the steady state flux, C_d is drug donor concentration.

The permeation of Mn++ and Fe++ across the formulation to water were studied spectrophotomically, from the permeation profiles, Mn++ and Fe++ were calculated the permeation curves which are shown in Figures 12 and 13.

From the results, it is observed that the permeation coefficient (P) depends on the type and the

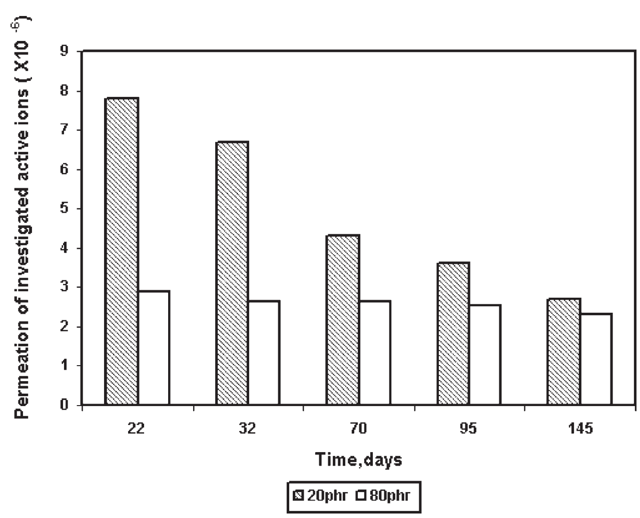

Figure 12 The permeation curve of manganese/water system.

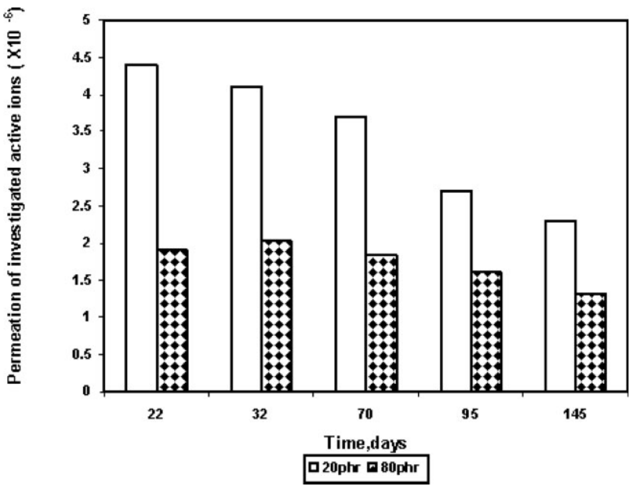

Figure 13 The permeation curve of iron/water systems.

concentration of the released material. Therefore, it is easy to study the release of manganese and iron using conventional release experiments as described by Marson.[8]

CONCLUSIONS

1. Controlled release system is a good technique used for controlling the release of micronutrient elements for plant nutrition such as manganese chloride and iron chloride.
2. SBR can be used as a binding matrix for manganese chloride and iron chloride.
3. The releases of the investigated active agents depend on environmental temperatures and the type of the aqueous media.
4. The permeation coefficient of the released ions depends on their type and concentration.

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