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The Repercussions of the Combined Use of Potassium Iodate and Chitosan Iodate on the Controlled Fractionation of Iodine

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ABSTRACT

Background: Iodine is found in soils in both inorganic and organic forms [Iodate-(IO_3^-) and Iodide-(I^-)]. Iodine is highly prone to leaching and volatilization which results in iodine depletion in soils. Crops cultivated in these soils will be lacking in iodine and humans and animals eating food grown in these soils will be deficient in iodine. Numerous studies have focused on the process by which iodine is absorbed from the soil, but there is still paucity of knowledge on different fractions of iodine in soils.

Methods: In our work, we assessed different fractions of iodine (Water Extractable, Exchangeable, Organic bound, Oxide bound and Residual iodine) in soil from different sources of chitosan and potassium iodate alone and combinations. The incubation experiment was carried out in the department of soil science and agricultural chemistry, Tamil Nadu Agricultural University, Coimbatore in 2022. Potassium iodate and chitosan were applied in the form of soil alone, soil drenching and chitosan iodate complex at different stages of incubation.

Result: The results suggested that combination and potassium iodate and chitosan complex has increased the iodine stability throughout the incubation experiment. As electrostatic interaction between chitosan and iodate prevents volatilization and gradually stabilizes the availability of iodine. Our findings offer more details on iodine mobility and behaviour in soil when it is used alone and combination with chitosan at different rates.

Key words: Biofortification, Chitosan, Fractionation, Iodine, Potassium.

INTRODUCTION

Iodine was discovered by Courtois in 1811, a violet vapor arising from seaweed ash while manufacturing gunpowder for Napoleon's army. Gay-Lussac identified it as a new element and named it as Iodine. In 1895, Baumann founded iodine in thyroid gland. The earth's iodine (as iodide) is extensively spread but unevenly distributed because iodine is a rare element that is primarily found as a salt, it is referred to as iodide rather than iodine Due to the presence of negative charge on iodine it is highly susceptible to leaching. Further iodine is also highly prone to volatilization loss due to biochemical and physiochemical properties of soil (Roulier *et al*., 2019). Indian soils in average contain only 3 mg kg^{-1} of total iodine which is less than its critical level (5 mg kg^{-1}). Despite the fact that higher plants do not consider iodine to be a micronutrient, living organisms require it. Iodine is also necessary for the development of nerve tissue and brain during pregnancy and early years of a child's life (Godswill *et al*., 2020).

An essential mineral, iodine is used by the thyroid gland to make thyroid hormones that control many functions in the body including growth and development. Because huamn body does not produce iodine, it needs to be supplied by foods and beverages. When iodine intake is poor, the body cannot produce enough thyroid hormones. Iodine deficiency in pregnancy is a worldwide problem and has become a global public health concern since it is identified as the leading cause of preventable brain damage in newborns and infants due to inadequate intake. Major international efforts are being made to help reduce the problem, mainly through the use of iodized salt and supplements. Hypothyroidism, thyroid gland enlargement (goiter) and weight gain are other conditions that may result from too little iodine intake.

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Iodine has several oxidation states and its behavior in soil is complicated by factors such as soil composition, texture, pH and redox processes (Nieder *et al.*, 2018). Depletion of surface soil iodide due to leaching, flooding and erosion results in increased iodide deposition in seas. Sea water iodide ions are converted to elemental iodine, which is subsequently volatilized into the atmosphere until rain returns it to the land. In many areas, the iodine cycle is sluggish and incomplete, resulting in iodine depletion in soil and drinking water (MacKeown *et al.*, 2022). Iodine in soil undergoes physical, chemical and biological transformations as part of its normal biogeochemical cycle, which can limit its transfer to plants but still significantly increasing its environmental mobility (Liu *et al.*, 2023). So it is quite important to study the nature and behavior of iodine in soil to know its various losses and also to minimize the losses to increase its availability in soils.

As a result, in the current investigation, an incubation experiment was conducted to determine the mobility of iodine in soil under controlled condition by applying iodine at various rates and combinations. Chitosan was also applied as one of the treatment as it is having the capacity to complex iodine thereby reducing its losses.

MATERIALS AND METHODS

To examine the iodine release pattern, an incubation experiment was conducted with ten treatments with 3 replications under completely randomized design with potassium iodate and chitosan. Chitsoan product was purchased from Kerala Marine Hydrocolloids with a molecular weight of 501.486 g/mol and more than 75% deacetylation. Sigma Aldrich company supplied potassium iodate containing 59% iodine and 18% potassium The treatments are as follows; T_1- KIO_3 Soil Application (SA)- 5 kg ha^{-1} , T_2- Chitosan-KIO_3 Complex-5 Kg ha^{-1}, T_3- Soil Drenching (SD)-KIO_3-0.2% at 60 and 90 DAI ,T_4- KIO_3- Soil Application at 5 $Kgha^{-1}$ + Soil Drenching -KIO_3- 0.2% at 60 and 90 DAI, T_5- Chitosan-KIO_3 Complex-5$Kgha^{-1}$ + Soil Drenching-KIO_3-0.2% at 60 and 90 DAI, T_6- KIO_3- Soil Application- 5 $Kgha^{-1}$ + Soil Drenching-KIO_3- 0.3% at 60 and 90 DAI, T_7- Chitosan-KIO_3 Complex-5 $Kgha^{-1}$ + Soil Drenching -KIO_3-0.3% at 60 and 90 DAI, T_8- Chitosan-KIO_3 Complex-10 $Kgha^{-1}$ + Soil Drenching -KIO_3-0.3% at 60 and 90 DAI, T_9- Chitosan Spraying (control) and T_{10}- Water Spraying (Absolute Control). An unfertilized surface soil was collected from Viraliyur farmer's field belonging to Palaviduthi soil series taxonomically *Typic Rhodustalf*. The soil was air dried and sieved to < 2 mm. The fertilizer sources such as Urea, single super phosphate, muriate of potash, chitosan and potassium iodate were added in 200 ml plastic cups containing 100 g soil and thoroughly mixed as per the treatments. After thorough mixing, distilled water was added to bring the gravimetric water content of soil to field capacity. The moisture content was maintained throughout the experimental period by correcting the water loss periodically. After two days of incubation potassium iodate and the chitosan iodate complex solution was fertilized into the soil. The soil is neutral in pH and non saline in EC. The experimental soil contains 1.33 mg kg^{-1} of water extractable iodine, 0.24 mg kg^{-1} of exchangeable iodine, 1.21 mg kg^{-1} of organic matter iodine, 0.67 mg kg^{-1} of oxide bound iodine, 0.21 mg kg^{-1} of residual iodine Soil samples were collected during 40, 80 and 120 days after incubation and analyzed for different iodine fractionation (Table 1). The iodine fractions was measured by following the procedure of Duborska *et al.* (2020) and iodine concentration was measured using inductively coupled plasma-optical emission spectrometry by following procedure of Knapp *et al*. (1998). The programme IBM SPSS® Statistics, version 25 was used to run all statistical tests.

RESULTS AND DISCUSSION

Water extractable iodine

In relation to the allocation of iodine in various forms, it is observed that the water extractable and exchangeable fractions exhibit higher accessibility for crop absorption in comparison to other fractions. The water-soluble iodine concentration exhibited a decline from the 40^{th} day of incubation to the 120^{th} day of incubation across all treatments, with the exception of the treatment including the application of potassium iodate alone by soil drenching at 60 and 90 days after incubation (DAI) (Table 2). The application of KIO_3 alone by soil drenching resulted in a rise in the observed parameter from the 40^{th} day after incubation (DAI) to the 80^{th} DAI, followed by a subsequent drop from the 80^{th} DAI to the 120^{th} DAI, as presented in Table 2. The application of iodate by soil drenching may have resulted in an enhancement in the iodine content that can be extracted from water samples at the 80^{th} day after incubation (DAI). Furthermore, a more pronounced drop in water extractable iodine was observed throughout the later phases of the experiment, namely between the 80^{th} and 120^{th} days after incubation (DAI). In contrast, the use of Cs-KIO_3 in isolation, as well as the combined application of Cs-KIO_3 and SD-KIO_3, resulted in a reduction in the depletion of iodine that is

Table 1: Fractionation of Iodine.

Fractions	Extracting reagent
Water extractable Iodine	Distilled water
Exchangeable Iodine	1M Neutral normal ammonium acetate
Oxide bound Iodine	0.04% Hydroxylamine hydrochloride
Organic bound Iodine	5% Tetra methyl ammonium hydroxide solution (Extraction)
Residual Iodine	5% Tetra methyl ammonium hydroxide solution (Digestion)

extractable in water for the whole duration of the incubation period, as compared to other treatments. The observed phenomenon can be attributed to a decrease in the rate of volatilization of iodate fertiliser when it is co-applied with chitosan, as opposed to its application in isolation. (Rakoczy-Lelek *et al.*, 2021).

Exchangeable Iodine

The combined treatments of $CsKIO_3$ and SD-KIO_3 exhibited the greatest levels of exchangeable iodine content during all phases of incubation. Regardless of the treatments used in the incubation research, the levels of exchangeable iodine generally exhibit a decline during the course of incubation period, with the exception of the treatment including sole soil drenching of potassium iodate. In all phases of incubation, the rate of decline in exchangeable iodine was seen to be lower for the treatments including Chitosan alone, as well as the combined treatments of Cs-KIO_3 and SD-KIO_3, when compared to the rate of decrease in water extractable iodine. In contrast, the treatments using SA-KIO_3 alone and the combination of SA-KIO_3 and SD-KIO_3 resulted in the greatest reduction in exchangeable iodine compared to water extractable iodine, as seen in Fig 1. The preservation of exchangeable iodine in chitosan applied treatments may be attributed to the robust interaction between chitosan and iodate, as shown by Andreica *et al*. (2020). Among the various treatments, the application of Chitosan-KIO_3 complex at a rate of 10 kg ha^{-1} combined with SD-KIO_3 at a concentration of 0.3% at 60 and 90 days after incubation (DAI) treatment resulted in a smaller reduction in exchangeable iodine levels compared to other treatments. Specifically, there was an 11.4% decrease in exchangeable iodine levels from the 40^{th} to the 80^{th} DAI and a 9.6% decrease from the 80^{th} DAI to the 120^{th} DAI. Following this, the application of Chitosan-KIO_3 complex at a rate of 5 kg ha^{-1} combined with SD-KIO_3 at a concentration of 0.3% at 60^{th} and 90^{th} DAI showed a 20.9% decrease in exchangeable iodine levels from the 40^{th} to the 80^{th} DAI and a 14.7% decrease from the 80^{th} DAI to the 120^{th} DAI.

Iodine bound to oxides

Following the extraction of water-extractable and exchangeable iodine, the soil underwent an additional step in which hydroxylamine hydrochloride was introduced to extract oxide-bound iodine from the existing pool of soil iodine. In the current investigation, the largest proportion of oxide bound iodine was seen in the treatment involving the application of SA-KIO_3- 5 kg ha^{-1} + SD-KIO_3- 0.3% at 60 and 90 days after incubation(DAI) treatment. This was followed by the treatment involving SA-KIO_3- 5 kg ha^{-1} + SD-KIO_3-0.2% at 60^{th} and 90^{th} DAI. Conversely, the lowest value was observed in the control treatments without any additional substances applied (Table 3). The amount of oxide bound iodine was found to be higher at the 40^{th} day after incubation (DAI) compared to the 80^{th} and 120^{th} DAI for all treatment groups. A contrasting pattern in the rate of decline was seen in the concentration of iodine bound to oxides, as compared to the other fractions. The rate at which oxide bound iodine decreased was found to be higher in the chitosan treatment alone, as well as in the combined Cs-KIO_3 and SD-KIO_3 treatments, with reductions ranging from 18% to 33% between the 40^{th} and 80^{th} days after incubation (DAI) and from 22% to 36% between the 80^{th} and 120^{th} DAI. In contrast, the rate of decrease in oxide bound iodine was relatively similar for the SA-KIO_3 and SD-KIO_3 treatments alone, with reductions of approximately 15% to 16% between the 40^{th} and 80^{th} DAI and 17% to 18% between the 80^{th} and 120^{th} DAI. According to Kohler *et al*. (2019), the presence of oxides in soil leads to a greater likelihood of iodine binding when iodine is added to the soil.

Table 2: Effect of potassium iodate and iodate chitosan complex on water extractable iodine content (mg kg^{-1}) at different stages of incubation.

Treatments	40^{th} DAI	80^{th} DAI	120^{th} DAI	Treatment mean
T_1- Soil application (SA)- KIO_3- 5 kg ha^{-1}	58.21^{a}	41.39^{a}	26.75^{cd}	42.12
T_2- Chitosan-KIO_3 complex ($CsKIO_3$)- (SA) -5 kg ha^{-1}	41.18^{c}	33.12^{c}	25.86^{f}	32.39
T_3- Soil Drenching (SD)-KIO_3-0.2% at 60 and 90 DAI	1.85^{d}	2.13^{d}	1.55^{g}	1.60
T_4- SA- KIO_3-5 kg ha^{-1} + SD-KIO_3- 0.2% at 60 and 90 DAI	58.83^{a}	43.87^{ba}	27.08^{c}	43.26
T_5- Chitosan-KIO_3 complex ($CsKIO_3$) - (SA)-5 kg ha^{-1} + SD-KIO_3 -0.2% at 60 and 90 DAI	42.53^{c}	32.97^{c}	23.95^{ef}	33.15
T_6- SA- KIO_3-5 kg ha^{-1} + SD-KIO_3- 0.3% at 60 and 90 DAI	59.06^{a}	45.86^{ab}	32.62^{b}	45.85
T_7- Chitosan-KIO_3 complex ($CsKIO_3$) (SA)-5 kg ha^{-1} + SD-KIO_3 -0.3% at 60 and 90 DAI	47.36^{b}	35.44^{c}	27.29^{de}	36.03
T_8- Chitosan-KIO_3 complex ($CsKIO_3$) - (SA)-10 kg ha^{-1} + SD-KIO_3 -0.3% at 60 and 90 DAI	59.92^{a}	46.89^{a}	37.97^{a}	47.26
T_9- Chitosan spraying	1.97^{d}	1.53^{d}	1.19^{g}	1.93
T_{10}- Water spraying	1.82^{d}	1.45^{d}	1.02^{g}	1.47
Mean	37.27	28.36	20.52	28.50
S.Ed	1.64	1.24	0.84	
C.D(0.05)	3.42	2.60	1.76	

Iodine bound to organic matter

The presence of organic matter iodine in soil is indicative of its unavailability and it has been seen to exhibit significant variation across different sources of chitosan and potassium iodate during the incubation process. The use of chitosan resulted in an elevation of the organic bound iodine in both Cs-KIO_3 and SD-KIO_3 treatments, hence reducing the adsorption of iodine by oxides. The rate of decline in organic bound iodine was higher in treatments where KIO_3 was applied to the soil alone, as well as in treatments where KIO_3 was applied in combination with soil application (SA-KIO_3) and soil drenching (SD-KIO_3) treatments (Fig 2). The lack of chitosan in the soil leads to a faster rate of decline in soil and soil drenching of potassium iodate. This is attributed to the reduction in soil binding affinity to organic bound iodine, as discussed by Dávila Rangel *et al*. (2020). Additionally, it was observed that the magnitude of loss was greater between the 40th and 80th days after initiation (DAI), whereas it was comparatively lower between the 80th and 120th DAI for the Cs-KIO_3 and SD-KIO_3 treatments. This observation demonstrates the long-term stability of iodine in chitosan-based materials.

Residual iodine

The residual iodine, which was previously unavailable, has been extracted using Tetra Methyl Ammonium Hydroxide Solution. When potassium iodate alone was drenched to

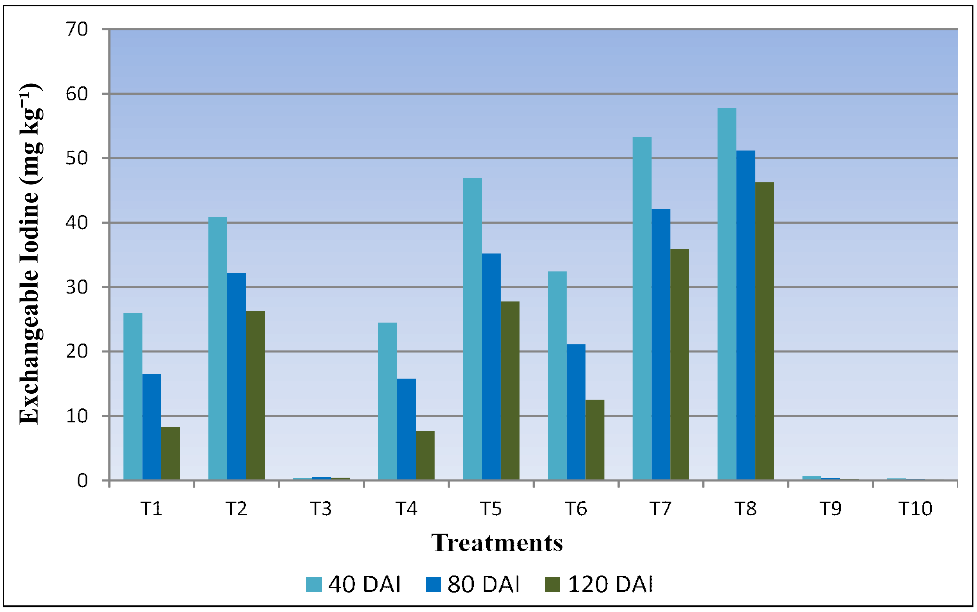

Fig 1: Effect of potassium iodate and iodate chitosan complex on exchangeable iodine content (mg kg^{-1}) at different stages of incubation.

Table 3: Effect of potassium iodate and iodate chitosan complex on oxide bound iodine content (mg kg^{-1}) at different stages of incubation.

Treatments	40th DAI	80th DAI	120th DAI	Treatment mean
T_1- Soil application (SA)- KIO_3- 5 kg ha^{-1}	66.72^{b}	55.43^{b}	45.32^{a}	55.82
T_2- Chitosan-KIO_3 complex (CsKIO_3)- (SA) -5 kg ha^{-1}	21.09^{e}	14.05^{e}	8.89^{d}	14.68
T_3- Soil Drenching(SD)-KIO_3-0.2% at 60 and 90 DAI	0.57^{f}	0.84^{f}	0.62^{e}	0.68
T_4- SA- KIO_3-5 kg ha^{-1} + SD-KIO_3- 0.2% at 60 and 90 DAI	66.51^{b}	56.08^{ab}	46.13^{a}	56.24
T_5- Chitosan-KIO_3 complex (CsKIO_3) - (SA)-5 kg ha^{-1} + SD-KIO_3 -0.2% at 60 and 90 DAI	23.65^{e}	14.53^{e}	8.42^{d}	15.53
T_6- SA- KIO_3-5 kg ha^{-1} + SD-KIO_3- 0.3% at 60 and 90 DAI	70.32^{a}	59.37^{a}	49.02^{a}	59.57
T_7- Chitosan-KIO_3 complex (CsKIO_3) (SA)-5 kg ha^{-1} + SD-KIO_3 -0.3% at 60 and 90 DAI	28.51^{d}	21.43^{d}	15.34^{c}	21.76
T_8- Chitosan-KIO_3 complex (CsKIO_3) - (SA)-10 kg ha^{-1} + SD-KIO_3 -0.3% at 60 and 90 DAI	41.23^{c}	33.45^{c}	25.98^{b}	33.55
T_9- Chitosan spraying	0.61^{f}	0.48^{f}	0.32^{e}	0.47
T_{10}- Water spraying	0.55^{f}	0.42^{f}	0.25^{e}	0.41
Mean	31.98	25.61	20.03	25.87
S.Ed	1.58	1.33	1.04	
C.D (0.05)	3.30	2.77	2.17	

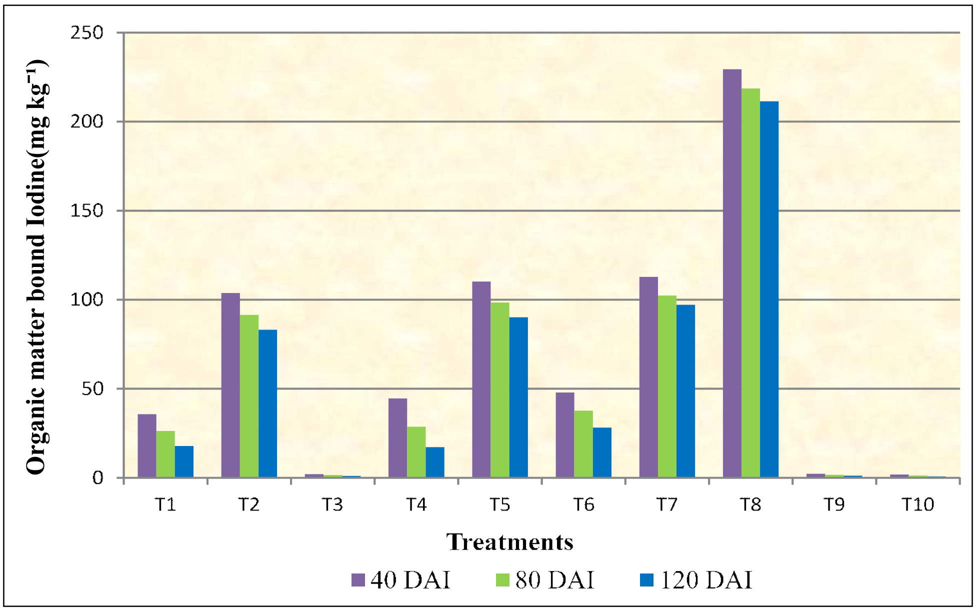

Fig 2: Effect of potassium iodate and iodate chitosan complex on organic matter bound iodine content (mg kg^{-1}) at different stages of incubation.

Table 4: Effect of potassium iodate and iodate chitosan complex on residual iodine content (mg kg^{-1}) at different stages of incubation.

Treatments	40th DAI	80th DAI	120th DAI	Treatment mean
T_1- Soil Application (SA)- KIO_3- 5 kg ha^{-1}	22.97^e	14.32^e	7.65^e	14.98
T_2- Chitosan-KIO_3 Complex ($CsKIO_3$)- (SA) -5 kg ha^{-1}	25.81^d	19.91^d	13.65^d	19.79
T_3- Soil Drenching(SD)-KIO_3-0.2% at 60 and 90 DAI	0.52^f	1.18^f	0.75^d	0.82
T_4- SA- KIO_3-5 kg ha^{-1} + SD-KIO_3- 0.2% at 60 and 90 DAI	39.48^b	28.51^b	16.44^b	28.14
T_5- Chitosan-KIO_3 Complex ($CsKIO_3$) - (SA)-5 kg ha^{-1} + SD-KIO_3 -0.2% at 60 and 90 DAI	36.51^c	28.23^c	20.89^c	28.54
T_6- SA- KIO_3-5 kg ha^{-1} + SD-KIO_3- 0.3% at 60 and 90 DAI	41.04^b	31.12^b	21.51^b	31.22
T_7- Chitosan-KIO_3 Complex ($CsKIO_3$) (SA)-5 kg ha^{-1} + SD-KIO_3 -0.3% at 60 and 90 DAI	38.43^c	32.98^b	26.31^b	32.57
T_8- Chitosan-KIO_3 Complex ($CsKIO_3$) - (SA)-10 kg ha^{-1} + SD-KIO_3 -0.3% at 60 and 90 DAI	48.38^a	41.53^a	34.78^a	41.56
T_9- Chitosan spraying	0.30^g	0.21^g	0.13^f	0.21
T_{10}-Water spraying	0.19^g	0.11^g	0.06^f	0.12
Mean	25.36	19.81	14.22	19.80
S.Ed	1.20	0.95	0.73	
C.D(0.05)	2.50	1.99	1.51	

the soil at 60 and 90 days after incubation application (DAI), the residual iodine content increased from the 40th to the 80+ DAI, but decreased from the 80th to the 120th DAI. The highest residual iodine content was observed in the Chitosan-KIO_3 complex at a rate of 10 kg ha^{-1}, combined with SD-KIO_3 at a concentration of 0.3%, at both 60th and 90th DAI. This was followed by the Chitosan-KIO_3 complex at a rate of 5 kg ha^{-1}, combined with SD-KIO_3 at a concentration of 0.3%, at 60 and 90 DAI, throughout all stages of incubation (Table 4). The rate of decrease in residual iodine content during all stages of incubation was higher in treatments where KIO_3 was applied to the soil alone, as well as in treatments where SA-KIO_3 and SD-KIO_3 were combined. Compared to chitosan-based applications, both soil and foliar application of potassium iodate fertilizer showed instability, resulting in greater loss in SA-KIO_3 and SD-KIO_3 treatments and higher retention in chitosan-based treatments (Sharif *et al.*, 2018).

CONCLUSION

The distribution of different iodine fractions in soils indicated that the water extractable, exchangeable, organic bound and residual iodine are dominant in combined Cs KIO_3 and SD-KIO_3 treatments, whereas the oxide bound iodine are dominant in combined SA-KIO_3 and SD- KIO_3 treatments in all the stages of incubation. Further the average distribution of iodine in chitosan alone and combined Cs-KIO_3 and SD-KIO_3 treatments follows the order of organic bound iodine > exchangeable iodine > water extractable iodine > residual iodine > oxide bound iodine. Similarly for SA- KIO_3 alone and combined SA-KIO_3 and SD- KIO_3 treatments increasing order of oxide bound iodine> water extractable iodine> organic iodine> residual iodine > exchangeable iodine is recorded throughout the incubation period. To conclude the application of chitosan along with potassium iodate has increased the iodine fractions in soil by preventing volatilization and leaching.

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Data availability

All datasets generated or analyzed during this study are included in the manuscript.

Ethics statement

This article does not contain any studies with human participants or animals performed by any of the authors.

Conflict of Interest

The authors declare that there is no conflict of interest.

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