

## Removal and Kinetic Studies of the Carcinogen Bromate Ion in Drinking Water Using Modified Date Seeds and Granular Activated Carbon

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**Abstract:** For the first time, we explore the efficacy of modified date seeds on the removal of the carcinogenic bromate ion from drinking water. As a way of checking the validity of this novel application of date seeds, we also test the capability of granular activated charcoal on the adsorption-reduction processes of the bromate removal in an identical system parameters. Special emphasis was given to the kinetics and the mechanism of bromate ion reduction and the formation of its conjugate bromide ion. For brevity purpose, only three well-established kinetic models were applied to the experimentally obtained data. We found that both the reduction and formation mechanisms of bromate and bromide ions follow pseudo-second order in the presence of the modified date seeds. However, the same adsorption-reduction process was observed to follow intraparticle diffusion kinetics in the presence of the granular activated carbon. Interestingly, the removal kinetics of bromate ion was acknowledged to be faster using the modified date seeds in the first stages (1-5 h) of the process though in the long run (after 24 h) the efficiency of the granular activated carbon was higher. In both systems, the removal efficacies were quite significant.

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### 1. Introduction

The presence of bromate ion in drinking water constitutes direct risk to human consumption due to its potential carcinogenic effects [1-5]. Bromate ion has already been considered as group 2B carcinogen by several international health organizations [3] as it has been suspected to cause cancer in  $10^{-4}$  life time exposure [4]. Various gastrointestinal toxicity symptoms including vomiting, diarrhea, nausea, abdominal pain and a possible effect on kidney and nervous system malfunctioning were all related to the consumption of high dose of bromate ion in fluids [5]. It is therefore of high interest to us to probe efficient, cost-effective, and widely accessible materials to use them for the removal of bromate ions from drinking water.

The formation of bromate ion in drinking water is linked to the ozonation treatment commonly used as an antimicrobial disinfectant and/or effective oxidizing agent for the removal of pollutants [6,7]. Furthermore, it has been reported that the ozonation results in the generation of bromate ion when the level of initial bromide salts present in ground water exceeds 20 ppb [8-10]; typical average concentration of bromide ion in natural water is  $\sim 100$  ppb [11]. The mechanism of bromate ion formation undergoes different cascading and complex steps manifested via

interactions with molecular ozone and hydroxyl radicals [8-10].

Many research groups have utilized different methods for the elimination of bromate ion once it has been formed as a result of the ozonation process. Techniques employed for this purpose include zero-valent iron [12,13], UV irradiation [14], filtering by reverse osmosis [15], high-energy electron beam irradiation (HEEB) [16], granular activated carbon [17,18] and others. However, most of these methods are accompanied by operational problems such as high maintenance costs, secondary pollution and complicated procedures involved in the treatment which limits their applicability for use on commercial scale [19]. For the first time we use chemically modified date seeds to remove bromate ions from aqueous solutions. We also aim to examine the adsorption-reduction process of granular activated charcoal as a means of substantiating the soundness of the removal efficiency of bromate ions by the modified date seeds. Special emphasis was given to the study of the kinetic behavior of the reduction of bromate ions and its reversal to bromide ions. In this present work, a number of well-established kinetic models were applied to determine the mechanism of the adsorption-reduction processes in both the modified date seeds and the granular activated charcoal systems. With the use of those models

important kinetic parameters such as rate constants were also extracted.

## 2. Experimental

### 2.1 Materials

KBrO<sub>3</sub> (Panreac, 99%), FeSO<sub>4</sub>.7H<sub>2</sub>O (BDH, 99.5%), Acetone (Holyland SA, 99.99%) and HCl (SD Laboratories, Mumbai, India, 35-38%) were used as received. Fresh Ajwa date seeds were collected from one of the date factories based in Madinah, KSA and the granular activated charcoal (LR 2.0 mm – 5.0 mm SD) was purchased from Fine-Chem Ltd, Mumbai, India.

### 2.2 Procedures

**2.2.1 Chemical modification of date seeds:** date seeds were chemically treated in two steps. First, a thorough cleaning of the seeds were carried out by mixing 10 g of ground date seeds in 200 ml of acetone and distilled water by a ratio of 1:1 and then the mixture in well-lid flask was placed in a temperature controlled shaker (GFL, D-30938 Burgwedel, Germany) at a temperature of 45 °C with a shaking rate of 150 rpm for half an hour until a reddish brown color of the mixture was observed due to impure materials. The date seeds were removed from the mixture and then washed with large quantity of deionized water and dried. The same procedure was repeated for three times until the mixture became colorless and the date seeds were completely cleaned from any impurities. Finally, the dry clean date seeds were incubated at 50 °C temperature for 24 h. In the second step, the date seeds were treated with a ten-fold amount of 0.1 M FeSO<sub>4</sub>.7H<sub>2</sub>O solution in column at 45 °C followed by a thorough washing with deionized water until the pH of the mixture was 7. The date seeds were removed, washed, dried and kept at a temperature of 50 °C for 24 h.

**2.2.2 Modification of the granular activated charcoal:** 10 mg of the activated charcoal was treated with ten-fold 0.1 M HCl in a column followed by a thorough washing with deionized water until a pH7 was reached. The charcoal was then dried and kept at temperature of 50°C for 24h.

### 2.2.3 Removal of bromate ion

The removal of bromate ion from aqueous solutions by the modified date seeds and granular activated charcoal was carried out as follows. First, 15 ml aqueous solutions with concentrations of 51 ppb bromate ion were separately added into tubes containing 10 mg/ml of each of the modified date seeds and charcoal. The tubes were then placed in the temperature controlled shaker at room temperature and a shaking speed of 250 rpm for contact times at 0.25, 0.5, 0.75, 1, 2, 3, 4, 5, and 24 of an hour. After each contact time, the solution was filtered and injected to Ion Chromatography

(Metrohm, 881Compact IC pro –Anion MCS, Switzerland) for the measurement of bromate and bromide ions concurrently.

## 3. Results and Discussion

### 3.1 Effect of contact time and absorbent

In this section, we explore the effect of contact time and the nature of absorbent on the removal capability of bromate ion in aqueous solutions. Fixed concentrations of aqueous solutions containing bromate ion were used. The progress of bromide ion formation was monitored at various contact times simultaneously with the reduction profile of bromate ion. Fig. 1 represents the raw experimental data of the sorption-reduction of bromate ion obtained using both the modified date seeds (MDS) and the acid treated granular activated charcoal (AGC) as a function of contact time. For comparison purposes, the parameters controlling the sorption processes of both systems were kept identical.

The initial concentration of bromate ion used was fixed at 51 ppb for an overall duration of 5 hour contact time,  $t_c$ , as annotated in Fig.1. All measurements were made using Ion Chromatography machine at room temperature and pH 7 resembling the natural conditions of drinking water. For the first contact hour, measurements were recorded in every 15 min to scrutinize the reduction-adsorption process of bromate ion at early stages. Subsequent measurements were made at one hour intervals. For the ease of visual manifestations, the profile of bromide ion formation as a function of contact time was shown in the same figure as the reduction of bromate ion (see Fig.1). To avoid confusion, different symbols were used to represent each data series as explained in the legend. For all data series in Fig.1, data points were averaged over three measurements with an overall standard deviation of  $\sigma \approx 0.3 \pm 0.1$  showing a great degree of reproducibility.

At a close scrutiny of the data in Fig.1, we can make three main remarks. First, it can easily be observed that the kinetics of bromate removal by the modified date seeds and the granular activated charcoal follow different patterns. Second, the significance of the use of the modified date seeds can be attributed to its effective removal of bromate ion by a factor of two for the first contact time in comparison to the granular activated charcoal. As it could obviously be seen in Fig.1, the amount of dissolved bromate ion was rapidly reduced to ~ 50% of its initial concentration within the first contact hour when the modified date seeds were utilized as an absorbent.

However, by using the acid treated granular activated charcoal as an absorbent the

amount of bromate ion reduced fell down only to ~26.5% its initial concentration within the same time period; approximately half the amount reduced in the presence of the modified date seeds. Third, we stress on the relatively fast reduction process in the presence of the modified date seeds in contrast to the granular activated charcoal within the boundaries of the experimental contact times of the first five hour period; no action of the granular charcoal was observed for the first 15 min contact time. In addition, the behavior of the bromate ion reduction as well as the bromide ion formation processes when used the granular activated charcoal goes through an inflection point immediately after the equilibration plateau followed by a subsequent gradual fall (in bromate ion reduction) and a corresponding rise (in bromide formation) starting at the third contact hour. Nevertheless, measurements made after 24 h contact time indicated that the bromate removal efficiency by the granular activated charcoal was ~ 99.9% compared to ~ 70% by the modified date seeds. In the light of this last remark, one may question the significance of the use of the modified date seeds. Presumably, considering the speed of

bromate ion removal in a significantly short time (within one hour contact time) with the added advantage of being cost effective, widely available and naturally abundant - on top of its efficacy to lower bromate ion to below accepted limits in drinking water - one may seem to be convinced that the benefits of using the modified date seeds as a removal bromate ion agent might outweigh its limitations. As a result, this novel and economically affordable absorbent maybe a potentially promising tool to use in water purification processes. In future works, we plan to study the interaction mechanisms between bromate ions and the modified date seeds to shed more light on the underpinning chemistry affecting the chemical reduction of bromate ion in the presence of the modified date seeds.

The contrast in bromate ion reduction behavior as shown by the two sorption-reduction processes based on the absorbents used here, namely the modified date seeds and the granular activated charcoal, may be due to different kinetic mechanisms. This will further be discussed in the following section by applying various kinetic models to the raw data represented in Fig.1.

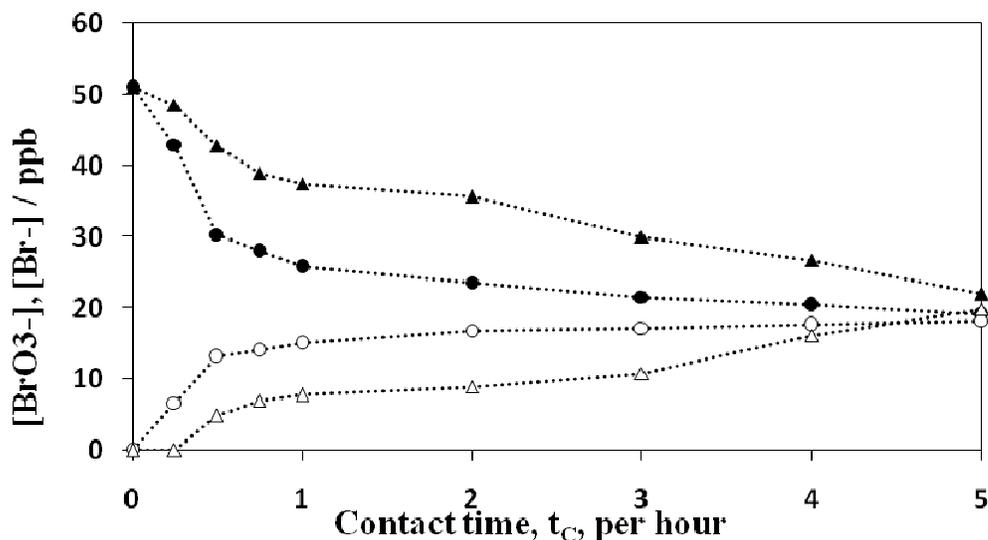


Fig.1: Concentration profile for the chemical reduction of bromate ion and the formation of bromide ion in ppb as a function of contact time in hours. Filled symbols (●,▲) are used for the formation progress of bromide ions while the open symbols (○,△) represent concentrations of bromate reduced as time progresses. Circles, filled or open are used for the data acquired using date seeds. The triangles are on the other hand used for the data obtained using the granular activated charcoal.

### 3.2 Kinetic Modeling of Adsorption-Reduction Processes

Kinetic modeling is considered as one of the crucial characteristics in understanding the mechanisms and the rate of chemical reactions. We now turn to applying some of the well-established kinetic models on the data in Fig.1. For brevity purpose, only three different models were used to investigate the mechanism of the bromate ion reduction and the formation of bromide ion in both modified date seeds (MDS) and granular activated charcoal (AGC) systems. With the use of these models, important information such as rate constant parameters can be extracted. Eqs. 1-3 describe pseudo-first order, pseudo-second order and intraparticle diffusion models, respectively [17].

$$\ln(C_e - C_t) = \ln C_e - k_1 t \quad (1)$$

$$\frac{t}{C_t} = \frac{1}{k_2 C_e^2} + \frac{1}{C_e} t \quad (2)$$

$$(C_e - C_t) = k_p t^{1/2} \quad (3)$$

where  $C_t$  and  $C_e$  are concentrations at time  $t$  and at equilibrium and;  $k_1$ ,  $k_2$  and  $k_p$  are rate constants of

pseudo-first order, pseudo-second order and intraparticle diffusion kinetics and  $t$  is the controlled contact time. The validity of these models can be tested by linear plotting of  $\ln(C_e - C_t)$  vs  $t$  for pseudo-first order, Eq.1,  $t/C_t$  vs  $t$  for pseudo-second order, Eq.2, and  $(C_e - C_t)$  vs  $t^{1/2}$  for the intraparticle diffusion kinetic processes, Eq.3. From the slope and the intercept of the linear plots, technologically important kinetic parameters (the rate constants and equilibrium concentrations) are determined.

The data in Fig. 1 was fitted to Eqs.1-3 for both systems i.e. the modified date seeds and the granular activated charcoal. We found that the kinetics of bromate ion reduction as well as the accompanying formation of bromide ion follow pseudo-second order kinetics for the experiments carried out in the presence of the modified date seeds as shown in Fig. 2; Fig.2a shows the linear plots of Eq.2 for bromide reduction whereas Fig.2b stands for the same plot for the formation of bromide ion.

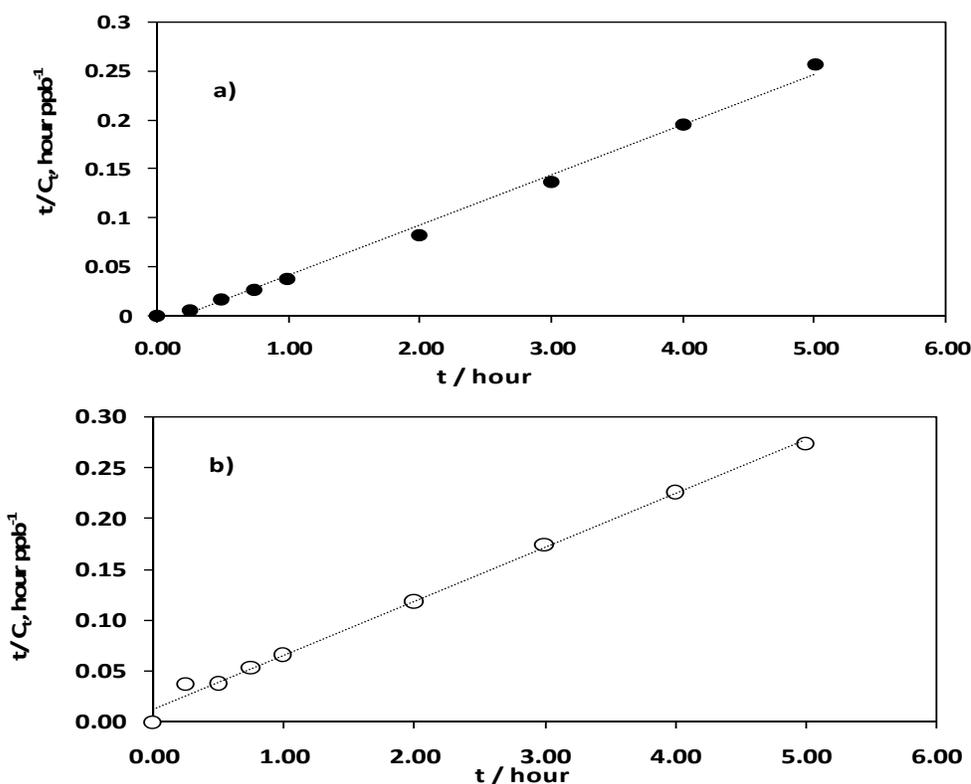


Fig. 2: shows the fitted data of Fig. 1 to Eq.2. a) Represents adsorption-reduction process of Bromate ion and b) represents the kinetics of the formation of bromide ion.  $C_t$  and  $t$  have their usual meaning as described in the text.

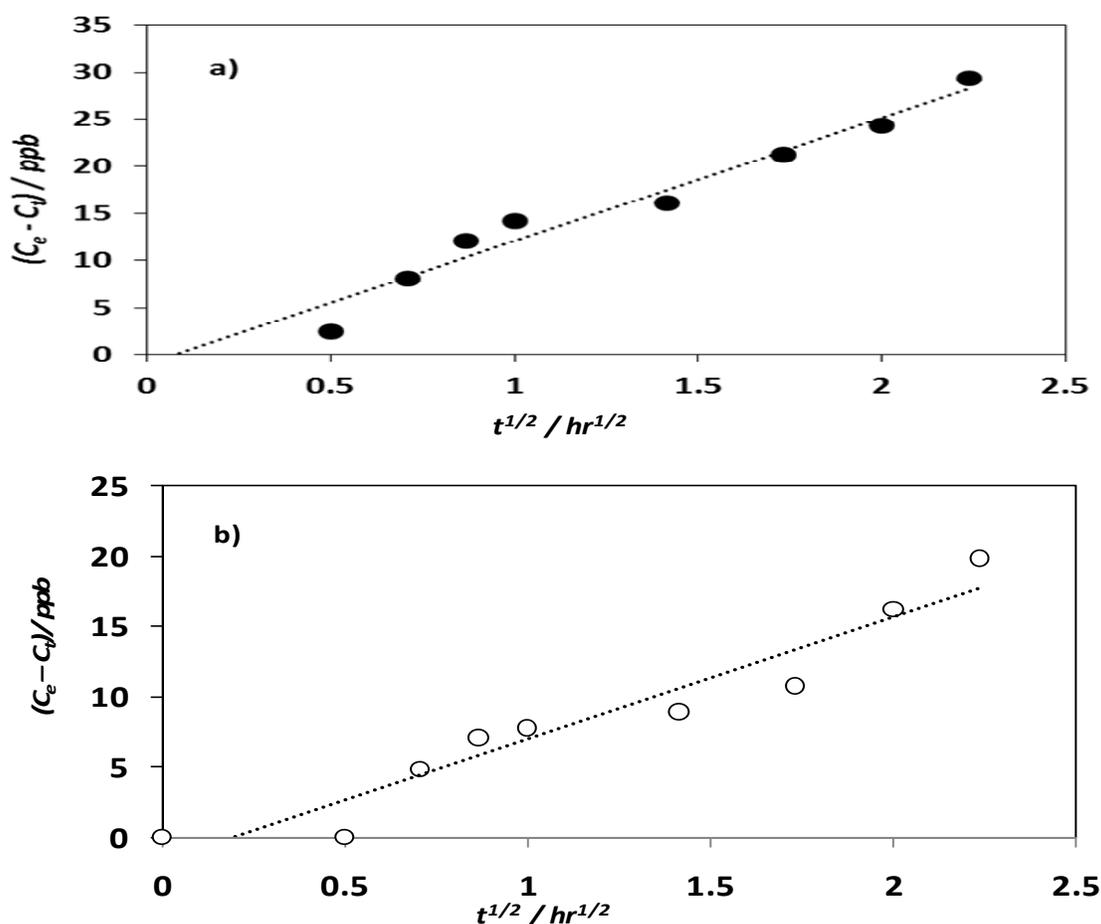


Fig.3: Fitting intraparticle diffusion model to the experimental data of Fig.1 obtained using the granular activated charcoal. a) Represents bromate ion reduction and b) represents bromide ion formation.

Co-ordination coefficients of  $R^2 = 0.994$  and  $R^2 = 0.995$ , respectively, for bromate ion reduction and bromide ion formation indicate quasi-perfect fit of the pseudo-second order equation to the experimental data. The values of rate constants calculated from the intercept of the linear graphs (Fig.2a and Fig2b) for the removal of bromate ion and bromide ion formation are  $0.16 \text{ ppb}^{-1} \text{ hr}^{-1}$  and  $0.35 \text{ ppb}^{-1} \text{ hr}^{-1}$ , respectively. The equilibrium concentration calculated using Eq.2 matches experimental values measured; an additional confirmation factor for the validity of analysis. By contrast, it was found that the kinetics followed by the adsorption-reduction process of both bromate ion reduction and bromide ion formation for the data obtained using the acid treated granular activated charcoal best fits to Eq.3, i.e. undergoes intraparticle diffusion mechanism (Fig. 3a and Fig.3b). This behavior may be due to

the interaction between bromate ion and the charcoal and/or due to the diffusion-driven transportations dictated by the pore sizes of the granules.

Similar to the fitting results in Fig.2, the co-ordination coefficients acquired for Fig.3 were  $R^2 = 0.97$  and  $R^2 = 0.93$  for bromate ion reduction and the concurrent formation of bromide ions, respectively. One may conclude from this that the kinetic mechanism of bromate ion removal under the granular activated charcoal may be influenced by the interactive forces between bromate ions and the protonated surface of the acid treated charcoal. This kinetic behavior may also be attributed – as indicated above – to the nature of pore sizes of the charcoal where bromate /bromide ions are subjected to diffusional restrictions. Using Eq.3, intraparticle diffusion rate constants were calculated from the slope of the linear plots shown

in Fig.3 and were found to be 13.1 ppb hr<sup>-1/2</sup> for the removal of bromate ion and 8.67 ppb hr<sup>-1/2</sup> for the formation of bromide ions.

#### 4. Conclusion

For the first time, the removal efficiency of bromate ion by economically affordable and chemically modified date seeds was probed. As a means of validity checking, the removal action of granular activated charcoal was also investigated. The adsorption-reduction process of bromate ion and formation of its conjugate ion, i.e. bromide ion, was explored at various contact times. For the purpose of understanding the mechanism of kinetic behavior of the reduction process in the presence of modified date seeds and granular activated charcoal, different models were fitted to the experimental data measured at pH 7 and room temperature. It was found that for the modified date seeds, the adsorption-reduction process of the bromate ion reduction (formation of bromide ions) follows pseudo-second order mechanism. In contrast, for the granular activated charcoal, the adsorption-reduction process of bromate ion was seen to undergo intraparticle diffusion kinetics. With the help of fitting the widely accepted kinetic models, we were able to determine the rate constants of the adsorption-reduction process in both the modified date seeds and the granular activated charcoal systems. In terms of removal efficiency, bromate ions initially present were observed to fall to ~ 50% (of initial amount) within the first contact hour when subjected to the modified date seeds compared to the efficiency of ~ 27% (of initial amount) removal yield for the granular activated charcoal. Notwithstanding, the charcoal removal of bromate ion was found to be ~ 99.9% of the initial amount of bromate ion after 24 hr contact time period whereas modified date seeds were only able to reduce the amount of bromate ions to ~ 70% of initial concentration. Apparently, the removal efficiency of both systems was quite significant. This may pave the way for the cheap and widely available modified date seeds to be used as an adsorbent in water purification process.

#### 5. Acknowledgement

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