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Bromate removal from water using granular activated carbon in a batch recycle

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ABSTRACT

The treatment of water polluted with bromate ions using GAC (granular activated carbon) was studied. As bromate ion is not a natural component of water, but it may be formed during the disinfection processes of drinking water, the level of bromate concentration according to WHO regulation in drinking water must be below l0 μg/l, and in view of this very low permissible concentration and the practical limitation of bromate available treatment processes, the adsorption of bromate in a GAC bed reactor and the effect of different parameters on the rate of bromate removal such as initial bromate concentration, solution flow rate, column contact time and temperature were investigated. It was found that the rate of bromate removal is increased by increasing the column contact time and temperature but decreased by increasing initial bromate concentration and solution flow rate. The removal of bromate from water using a granular activated carbon bed reactor was found to be an efficient technique for the removal of bromate ions, as high removal rate up to 95% was achieved. The present data suggest the use of flow rates in operating continuous reactors in order to obtain a high degree of bromate removal.

Keywords: Bromate; Adsorption; Desalination; Drinking water

1. Introduction

Throughout the world consumers demand is expanding for a higher level of water quality and quantity. The source of water greatly varies from country to country and in some areas desalination of seawater is the dominant process for potable water. Desalination is a process that removes dissolved minerals (including but not limited to salt) from seawater, brackish water, or treated wastewater. The potential for the increased use of desalination in the Middle East is significant. The opportunities are great for providing water supply from seawater and brackish water desalination as well as recovering wastewater.

Recently a great concern has been raised about bromate ions (BrO_3^-), as the bromate ions were found in potable water produced from salty sources [1]. Bromate is formed in drinking water during the disinfection of water containing bromide. Disinfection is carried out by:

- Ozonation, during the chemical oxidation of natural waters that contains Br^- by O_3 and OH•, BrO_3^- is formed at concentrations from 1 to 50 μg/l in full-scale drinking water plants [2–9].
- Sodium hypochlorite solutions, especially when produced by electrolyzing seawater or during chlorination of sea water using Cl_2, BrO_3^- is formed at a concentration 65 mg/l [10,11].

BrO_3^- has been shown to cause kidney and renal cell tumors in laboratory animals fed with aqueous bromate [12,13]. BrO_3^- does this directly or indirectly by causing oxidation of the lipids in cell membranes to produce active oxygen species, which in turn produce damage in macromolecules such as DNA. This anion is also genotoxic in vitro and in vivo, although this has been confirmed to cause primarily physical damage in chromosomes [14]. Bromate has been classified into group 2B as a possibly genotoxic human carcinogen [15,16].

The United States Environmental Protection Agency (US EPA) performed a risk assessment for a 70-kg adult drinking 2 L of water per day with a bromate concentration of 5 μg/l. The lifetime risk was calculated to be 10^{-4}, meaning that one person per every 10,000 people would develop cancer via bromate ingestion [17].

The removal of bromide has particular significance with respect to obtaining control over formation of brominated disinfection by-products. For example, observations in a number of regions indicate that a reduction in natural organic matter (NOM) prior to chlorination does not result in a corresponding reduction in brominated disinfection by-products if the bromide levels are not reduced as well [18]. This can produce conditions that limit the extent to which reductions in total trihalomethane formation can be achieved. Therefore, the ability to remove bromide would be an additional asset in meeting regulatory requirements. It has also been found that chloride and bromide ions deeply inhibit the rate of degradation of chloroform and tetrachloromethane [19].

Several researchers have studied the adsorption by activated carbon (granular or powder) [20–22]. They found that a number of factors affect the efficiency of bromate reduction by GAC including carbon surface chemistry, solution pH, and the presence of natural organic matter (NOM) and other anions. The mechanism of BrO_3^- removal by activated carbon has been postulated to be adsorbed, reduced to hypobromite (BrO^-) and finally reduced to bromide (Br^-) on the activated carbon surface. The mechanism by which BrO_3^- is removed by activated carbon has also been analyzed by other researchers [13,20,22], especially with reference to the surface conditions and properties of many forms of activated carbon including granular activated carbon (GAC) and powdered activated carbon (PAC).

The aim of this work is to investigate the effect of different parameters, such as bromate ion concentration, solution flow rate, contact time and temperature on the rate of removal of bromate ions using an activated carbon bed reactor in a batch recycle reactor. Previous studies were conducted in a simple batch reactor. Therefore the present work throws some light on the role of fluid motion in the rate of bromate removal.

2. Experimental technique

The apparatus (Fig. 1) consists of a plexiglass column of 10 cm diameter and 50 cm height, the bed height of the activated carbon is 30 cm, two perforated plates are used: one at the bottom, as a support for the activated carbon bed, and the other at the column outlet to prevent any migration of the activated carbon granules. A 0.2 hp plastic centrifugal pump was used to circulate the bromate solution between 10 L plexiglass storage tank and the column. The experimental set up was equipped with a temperature controller system to enable studying the effect of temperature on the reaction kinetics.

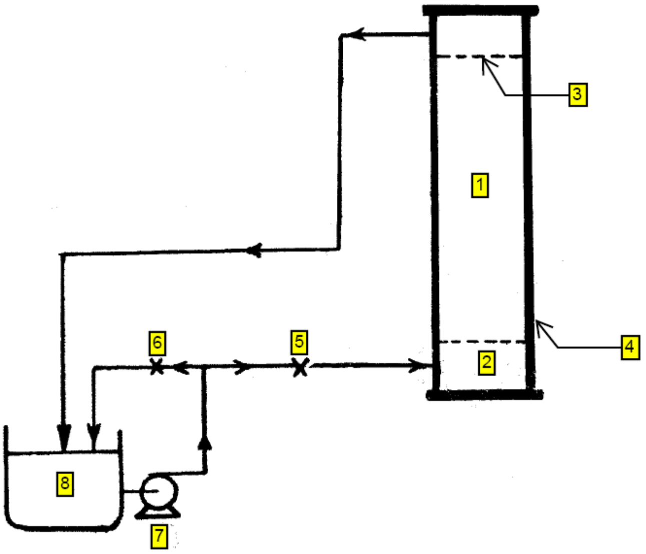

Fig. 1. Apparatus (1) GAC bed; (2) Glass beads; (3) GAC bed supports; (4) Plexiglas column; (5,6) Ball valves ; (7) Plastic centrifugal pump; (8) Plexiglass storage tank.

Before each run, the solution flow rate was measured using a roatameter and adjusted at the required values by means of a bypass and ball valve, respectively.

The rate of bromate removal was followed by measuring the change in concentration of the bromate solution with time using UV spectrophotometer. Before each run, 10 L of fresh bromate solution were placed in the storage tank. The source of bromate ions is potassium bromate. Bromate ion standards were prepared by dilution from a bromate ion stock solution. The 1.00 g/L bromate ion stock solution was prepared by dissolving 0.131 g of potassium bromate (purity 99.88%) in 100.0 mL of distilled water (DW). The second stock solution was prepared by diluting a 1.00 mL of 1.00 g/L bromate ion stock solution in 100.0 mL of DW to a final concentration of 1.00×10^{-2} g/L. The bromate ion stock solutions were stored at 4°C for a maximum of 21 days.

The flow rate was measured with a roatameter and adjusted at the required value by means of a bypass and ball valve, respectively. After that the solution was subjected to circulation at the required flow rate. Samples of the solution (5 ml) were withdrawn at regular time intervals of 5 min at different solution flow rates. Samples were analyzed using UV spectrophotometer and the rate of bromate removal was followed through following the change in the bromate concentration. Experiments were carried out at temperature 20±1°C and pH 6.5.

The ranges of the studied variables are:

1. Solution flow rate: 333, 285, 250, 200, 167, 78, 14 cm^3/s.
2. Initial bromate concentration: 1, 2, 3, 5, 7, 10 ppm.
3. Contact time from 0.2, 0.23, 0.26, 0.33, 0.39, 0.84, 4.67 min.
4. Temperature 25, 30, 40, 60°C.

The activated carbon used was Norit Nederland B.V – NRS Carbon GA (0.5–2.5), iodine number 850, total surface area 975 m^2/g, apparent density 500 kg/m^3, particle size 0.5–2.5 mm.

3. Results and discussion

Figs. 2 and 3 show the effect of different bromate concentrations on the rate of bromate removal on activated carbon. The data show that as the the bromate concentration increased from 1 to 10 ppm, the rate of bromate removal decreased from 95 to 63%. To explain this result the mechanism of bromate removal [22] should be recalled first, bromate removal takes place via:

(i) Physical adsorption of bromate ions on the active adsorption sites of activated carbon.
(ii) Removal of bromate ions through the limited ion exchange capacity available on the pores of activated carbon granules.
(iii) Surface reduction of BrO_3^- to Br^- occurred with bromine ($HOBr/OBr^-$) as intermediate, through a transient chemi-sorption step. These reactions are interfacial reactions involving the interaction of surface bound carbon groups with dissolved bromide species.

The decrease in the rate of bromate removal with increasing the bromate concentration may be explained as follows. Adsorption involves liquid phase diffusion of the adsorbate (external diffusion) followed by internal diffusion (intraparticle diffusion); although bromate concentration is extremely low in the solution bulk, conditions differ in the narrow capillary pores of carbon particles, the limited volume of the capillary pores increases the apparent concentration of bromate inside the capillary. The increase in bromate concentration inside the capillaries leads to a pronounced interionic attraction which decreases the activity and diffusivity of bromate [23] with a consequent decrease in the rate of adsorption, i.e. the rate of bromate adsorption becomes controlled by intraparticle diffusion. This retarding effect increases in magnitude with increasing the initial bulk bromate concentration.

Figs. 4–9 show that, contrary to expectations, as the bromate solution circulation rate increased the rate of bromate removal decreased. For the initial bromate concentrations 2, 5, 10 ppm the rate of removal decreased from 95.5 to 55, 94 to 54 and 76 to 41% respectively, as the flow rate increased from 14 to 333 cm^3/s. It was expected that the rate of bromate removal would increase by increasing the solution flow rate in view of the increase in the rate of mass transfer of bromate ions to the solid carbon particles. The decrease in the % bromate removal

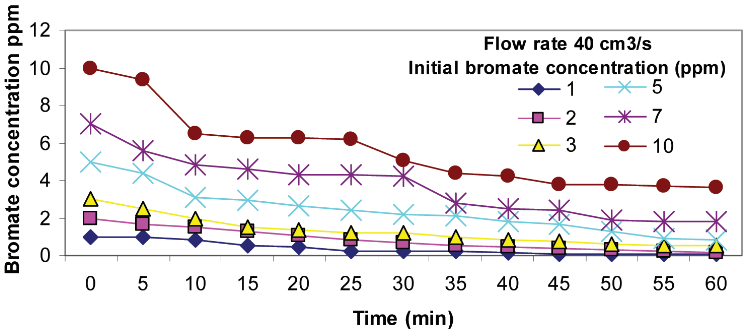

Fig. 2. Bromate concentration time data for different initial bromate concentrations.

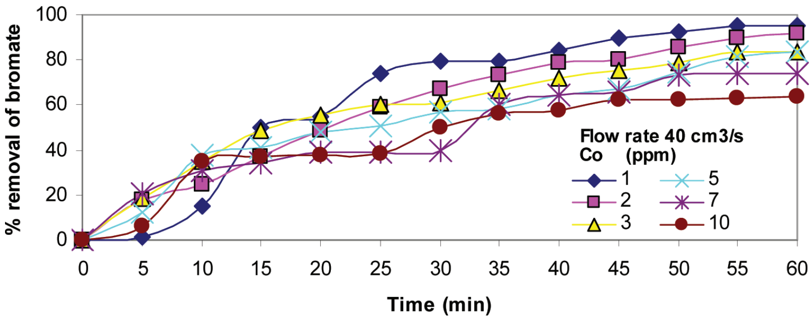

Fig. 3. Effect of different initial bromate concentrations on % removal of bromate.

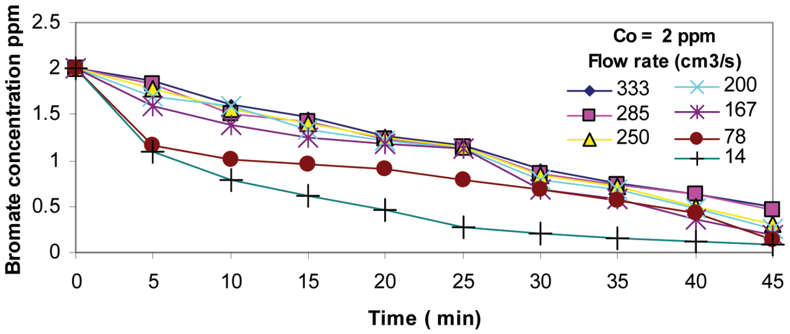

Fig. 4. Concentration time data for different solution flow rates at bromate C_o 2 ppm.

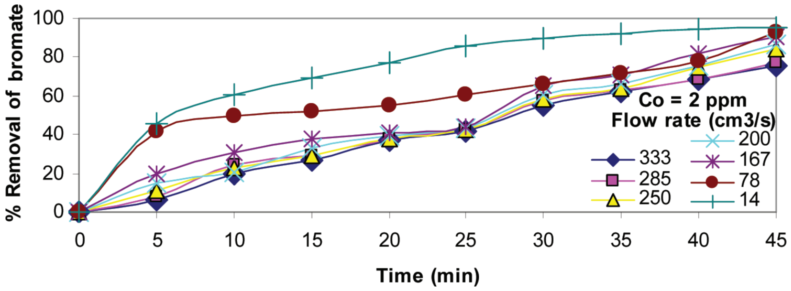

Fig. 5. Effect of different solution flow rates on % bromate removal at C_o 2 ppm.

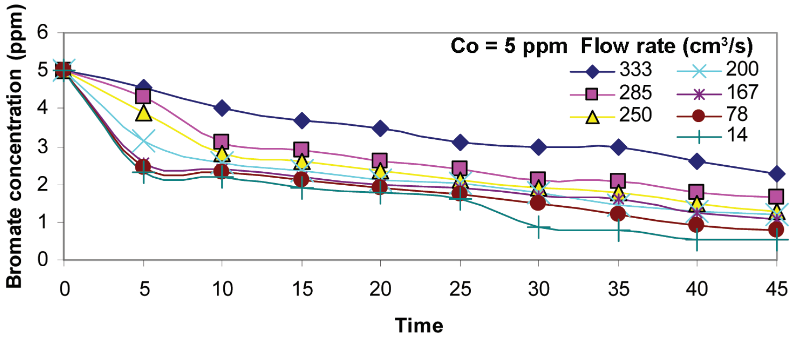

Fig. 6. Concentration time data for different bromate solution flow rates at C_o 5 ppm.

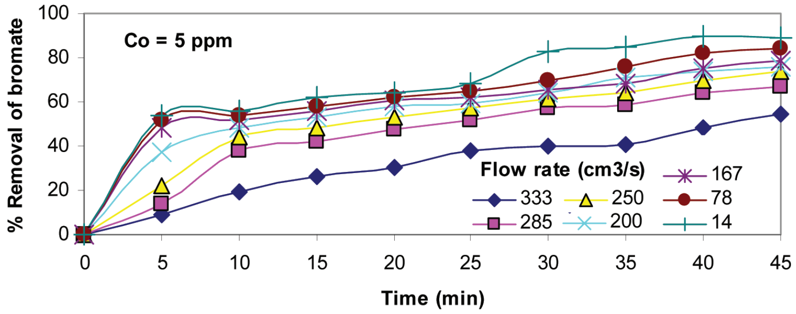

Fig. 7. Effect of different solution flow rates on % bromate removal at C_o 5 ppm.

with increasing the flow rate may be explained in terms of the fact that physical adsorption of bromate on carbon plays a major role in bromate removal. It seems that the high shear stress associated with high flow rates leads to adsorption of the weakly bonded bromate ions from the graphite particles. The effect of the solution flow rate on the rate of bromate removal can be expressed in terms of the residence time of the solution in the column — the lower the flow rate, the higher the residence time and the higher the degree of bromate removal and vice versa.

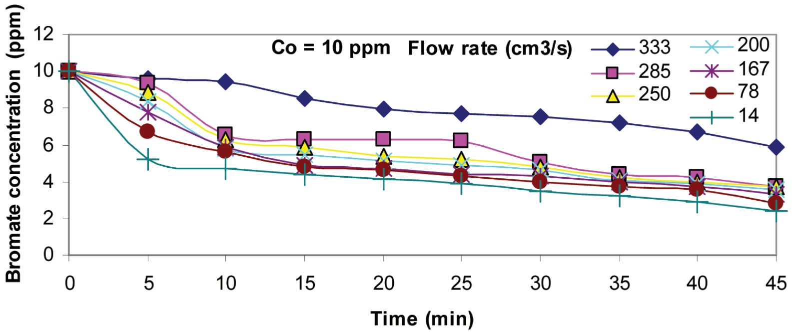

Fig. 8. Concentration time data for different solution flow rates at C_o 10 ppm.

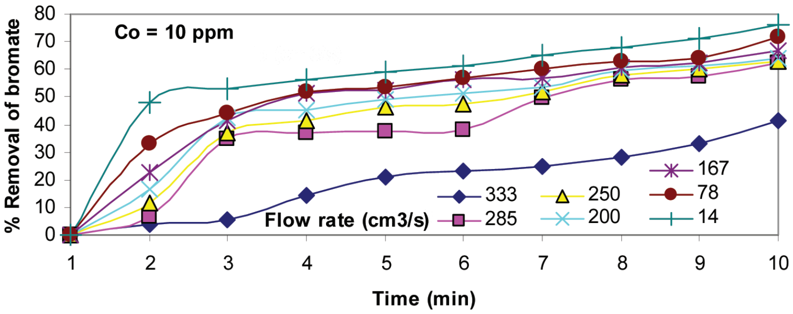

Fig. 9. Effect of different solution flow rates on % bromate removal at C_o 10 ppm.

Fig. 10 shows that the % removed bromate increased from 40 to 95% by increasing the column contact time from 0.19 to 4.67 min. This result is in consistent with the previous studies [20].

Fig. 11 shows that as the temperature increased from 25 to 60°C, the % of removed bromate increased by about 20%. The present finding is in consistent with the previous studies [24] and will be more lighted in view of the kinetic study for the bromate removal with increasing temperature, as illustrated in Figs. 12 and 13.

The above modest increase in the rate of bromate removal with increasing temperature is the outcome of the following opposing effects:

(i) The increase of temperature increases bromate diffusivity according to the Stokes–Einestein equation, with a consequent increase in the rate of diffusion of bromate to carbon particles and consequently the rate of adsorption increases.

(ii) The increase of temperature in the case of physical adsorption, as in the present case, leads to desorption of bromates from the carbon particles.

It seems that under the present set of conditions, the enhanced diffusion (effect i) outweighs desorption (effect ii). The present finding is consistent with previous studies [22].

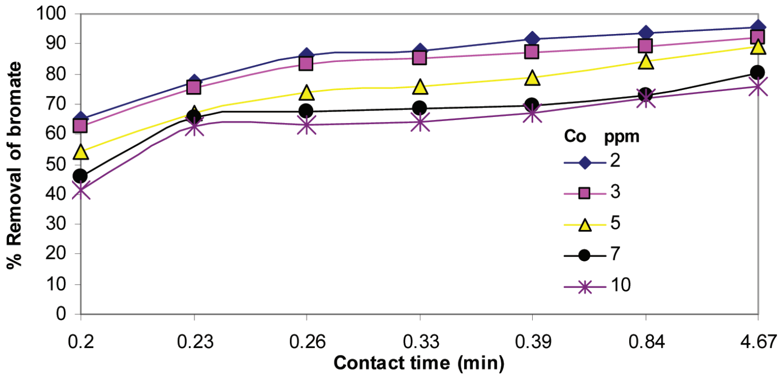

Fig. 10. Effect of column contact time on the % removal of bromate.

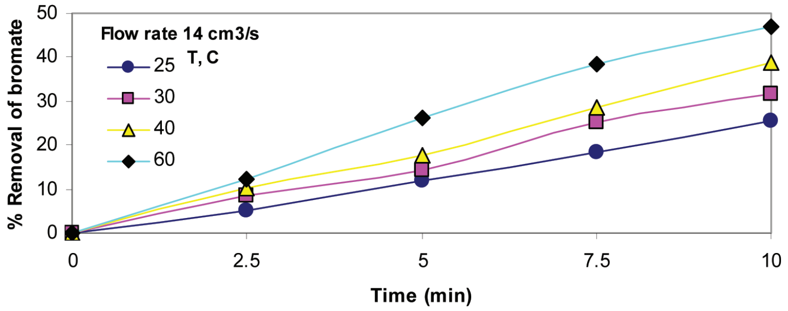

Fig. 11. Effect of temperature on the % removal of bromate.

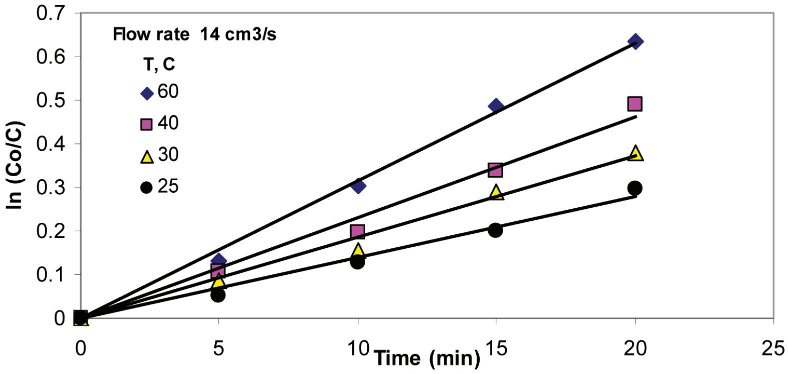

Fig. 12. ln(C_o/C) vs. time for different temperatures

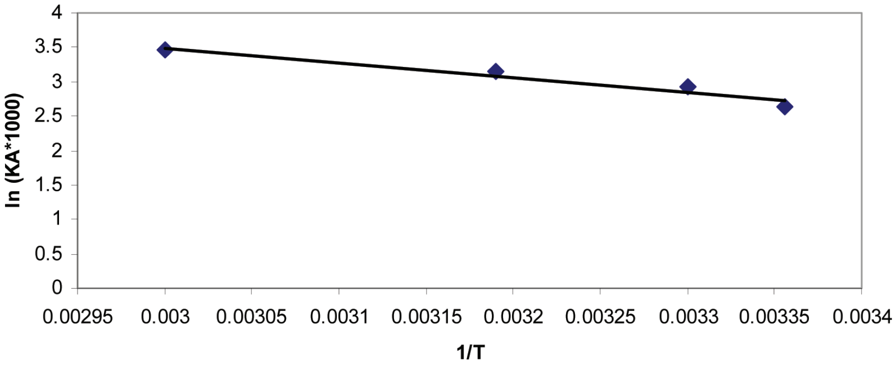

Fig. 13. Determination of activation energy from Arrhenius equation.

To substantiate the above argument that diffusion and physical adsorption are involved in the process, the activation of bromate removal was calculated from Arrhenius equation:

$$KA = A_0 e^{(-E/RT)} \tag{1}$$

Figs. 12 and 13 show that the volumetric mass transfer coefficient increases with temperature increasing with an activation energy of 4.23 Kcal/mol. The relatively small value of the activation energy confirms the fact that the process of bromate ion removal by adsorption using activated carbon is a physically controlled process [24] where diffusion and physical adsorption are involved.

4. Conclusion

The removal of bromate ions by activated carbon adsorption was found to be an efficient technique in view of the fact that bromate removal up to 95% was obtained. The study of the effect of different parameters such as initial bromate concentration, solution flow rate, contact time and temperature revealed that:

(i) Increasing initial bromate concentration from 1 to 10 ppm decreases the % removal of bromate by 22%.
(ii) Increasing the solution flow rate from 14 to 333 cm^3/s leads to unexpected decrease in the rate of bromate removal by 44%.
(iii) Increasing the column contact time from 0.2 to 4.67 min increases the removal of bromate by 45%.
(iv) The increase of temperature was found to increase the volumetric mass transfer coefficient with an activation energy 4.23 k.cal/mol. The % removal of bromate was found to increase by about 20% as the temperature increased from 25 to 60°C.
(v) The low value of the activation energy and the effect of the solution flow rate on bromate removal lend support to the fact that bromate removal by adsorption on carbon takes place through physical adsorption.
(vi) An important implication of the present results is that continuous reactors should be operated using extremely low flow rates in order to obtain a high degree of bromate removal per pass.

Symbols

A — Bed active area, cm^2
A_o — Arrhenius constant (frequency factor)
C — Concentration at any time, ppm
C_o — Initial concentration, ppm
D — Diffusivity, cm^2/s
E — Activation energy, K.cal/mol
KA — Volumetric mass transfer coefficient, cm/s
R — Gas constant
T — Temperature, °K
t — Time, min
δ — Diffusion layer thickness, cm
μ — Solution viscosity, g/cm.s

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