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Egypt. J. Rad. Sci. Applic. **Vol. 33,** No.1, pp. 19-25 (2020)

Egyptian Journal of Radiation Sciences and Applications

Effect of Silica Gel on the Electrical Conductivity of ɣ- irradiated Pure Water: A Radiation Chemical Study

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EFFECTS of silica gel (SG) and its particle size on the radiation-induced electrical conductivity (RIC) and pH of pure water were studied. RIC of pure water in the absence of SG increases as absorbed dose increases. In the presence of SG the values of the RIC are higher than the corresponding values in the absence of SG up to 12.28kGy, which reflects the induced catalytic effect of irradiated SG. Moreover, the particle size of SG seems to affect the RIC of water. Therefore, as the particle size decreases, the RIC increases (below18.99kGy). Also, it was observed that the pH values decrease as the RIC increases and vice versa. The RIC and variation of pH in the studied samples are related to the radiation induced formation of H_2O_2 and H_3O^+. The induced catalytic effect of SG is related to the radiation-induced formation of electron/ +ve hole (e/ h+) pair during ɣ-radiolysis of SG. Therefore, the RIC increases (pH values decrease) as particle size of SG decreases (surface area increases).

Keywords: Electrical conductivity, ɣ-radiolysis, Particle size, pH, Silica gel, Water.

Introduction

Since the start of radiation chemistry, several workers have studied, extensively, the mechanisms of water and aqueous solutions radiolysis (Spinks & Woods, 1990a; Le Caër, 2011; Sanguanmith et al., 2018; Svoboda et al., 2020). Consequently, it is believed that radiolysis of water leads to the formation of radical and ionic species (H, OH, e^-_{aq}, $HO_2^{\cdot}$, H_3O^+, OH^-) and molecular products (H_2O_2, H_2).

$$H_2O \;\; W{\rightarrow} \; H, OH, e^-_{aq,} \; HO_2^{\cdot}, H_3O^+, OH^-, H_2O_2, H_2$$

Many researchers studied the effects of ionizing radiations on heterogeneous catalysis (Krohn, 1963; IAEA, 1963). Coloration of inorganic solids by ionizing radiations has been well-known and studied for many years. The possibility that defects associated with such color, can be related to the processes of adsorption and catalysis, has been suggested (Kohn, 1959). Silica gel has been found to exhibit a high catalytic activity in the formation of hydrocarbons from CO and H_2 under electron beam irradiation at 300°C (Nagai et al., 1977). The radiolysis of water/ SG system is of a significant importance and is complex. Product formation by water radiolysis, at the interface between solids and water, was examined (Dzaugis et al., 2015). Maeda and co-workers have studied the formation of H_2 by ɣ-irradiation of SG and metal oxides in water (Maeda et al., 2005). Upon exposure to a high energy radiation, H atoms are produced with significant yields in silica samples pretreated at 150°C (Guohong et al., 1997; Rotureau et al., 2006). Brewer and Elvington used a complex supramolecular of ruthenium and rhodium in the study of water decomposition under the action of radiant energy (Brewer & Elvington, 2006). Higher values of radiolyitc yield of H_2 due to energy transfer from zeolite to absorbed water were recorded (Nakashima & Masaki, 1996). Seino et al., recorded that the nanoparticles of TiO_2 and Al_2O_3 dispersed in water lead to a significant increase of radiolytic yields of H_2. They also

noted that the yield of H_2 depends on ɤ- radiation absorbed dose and metal oxide particle size (Seino et al., 2001a, b). Yoshida and collab obtained H_2 by ɤ- irradiation of water in the presence of Al_2O_3 particles of different diameters. The maximum yield of H_2 produced was 3.48µmol/cm³ for water containing Al_2O_3 particles (with diameter of 3µm) , value three times higher than the one obtained for the systems with pure water (Yoshida et al., 2007). It was concluded that the absorption of radiation energy is partitioned between the solution and the solid particles (Fryberger et al., 1997).

The catalytic effect of SG is related to the radiation-induced formation of electron / +ve hole (e /h+) pair during ɤ-radiolysis of SG:

$$M \quad W \rightarrow e^- + h^+$$
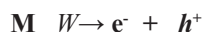
where, M stands for SG.

The radiolysis of an oxide causes electronic excitations, which promote an electron from the valence band to the conduction band, leaving a hole in the valence band. The absorbed radiation energy in SG, crosses the solid-liquid interface and appears in the aqueous phase as solvated electrons (Schatz et al., 1998). On the other hand, +ve holes, remain trapped in the silica particles (Dimitrijevic et al., 1999). In the pulse radiolysis of aqueous suspensions of nanometer-silica, electrons formed in the particle migrate out in the bulk water (Schatz et al., 1998). It is worthwhile to mention that the hydrated electron e^-_{aq} is of a great importance in radiation chemistry where the excited electrons tend to be solvated in water.

$$e^- + n\,H_2O \rightarrow e^-_{aq}$$

It was reported that radiation energy absorbed by solids can be dissipated into three main channels: thermal, defect formation and luminescence. Defects formed in solids, by radiolysis, can participate in chemical reactions on the surface (Sophie Le Caër, 2011). It was concluded that irradiated surface plays a major role in the activation of adsorbate (Guohong et al., 1997). Therefore, in heterogeneous systems, there is a competition between surface reactions and the other energy dissipation channels (Sophie Le Caër, 2011). It was concluded that in an irradiated heterogeneous system, in the case of the two phases, each constitutes a significant fraction of the total mass, the ionizing energy is absorbed significantly by the two phases (Sophie Le Caër, 2011). The radiolysis of water can be strongly affected at solid/liquid interfaces, due to energy transfer from the solid to adsorbed molecules on the surface. This can be considered as a aradiation catalysis (Sophie Le Caër, 2011). The influence of high-energy electron beam (EB) radiolysis, in the dose range of 100 −1000kGy, on the physicochemical properties of silica-supported TiO2 was studied. The enhancement of activity was attributed to EB-induced defects. It has been found that the activity of the irradiated solid is a function of its surface area. It is concluded that during EB treatment, formation of defects in the bulk and on the surface of irradiated crystals occurs (Wronski et al., 2015). It is believed that the energy of the radiation creates displacements and dislocations in the irradiated solid, which converts the solid into a form that is more catalytically active (James, 1961). The most important effect of radiation on solids is the production of paramagnetic units such as F centers. These are electrons trapped in vacant anionic lattice sites (Kazanskyg, 1961; Clinical Documentary Report, 1963). The formation of F centers in the irradiated samples took place on the surface and in the bulk of silica-gel. The results seem to be of interest in connection with the increased catalytic activity of the irradiated silica-gel (Kazanskyg, 1961). Also, it was concluded that transfer of energy from the solid to the adsorbate enhances the yield of the various reaction products (James, 1961). The current study provides a general quantitative model for the RIC and pH changes in water as a function of SG particle size, after γ -irradiation.

Experimental

Different particle sizes of SG (A= ≤0.16mm, B= >0.16mm - 0.2mm, C= >0.2mm - ≤0.5mm, D= 0), were obtained by sieving SG from merk (mesh 60-120 for chromatographic use, UK) after washing by distilled water and drying at 100C°. The samples were ɤ-irradiated by a ^{60}Co source (India Gamma chamber 4000 A, India) at a dose rate of 1.42kGy h⁻¹. The samples were prepared by adding 20 ml of bi-distilled water (its specific conductivity does not exceed 0.5µS . cm⁻¹), to 2g of the SG with different particle size in 50ml glass bottle with stopper. The pH measurements were performed using an Orion Research model SA210 pH/meter. The measurements were carried out at room temperature after calibration using standard buffer solutions at pH 10.00, and pH 4.00. The

electrical conductivity was measured at room temperature using a Kent EIL5007 conductivity meter (Kent industrial measurements—Brown Boveri). The conductivity meter, with cell constant of 1cm^{-1}, was calibrated using NaCl standard solutions (Instruction Manual and Experiment Guide). The electrical conductivity of the irradiated solutions was measured immediately after irradiation at room temperature.

Results and Discussion

High -energy radiation induces defects in silica gel, which influence its catalytic property (Taylor, 1964; Per-olof et al., 1970). As mentioned previously, H_2O_2 is one of the main primary products of water radiolysis (Spinks & Woods, 1990a; Le Caër, 2011). It is well-known tha, H_2O_2 (weak electrolyte) has an acidic property (WWW. H_2O_2.com). Thus, radiation induced formed H_2O_2 can be related to the changes in both RIC and pH in the irradiated samples. Therefore, as the absorbed radiation dose increases the yield of H_2O_2, also, increases. Consequently, the RIC increases and the pH decreases. It was concluded that irradiation of pure water in a system leads to buildup of a steady-state concentration of H_2O_2 in solution and the continual escape of hydrogen and oxygen from the system (Genn, 2016).

It is well-known that H^+ and H_2O_2 are among the main radiolysis products of water (Spinks & Woods, 1990a; Le Caër, 2011). Moreover, H_2O_2 tends to associate and stabilize H^+ (Eq. 1) via the formation of Hydroxyoxidanium cation ($H_3O_2^+$) (https://pubchem.ncbi.nlm.nih.gov/compound/21026404). Hence, the recombination between H^+ and e^-_{aq} will be hindered, and consequently RIC will increase. Thus, both of H_2O_2 and $H_3O_2^+$ (acidic electrolytes) can affect the RIC and pH of the medium. It is well-known that H_2O_2 and $H_3O_2^+$ (https://pubchem.ncbi.nlm.nih.gov/compound/21026404) have acidic property and their free amount in the medium decreases the pH values.

$$H_2O_2 + H^+ \rightarrow H_3O_2^+ \qquad (1)$$

Figures 1-4 illustrate the effect of the absorbed radiation dose (kGy) on RIC (µS .cm^{-1}) and pH of pure water in the absence (Fig.1) and the presence (Fig. 2-4) of SG. It is clear that in all these Figures, the RIC curves are mirror images to those of pH. Generally, in all Fig. 1-4, when the RIC increases the pH decreases.
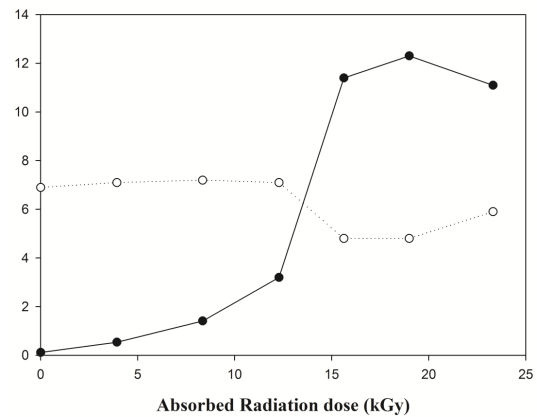

Fig. 1. Effect of absorbed radiation dose (kGy) on (●) RIC (µS .cm^{-1}) and (○) pH of pure water in the absence of SG (dose rate=1.42kGy/h).

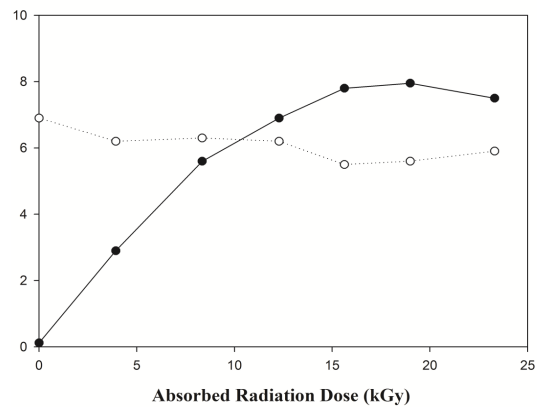**Fig. 2.** Effect of absorbed radiation dose (kGy) on (●) RIC (µS .cm^{-1}) and (○) pH of pure water in the presence of SG with particle size= ≤0.16mm (dose rate=1.42 kGy/h).

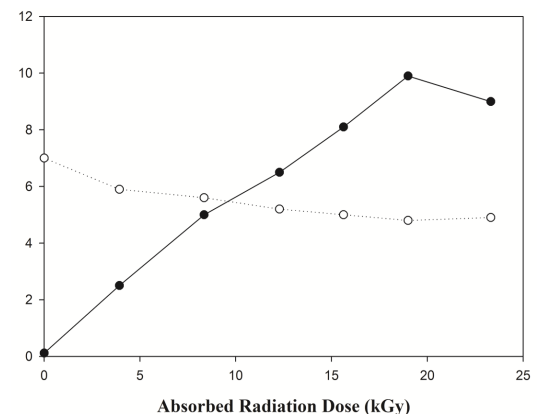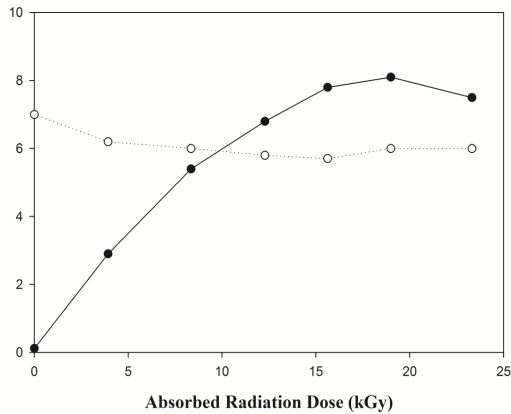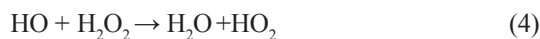**Fig. 3.** Effect of absorbed radiation dose (kGy) on (●) RIC (µS .cm^{-1}) and (○) pH of pure water in the presence of SG with particle size= >0.16mm - 0.2mm (dose rate=1.42kGy/h)

Fig. 4. Effect of absorbed radiation dose (kGy) on (●) RIC (µS .cm⁻¹) and (○) pH of pure water in the presence of SG with particle size= 0.2mm - ≤0.5mm (dose rate=1.42 kGy/h).

In the absence of SG

In the absence of SG (Fig. 1.), an increase in the RIC (a decrease in pH) was observed as the absorbed radiation dose increases up to about 19kGy. These trends are reversed at a higher dose (≈23kGy). Where, at dose >19 kGy, electrical conductive spices (H_2O_2 and $H_3O_2^+$) concentrations seem sufficient to be consumed in molecular-radical reactions (Spinks & Woods, 1990b) (Eq. 2-4), as well as radiation-induced decomposition reactions (Goldstein et al., 2007) (Eq. 5):

$$e^- + H_2O_2 \rightarrow HO^- + HO \qquad (2)$$

$$H + H_2O_2 \rightarrow H_2O + HO \qquad (3)$$

$$HO + H_2O_2 \rightarrow H_2O + HO_2 \qquad (4)$$

$$H_2O_2 + w \rightarrow 2 HO \qquad (5)$$

Therefore, a decrease in RIC (an increase in pH) was observed.

In the presence of SG

Comparing Fig. 1 with Figs. 2-4 reveals that in the presence of SG (Fig. 2-4), there is another mechanism, through which absorbed radiation dose affects RIC and pH of the medium. The radiation induced catalysis of SG is attributed to the generation of (e/ h+) pairs (Eq. 6) (Fryberger et al., 1997., Ogura et al., 1978), through which, energy absorbed by the solid is channeled to decompose (Christensen, 1965), or activation of the adsorbate for reaction with another species (Dimitrijevic et al., 1999).

$$SG\, w \rightarrow SG^+ + e^- \qquad (6)$$

where, SG^+ and e^- represent a positive hole (h^+) and a free electron(e^-) which can be solvated either by water molecules or traped on the surface by the silenol groups of the SG. Recombination of SG^+ and e^- (Eq. 7) leads to the excited states of SG (SG*) (Ogura et al., 1978):

$$SG^+ + e^- \rightarrow SG^* \qquad (7)$$

Oxidation of water or OH^- by the +ve hole (in the surface of irradiated SG) produces the hydroxyl radical (OH) (Eq. 8) (Eddy et al., 2015). Consequently, H_2O_2 is formed via recombination of two OH radicals (Eq. 9):

$$OH^- + {}^+ve\ hole\ (h^+) \rightarrow OH \qquad (8)$$

$$2\ OH \rightarrow H_2O_2 \qquad (9)$$

It should be mentioned that, in the presence of SG (Fig. 2-4), another mechanism was proposed for the formation of OH via the reaction of water with ³exciton on the surface of SG (Eq. 10) (Dimitrijevic et al., 1999):

$$^3exciton + H_2O \rightarrow HO + H \qquad (10)$$

where, (Eq. 10) can be followed by (Eq. 9) producing H_2O_2. Therefore, the yield of OH and, consequently, H_2O_2 are expected to be related to the particle size (surface area) of SG. Thus, these mechanisms are enhanced when the size of the SG particles decreases, i.e., surface area increases (Dimitrijevic et al., 1999).

Table 1 illustrates the effect of the SG particle size on the RIC of the irradiated water at different absorbed radiation doses. Up to12.28kGy, the RIC of irradiated samples, almost, increases as the particle size of SG decreases i.e., surface area increases (Table 1). This can be attributed to the increase of the number of +Ve holes in the surface of the irradiated SG as the surface area increases. It is worthwhile to mention that the silanol groups and residual water facilitate some form of hydration of free electrons on the gel (Ogura et al., 1978). Thus, the recombination of electron initially produced with +Ve holes will be suppressed. So, OH⁻ are then discharged by the +Ve holes on the oxide and as a result, OH radicals are produced (Christensen, 1965). Consequently, the yield of H_2O_2 increases (Eq. 9) (Spinks & Woods, 1990b).

TABLE 1. Effect of the SG particle size on the RIC of irradiated water at different absorbed radiation doses.

Silica Gel particle size(mm)	0kGy	3.93kGy	8.35kGy	12.28kGy	15.62kGy	18.99kGy	23.31kGy
0	0.12	0.54	1.41	3.20	11.40	12.30	11.10
≤0.16	0.12	2.90	5.60	6.90	7.80	7.95	7.50
>0.16 - 0.2	0.12	2.50	5.00	6.50	8.10	9.90	9.00
0.2 - ≤0.5	0.12	2.90	5.40	6.80	7.80	8.10	7.50

Also, it is apparent from this Table that in the absence of the SG, the RIC increases as absorbed dose increases. However, its values are less than in the presence of SG in the range 0 - 12.28kGy. This can be attributed to the radiation catalysis of SG. At higher doses than 12.28kGy, the situation is reversed, i.e., RIC values are greater in absence of SG. This can be attributed to the magnification of absorption effect of SG as the concentrations of H_2O_2 and $H_3O_2^+$ reach considerable values. Where, the concentrations of H_2O_2 and $H_3O_2^+$ seem to be enough to be affected by the adsorption property of SG i.e., the adsorption property competes with the catalytic property. Therefore, the RIC in the presence of ≤0.16mm SG is, no more higher than that of 0.2 - ≤0.5mm. So, ≤0.16mm SG tends to adsorb, efficiently, part of the formed H_2O_2 and $H_3O_2^+$ than 0.2 - ≤0.5mm SG. Generally, at higher doses than 12.28kGy the surface of the SG may be saturated with a lot of solvated electrons and other products, which hinders the formation of H_2O_2 via oxidation of OH^- by +ve hole (Eq. 8).

It should be mentioned that in the presence of SG (at doses above 12.28kGy), the maximum values of RIC are in the presence of >0.16 - 0.2mm SG, which reflects that the catalytic effect of >0.16 - 0.2mm SG superior to adsorption property, with respect to H_2O_2 and ($H_3O_2^+$).

In the absence of SG, the pH of the irradiated water seems to be constant up to 12.28kGy (Table 2). However, sharp decreases occur at higher doses. This can be attributed to the considerable increase in the concentration of hydroxyoxidanium cation ($H_3O_2^+$), as well as H_2O_2. For ≤0.16 and >0.16- 0.2mm particle sizes, the pH decreases as the absorbed dose increases, with a different manner relative to that observed in the absence of SG. It is worthwhile to mention that the pH values, in the presence of >0.16 - 0.2mm particle size are less than the corresponding values of other particle sizes, all over the dose range, which, reflects that the catalytic effect of >0.16 - 0.2mm SG is superior to adsorption property, with respect to H_2O_2 and $H_3O_2^+$. In the case of 0.2 - ≤0.5mm SG samples, after irradiation, the pH decreases, and its values seem to be constant, all over the absorbed dose range.

TABLE 2. Effect of the SG particle size on the pH of irradiated water at different absorbed radiation doses.

Silica Gel particle size(mm)	0kGy	3.93kGy	8.35kGy	12.28kGy	15.62kGy	18.99kGy	23.31kGy
0	6.90	7.10	7.20	7.10	4.80	4.80	5.90
≤0.16	6.90	6.20	6.30	6.20	5.50	5.60	5.90
>0.16 - 0.2	7.00	5.90	5.60	5.20	5.00	4.80	4.90
0.2 - ≤0.5	7.00	6.20	6.00	5.80	5.70	6.00	6.00

Conclusion

The results seem to be of interest in connection with the catalytic activity of the irradiated silica-gel in pure water. Not only the presence of SG affects the RIC and pH of the γ- irradiated pure water, but also, SG particle size. Generally, it can be concluded that the RIC and variation in the pH values in the studied samples are related to the radiation induced formation of H_2O_2 and $H_3O_2^+$ (acidic and electrolyte) according to their concentrations. Therefore, as H_2O_2 and $H_3O_2^+$ concentrations increase, RIC increases and pH decreases and vice versa. In the presence of SG, the formation of these products is catalyzed, specially, below 18.99 kGy. At higher doses, the concentrations of H_2O_2 and $H_3O_2^+$ build up and reach a value which can be decomposed by radiation chemical reactions. Moreover, at this condition i.e., high product concentrations, the adsorption property of the SG comes to play beside the catalytic effect of SG. The catalytic effect of SG is attributed to the radiation induced formation of electron/hole pair (e/ h+) during γ-radiolysis of SG. Therefore, the RIC increases (pH decreases) as the particle size of SG decreases (surface area increases), this can be attributed to the fact that the amount of e / h+ pairs depends on SG surface area. It is worthwhile to mention that, the +ve holes can oxidize OH⁻ anion to OH, which participate in the formation of H_2O_2 and $H_3O_2^+$. According to the enhancement of RIC of water in the presence of SG, dosimetric studies should be carried out based on this phenomenon.

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