Gamma Radiation's Influence on TiO_2 in Iron Oxidation within Aqueous Solution: Potential Photocatalytic Applications	ORAL Ph.D. Student: N Journal: YES

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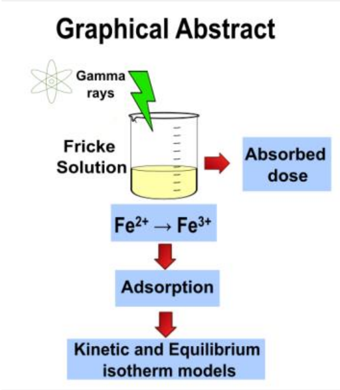

The impact of the adsorption process, under gamma radiation, when introducing TiO_2 semiconductor into the Fricke solution containing Fe^{2+} and Fe^{3+} ions, was investigated. The crystalline phase, purity, particle size distribution, and specific surface area of TiO_2 were measured. Based on experimental findings, it was observed that the pseudo second-order model offers a superior fit for the adsorption kinetics of both metal ions. Additionally, the Freundlich model better describes the adsorption equilibrium of Fe^{2+} and Fe^{3+} onto TiO_2. To evaluate the influence of TiO_2 on Fricke solution, suspensions containing 0, 50, and 100 mg of TiO_2 were irradiated with 100, 250, and 500 Gy using a ^{60}Co gamma source. The presence of TiO_2 in the Fricke solution alters the absorbed dose, likely attributable to the adsorption of Fe^{3+} ions onto TiO_2. Consequently, this indicates the need for additional experiments to quantify the reduction factor in absorbed dose resulting from this adsorption phenomenon.

Introduction

The Fricke solution serves to quantify the absorbed dose resulting from the interaction of gamma radiation with matter. Fricke dosimetry, also referred to as ferrous sulfate dosimetry, stands as one of the most extensively researched and commonly employed chemical dosimetry techniques [1]. This method hinges on the conversion of ferrous ions (Fe^{2+}) to ferric ions (Fe^{3+}) induced by ionizing radiation [2]. However, when this solution interfaces with a semiconductor such as titanium dioxide (TiO_2), the absorbed dose escalates owing to the generation of •OH radicals stemming from electron-hole pair formation on the semiconductor's surface. TiO_2 acts as a photosensitive semiconductor by absorbing electromagnetic radiation with enough energy to overcome its band gap [3].

Consequently, TiO_2 particles possess the capability to produce free radicals •OH and O^{2-}, rendering it widely applicable in organic matter decomposition, disinfection, and the elimination of viruses, bacteria, and other pathogens [4]. Extensive research has investigated the utilization of TiO_2 to enhance photocatalysis in water treatment processes [5].

Nonetheless, the adsorption mechanism and the impact of TiO_2 under gamma radiation on the Fricke solution remain unexplored, and this study aims to address that gap in research.

Material and Methods

The particle size, surface area, and purity of TiO_2 were analyzed using light scattering for particle size distribution, BET surface area measurement, and X-ray diffraction techniques. Fricke solutions were prepared following the ASTM E1026-04 standard. Fe^{2+} ions were measured according to Standard Method 3500-Fe B, while Fe^{3+} ions were determined using the thyocyanate colorimetric method.

For adsorption experiments, a suspension containing 10 g L^{-1} of TiO_2 in 1 M solution of Fe^{2+} or Fe^{3+} was stirred at 300 rpm. Samples were taken at various time intervals ranging from 2 to 300 min. Each experiment was conducted in triplicate. Adsorption isotherms were constructed using TiO_2 masses ranging from 30 to 200 mg in 10 mL of Fricke solution containing either 0.5 M Fe^{2+} or Fe^{3+}. Solutions were filtered and maintained at 20 ± 3°C with constant agitation in the dark. Solutions were irradiated using a self-contained ^{60}Co irradiator. The doses used were 100, 250, and 500 Gy and the TiO_2 mass applied were 0, 50, and 100 mg. Absorbed dose values were the response variable, with six repetitions performed for each TiO_2 mass level.

Results and Discussion

The results of the light scattering particle size distribution revealed that anatase is the dominant crystalline phase in the TiO_2; 80% of its particles are below 2.4 µm (d80), and 50% is below 1.4 µm (d50). XRD analysis indicated a purity of TiO_2 ranging from 99 to 100%. Additionally, BET analysis determined that specific surface area of TiO_2 was 111.203 m^2/g.

Table 1 presents kinetic and equilibrium adsorption parameters for Fe^{2+} and Fe^{3+} using pseudo-first order, pseudo-second order, Freundlich, and Langmuir models, respectively. The data indicate that the adsorption kinetics of both Fe^{2+} and Fe^{3+} with TiO_2 fit better to the pseudo-second order model, with respective R^2 values of 0.9727 and 0.9610. In the Freundlich model, the adsorption capacity (K_F) is higher for Fe^{2+} compared to Fe^{3+}, while the adsorption intensity (represented by the exponent "n") is similar between Fe^{2+} and Fe^{3+}. This suggests an inhomogeneous adsorption in multilayers due to an exponential distribution of active sites. The Langmuir model was discarded due to the obtaining of negative values for Langmuir constant (K_L) for Fe^{2+} and Fe^{3+} individual systems, which lacks chemical sense.

Figure 1 illustrates the correlation between the absorbed dose and the dose administered by the ^{60}Co source across various masses of TiO_2. It is evident that the presence of TiO_2 has no discernible impact on the absorbed dose up to an irradiation dose of 250 Gy. However, the sensitivity of the Fricke solution containing TiO_2 with increasing absorbed dose under gamma radiation is affected.

The likely explanation for these findings is that the adsorption of Fe^{3+} onto the surface of TiO_2 could diminishes its absorbance value. Given that absorbance is directly correlated with the absorbed Fe^{3+} in the catalyst, rather than indicating an increase in the oxidation of Fe^{2+} to Fe^{3+}. Consequently, the absorbed dose decreases compared to the measurement taken when there are no TiO_2 particles present in the Fricke solution.

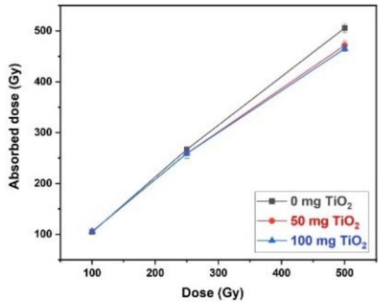

Figure 1. Absorbed dose vs. dose by ^{60}Co source for Fricke solutions with and without TiO_2.

Table 1. Kinetic and equilibrium adsorption models parameters for adsorption of metal ions onto TiO_2.

	Pseudo-first-order		Pseudo-second-order		Langmuir		Freundlich		
Metal ions	k_1 (min^{-1})	R^2	k_2 ($g\ mmol^{-1}\ min^{-1}$)	R^2	K_L ($L\ mmol^{-1}$)	R^2	K_F ($mmol\ g^{-1}\ mM^{-(1/n)}$)	n	R^2
Fe^{2+}	0.179	0.9354	34.547	0.9727	-2.5	0.9913	$2.8x10^8$	0.037	0.9893
Fe^{3+}	0.219	0.9449	31.875	0.9610	-3.2	0.9800	$3.4x10^{11}$	0.037	0.9755

Conclusions

The interaction between gamma radiation and an aqueous solution containing a semiconductor solid, such as TiO_2, constitutes a form of heterogeneous photocatalysis. The TiO_2 utilized is in the crystalline phase of anatase, with a purity ranging from 99 to 100%. It possesses a particle size (d50) of 1.4 µm and a particle size (d80) of 2.4 µm, along with a specific surface area of 111.203 m^2/g. Adsorption takes place when the semiconductor TiO_2 comes into contact with metallic ions Fe^{2+} and Fe^{3+} present in the Fricke solution. Both Fe^{2+} and Fe^{3+} individually exhibit pseudo-second-order kinetics when adsorbed onto TiO_2. The Freundlich model demonstrates a good fit for Fe^{2+} and Fe^{3+} systems with TiO_2. However, the Fricke dosimeter is found to be compromised in measuring the absorbed dose in the presence of TiO2, primarily due to the adsorption of Fe^{3+} ions onto the TiO_2. Therefore, further experiments with higher irradiation doses are necessary to determine the extent of this adsorption phenomenon's impact on the absorbed dose.

Acknowledgments

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