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Insights into Competitive Adsorption Between Nitrate and Oxalic Acid Over Tio$_2$ and Consequences for Photocatalytic Remediation

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Abstract **–**The adsorptive behaviour of nitrate and oxalic acid on TiO_2 in single and bi-component systems was studied. It was found that the Langmuir adsorption coefficient for nitrate is 4 times higher than that of the oxalic acid. However, the amount of oxalic acid adsorbed by TiO_2 was about 10 times greater than the amount of nitrate adsorbed. In the bi-component system, oxalic acid was preferentially adsorbed on the TiO_2 surface. Thus, in the presence of oxalic acid, adsorption of nitrate was inhibited and despite its higher Langmuir adsorption coefficient, at oxalic acid concentrations of 4 and 8 mM uptake was negligible. Consequently, the impact of inhibition on the adsorption of nitrate by oxalic acid could be responsible for low rate of photocatalytic remediation of nitrate in aqueous suspension of TiO_2. Therefore, enhancing adsorption of nitrate on TiO_2 through surface modification could be a key parameter for accelerating the photocatalytic reaction.

Keywords**:** TiO_2, adsorption, inhibition, nitrate, oxalic acid.

1. Introduction

Nitrate ions are the abundant components of industrial, agricultural and municipal wastewater streams and discharges from these source points result in excess concentrations in water supplies. High concentration of nitrate ions in drinking water source has been considered to be deleterious to human health as it can be transformed into carcinogenic compound and therefore, its removal from drinking water is essential. For this reason, heterogeneous photocatalytic remediation of nitrate on TiO_2 has been developed and emerged to be a promising advanced green remediation technology for denitrification of drinking water sources (Anderson, Fernandez-Garcia 2009). The technology exploits the oxidation and reduction potentials of the photogenerated holes and electrons that are simultaneously created in the solid following exposure to radiation of energy greater than the band gap. If suitable scavengers are available to trap the electrons and holes, the rate of recombination is reduced and consequently, redox reactions and proportianaly enhanced. In the case of photocatalytic remediation of nitrates, upon photo-excitation of TiO_2, the photogenerated electrons and positively holes can reduce and oxidise adsorbed nitrate and organic hole scavenger on the surface of TiO_2, respectively. To this effect and achieve effective photochemical conversions of these substances simultaneously, preadsorption of nitrate and organic species on the TiO_2 surface is a prerequisite step in the entire process, since interfacial charge carrier trapping needs to be very fast. More importantly, nitrate should be adsorbed more efficiently than an organic hole scavenger, since the interfacial transfer of electron occurs slower than the hole transfer (Hoffmann et al. 1995). However, it has been reported that organic hole scavenger was preferentially adsorbed on the surface of TiO_2 whereas the adsorption of nitrate was to a lesser extent or even inhibited (Li, Wasgestian 1998). With this observation, detail studies in the literature that elucidate how the two solutes behave under competitive conditions have not been well explored. Therefore, from the heterogeneous photocatalysis purview, it is of great interest to investigate the co-adsorption of nitrate and organic hole scavenger on TiO_2 surface, which can allow an understanding of the effect of organic hole scavenger on nitrate adsorption. The derived co-adsorption parameters may be a key in trying to develop improved photocatalysts for better performance in the photocatalytic remediation of nitrate that could be attained by enhancing nitrate adsorption capacity.

In the present paper, co-adsorption of nitrate and oxalic acid in aqueous suspension of TiO_2 is reported. This binary system was considered since this pair is often employed in the photocatalytic removal of nitrate, but few studies report on the strength or extent of adsorption of the two components when combined in a competitive environment.

2. Separate And Co-Adsorption Adsorption Test Of Nitrate And Oxalic Acid

The adsorption tests for single-component systems were conducted at constant temperature of 25 ± 0.1 °C and without pH adjustment using different initial concentrations of nitrate and oxalic acid. 0.25 g of P25-TiO_2 was thoroughly mixed in a series of capped 100 ml Pyrex bottles contained 25 ml of nitrate or oxalic acid solutions with concentrations in the range 10 – 100 mg/L ($1.61 \times 10^{-4} - 1.61 \times 10^{-3}$ mol/dm^3) and 0.001, 0.002, 0.004, 0.008 and 0.010 mol/dm^3, respectively, in a thermostat water bath/shaker for 24 h. After the 24 h shaking, the suspensions were centrifuged, filtered with syringe filter 0.45 μm (Millipore) and then then analysed for equilibrium concentrations of nitrate and oxalic acid were determined at 340 and 262 nm, respectively, using UV-visible spectrophotometer (*Lambda 25, PerkinElmer*). For nitrate, nitrate kit (spectroquant) was used for its residual concentration determination, whereas oxalic acid was based on its characteristic functionality.

To determine the maximum adsorption uptake for both nitrate and oxalic acid, the amount of nitrate and oxalic acid adsorbed per unit mass of TiO_2 (mol/g) was calculated using the expression (1)

$$q_e = (C_i - C_e)\, V/m \tag{1}$$

where q_e is the amount adsorbed at equilibrium (mol/g), C_i is the initial concentration (mol/dm^3), C_e is the solution equilibrium concentration (mol/dm^3), V is the volume of the aqueous phase (dm^3), and *m* is the mass of TiO_2 used.

In the co-adsorption experiment, a similar procedure was used. Solutions of oxalic acid (0.001, 0.002, 0.004 and 0.008 mol/dm^3) and fixed nitrate concentration of 100 mg/L (0.00161 mol/dm^3) were mixed with 0.25 g TiO_2. The equilibrium concentrations in the samples were determined in the same way as employed for the individual components.

2. 1. Error Analysis

The regression Chi-square (χ^2) test was employed as a criterion for fitting quality. The statistical analysis is based on the sum of the square of the differences between the experimental adsorption data and model calculated data, of which each squared difference was divided by the corresponding data obtained by calculating from models (Ho 2004). The chi-square can be presented by the following equation:

$$\chi^2 = \Sigma \left[\frac{(qee - qec)2}{qec} \right] \tag{2}$$

where q_{ee} is the equilibrium capacity of the adsorbent obtained from experiment (mol/g), and q_{ec} is the calculated equilibrium uptake according to the model (mol/g). A low value of χ^2 indicates that experimental data provides a good quality fit to the value from the model. Therefore, data were analysed to confirm the best-fit isotherms for the adsorption systems of both nitrate and oxalic acid.

3. Results and Discussion

3. 1. Individual Adsorption Isotherms Of Nitrate And Oxalic Acid

The equilibrium relationship between adsorbent and adsorbate is commonly established by adsorption isotherms and thus, is of great importance to heterogeneous photocatalysis. Equilibrium adsorption studies provide the uptake capacity of the adsorbent and delineate the surface properties and affinity of the adsorbent for an adsorbate *via* certain constants. With respect to this, Langmuir and Freundlich models, as the most frequently used isotherms, were employed to explore adsorption behaviour of TiO_2 towards nitrate and oxalic acid in single and bi-component systems. The commonly linearised Freundlich and Langmuir equations used are expressed in equation 3 and 4, respectively.

$$\log q_e = \log K_F + 1/n \log C_e \tag{3}$$

where qe is the adsorption capacity (mol/g); C_e is the equilibrium concentration (mol/dm^3), respectively; K_F and 1/n are the adsorption capacity and intensity of adsorption, respectively. The values of K_F and 1/n were determined from the intercept and slope respectively, of the logarithmic plot, whereas the expression below is the linearised Langmuir equation used-

$$C_e/q_e = (1/K_L q_m) + (1/q_m)Ce \tag{4}$$

where q_e is the amount of nitrate adsorbed at equilibrium (mol/g); C_e is the equilibrium concentration of nitrate and oxalic acid (mol/dm^3); K_L (dm^3/mol or M^{-1}) and q_m (mol/g) are the Langmuir constant and predicted maximum adsorption capacity. The constants q_m and K_L were determined from the intercept and slope of the linear plot of the experimental data of C_e/q_e *vs*. C_e.

Fig. 1a and b indicate that the uptake processes were continuous until saturation attained, suggesting conceivable monolayer coverage of both nitrate and oxalic acid onto the surface of the TiO_2. The equilibrium uptake, q_e, were 8.38×10^{-5} and 8.20×10^{-4} mol/g for nitrate and oxalic acid, respectively, confirming that the amount of oxalic acid adsorbed was about 10 times higher than the amount of nitrate adsorbed by TiO_2. Similarly, the isotherms given by the Langmuir equation for the two adsorbates are shown in Fig. 1c. Table 1 show the calculated values of Freundlich and Langmuir isotherm parameters for single-component adsorption experiments, which reveal that the adsorption data of both oxalic acid and nitrate were best fitted to the Langmuir model with a correlation coefficient, $r^2 > 0.99$. In addition, the smaller values of the χ^2 further reveal the agreement between the measured and Langmuir model-predicted uptake for both adsorbates, which characterise the quality of fit of the Langmuir isotherm model describing the data. However, it is obvious from the linearised Langmuir plot that nitrate has a strong affinity for TiO_2 as implied by the initial rise at low concentrations of adsorbate (Vimonses et al. 2009a, Vimonses et al. 2009b). Additionally, the extracted value of Langmuir adsorption coefficient, K_L, for nitrate is 4 times greater than that of oxalic acid (Table 1), suggesting that the strength of adsorption of nitrate was significantly greater than oxalic acid. Despite this, the amount of oxalic acid was adsorbed on the TiO_2 surface was much greater. This observation could be attributed to the formation of oxalate complexes at the surface of TiO_2, since $C_2O_4^{2-}$ is a good bidentate ligand (Robert et al. 2000, Thomas, Syres 2012, Mendive et al. 2009). The explanation could also be due to the ability of oxalic acid to bind *via* two adsorption routes, which are either by two carbonyl groups or one carbonyl and one hydroxyl groups (Fahmi et al. 1995, Mendive et al. 2007). This reflects that, at highest coverage, one oxalic acid conceivably covered 2 TiO_2 units, indicating it ability to reach more adsorption sites of TiO_2 than nitrate with monodentate characteristics.

Table. 1. Adsorption parameters for nitrate and oxalic acid on TiO_2.

	Freundlich					Langmuir			
	$q_{e\ (Expt)}$	K_f	n	r^2	χ^2	K_L	q_{max} (predicted)	r^2	χ^2
Nitrate	8.38×10^{-5}	9.24×10^{-4}	2.8	0.9333	5.62×10^{-3}	4672	9.49×10^{-5}	0.9977	1.0×10^{-4}
Oxalic acid	8.20×10^{-4}	5.0×10^{-3}	2.3	0.9252	1.89×10^{-2}	1137	9.0×10^{-4}	0.9905	4.3×10^{-4}

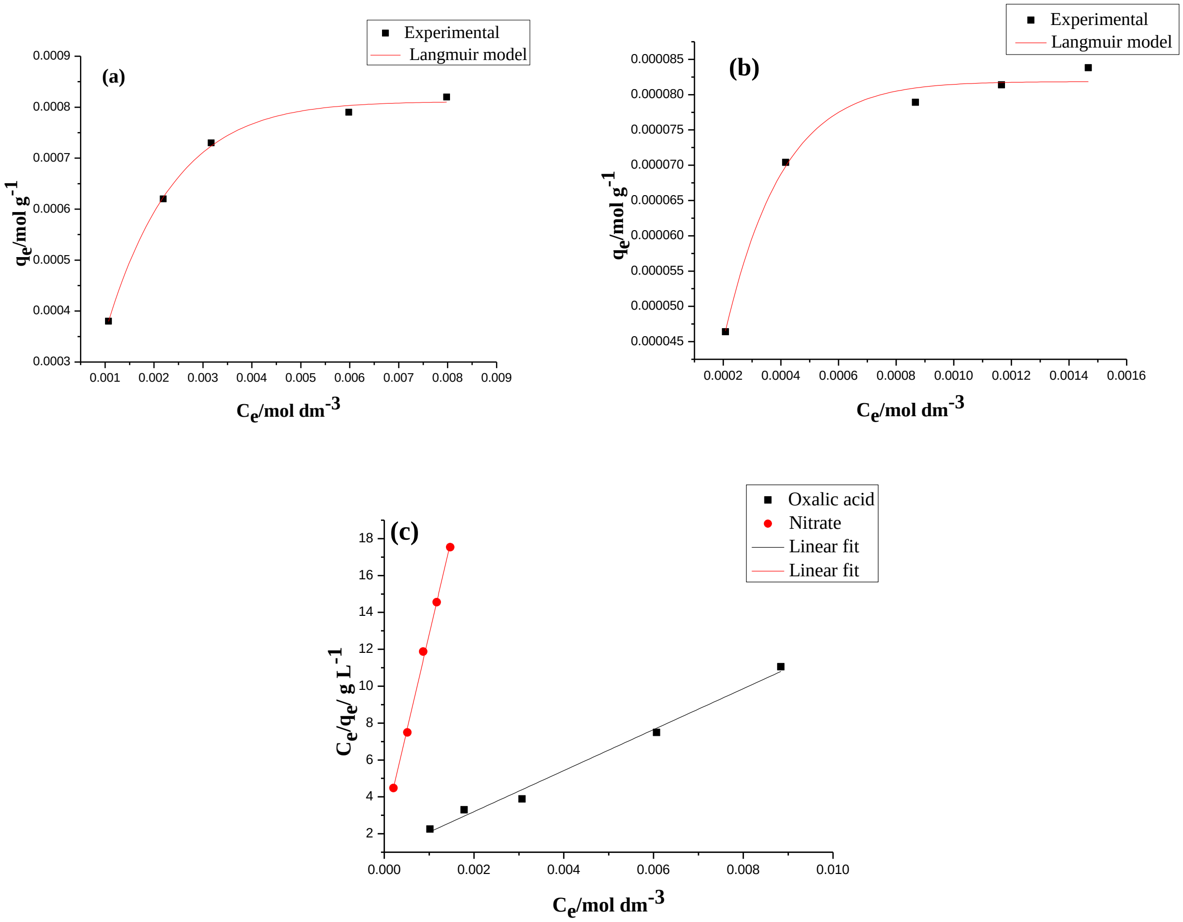

Fig. 1. (a) Oxalic acid and (b) nitrate adsorption isotherms (c) Langmuir plot for oxalic acid and nitrate.

3. 2. Co-Adsorption Isotherms Of Nitrate And Oxalic Acid

In heterogeneous photocatalytic remediation of nitrate using oxalic acid as hole scavenger, the nitrate (electron acceptor) and oxalic acid (electron donor) are presence together in the reaction. Accordingly, these two pollutants require adsorption sites on TiO_2 surface and would be doubtful if their respective ions are adsorbed in equal quantities and thus, competition is a relevant criterion to be investigated and quantified. To test the adsorption behaviour of nitrate in presence of oxalic acid or *vice visa*, the extended Langmuir isotherm for competitive adsorption developed by Jain and Snoeyink (1973) was applied.

Hence, the amount of oxalic acid adsorbed on TiO_2 surface upon competition with nitrate was calculated from equation (5), which can be expressed as-

$$q_{e,oxalic} = (q_{m,oxalic} - q_{m,nitrate})\ K_{L,oxalic}\ C_{e,oxalic} / (1 + K_{L,oxalic}\ C_{e,oxalic}) + (q_{m,nitrate}\ K_{L,oxalic}\ C_{e,oxalic}) / 1 + K_{L,oxalic}\ C_{e,oxalic} + K_{L,\ nitrate}\ C_{e,nitrate} \tag{5}$$

Similarly, the amount of nitrate adsorbed on TiO_2 in competition with oxalic acid was calculated from equation (6) written as-

$$q_{e,nitrate} = (q_{m,\ nitrate}\ K_{L,\ nitrate}\ C_{e,\ nitrate}) / 1 + K_{L,\ oxalic}\ C_{e,\ oxalic} + K_{L,\ nitrate}\ C_{e,\ nitrate} \tag{6}$$

where $q_{e,\ oxalic\ and}$ $q_{e,\ nitrate}$ are the amounts of oxalic acid and nitrate adsorbed per unit mass of TiO_2 at equilibrium concentrations of $C_{e,oxalic\ and}$ $C_{e,\ nitrate}$, respectively. $Q_{m,\ oxalic}$ and $q_{m,\ nitrate}$ are maximum amount of adsorption with complete monolayer coverage on TiO_2 with oxalic acid and nitrate, respectively, which are determined from single-component systems with their corresponding Langmuir constants.

Fig. 2 shows the adsorption behaviour of each in presence of both adsorbates. Compared to nitrate single-solute adsorption onto TiO_2 surface, competitive adsorption infers a significant decrease in uptake. Despite the low Langmuir coefficient for oxalic acid, it was preferentially adsorbed onto TiO_2 surface and adsorption of nitrate was strongly inhibited. The inhibition by oxalic acid in preventing nitrate adsorption increased from 12 to 93 % at 1.0 and 8.0 mM oxalic acid concentration, respectively. This implies that nitrate can only successfully compete with oxalic acid at low concentrations equal or lower than 1.0 mM, because even at 2.0 mM the inhibition effect reached 60 % (Fig. 2). However, at low concentration of oxalic acid, the amount of oxalic acid that could be adsorbed maybe insufficient to trap the photogenerated holes and as a result, effective nitrates reduction is limited. On the other hand, at high concentrations, because of the preferential adsorption of oxalic acid, nitrate adsorption is greatly inhibited and therefore, nitrate reduction cannot be efficiently performed due to reduced rate of acceptance of electrons. The dependence of nitrate reduction upon oxalic acid concentration is shown in equation 7, which indicates 2.5: 1 molar ratio of oxalic acid to nitrate. However, to avoid the likelihood of the photocatalytic reduction process ceasing due to rapid consumption of oxalic acid, the concentration needs to be double of the stoichiometric amount. Therefore, the concentration regions at which oxalic acid can produce desired reduction of nitrate is at minimum of 4.0 mM and 8.0 mM maximally against 1.61 mM of nitrate, concentration regions where oxalic acid prevented the adsorption of nitrate by 87 and 93 % inhibition, respectively (Fig. 2). Hence, the reported lower degradation rate of nitrate in aqueous suspension of TiO_2 (Anderson 2012) may be related to the low amount of nitrate adsorbed on the photocatalyst surface cause by preferential adsorption of oxalic acid. Consequently, to enhance the adsorption of nitrate in the photocatalytic reduction process without compromising the required oxalic acid concentration, surface modification of TiO_2 with a high surface area adsorbent such as an activated carbon might help in increasing adsorption capacity.

$$5H_2C_2O_{4(aq)} + 2NO_3^- + 2H^+ \xrightarrow{\qquad\qquad} N_2 + 10CO_{2(g)} + 6H_2O \tag{7}$$

4. Conclusion

The adsorption of nitrate and oxalic acid in aqueous suspension of TiO_2 was investigated both in single-solute and bi-solute systems. For single-solute adsorption, the results obtained fitted the Langmuir adsorption isotherm model, which suggests higher uptake of oxalic acid than nitrate despite its lower Langmuir adsorption coefficient. In the case of bi-component adsorption, it was found that nitrate adsorption onto TiO_2 was strongly inhibited in the presence of oxalic acid at stoichiometric amounts and above. This distinct inhibition effect imposed on nitrate may be attributed to the dissimilar ability of adsorption competition with oxalic acid on the surface of the photocatalysts. This better understanding of the adsorption behaviour of nitrate and oxalic acid in bi-component system is likely to be employed in surface modification of TiO_2 with high surface area materials, which may result in improvement in the uptake of nitrate without a compromise on the stoichiometric concentration of oxalic acid for enhanced photocatalytic remediation of nitrate.

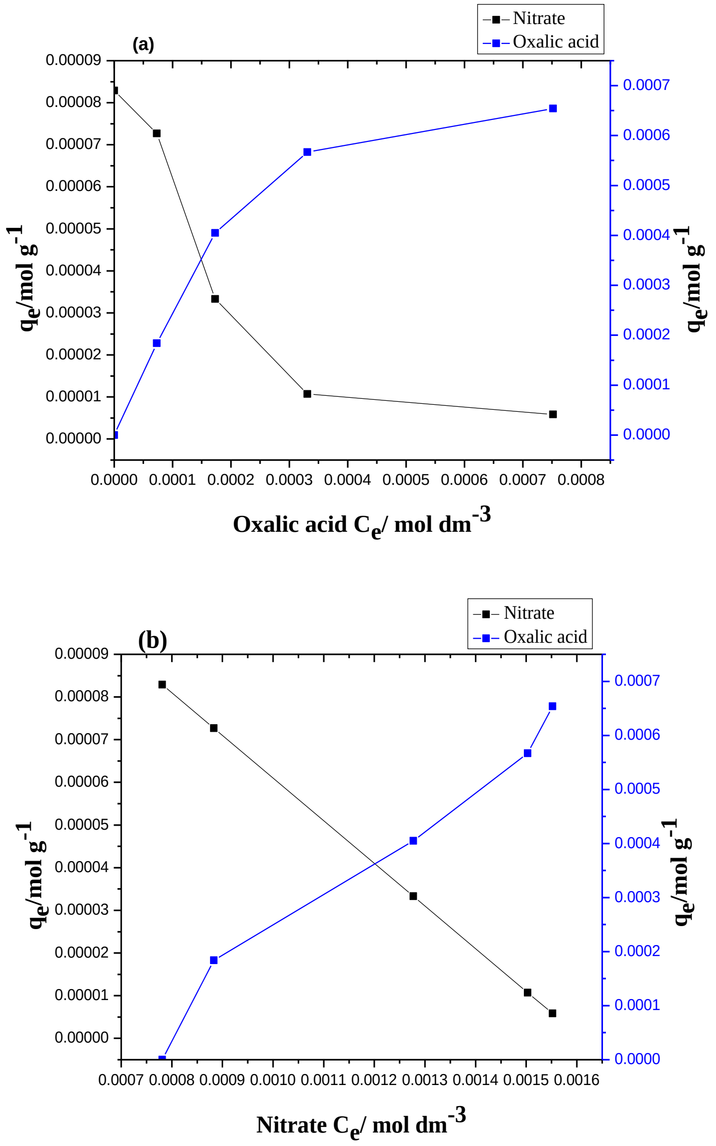

Fig. 2. (a) Co-adsorption isotherm of nitrate and oxalic acid as a function of equilibrium concentration of oxalic acid, (b) as a function of equilibrium concentration of nitrate.

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