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KINETICS DEGRADATION OF TNT FROM AQUEOUS SOLUTIONS USING CATALYTIC IONIC LIQUID

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ABSTRACT

The reduction of 2,4,6-trinitrotoluene (TNT) in aqueous solution with imidazolium chloride [BMIM][Cl] and its modified imidazolium tetracholoferrate [BMIM][$FeCl_4$] based ionic liquid were systematically investigated. The results showed that the pseudo first-order reaction law fit the reduction of TNT. The measured apparent rate constant (K_{obs}) of TNT on modified ionic liquid (0.0274 min^{-1}) was eleven fold than on ionic liquid (0.0025 min^{-1}) at 303 K. The apparent rate constant of TNT reduction on modified ionic liquid also can be improved by an increase in ionic liquid concentration (0.1, 0.4, 0.6, 1.2). It is found that [BMIM][$FeCl_4$] based ionic liquids has the best effect on the selective reduction of 2,4,6-trinitrotoluene (TNT) in aqueous solution at 303 K.

Key words: 2,4,6-Trinitrotoluene, Kinetics degradation, Catalytic ionic liquid, Imidazolium tetracholoferrate, Aqueous solutions, Green environment.

INTRODUCTION

2,4,6-Trinitrotoluene (TNT) is one of the most commonly used explosives for military and industrial applications. It is valued because of its insensitivity to shock and friction, which reduces the risk of unexpected detonations[1,2]. TNT exposure occurs occupationally during production and use as well as to the general public through contaminated drinking water, air, soil, foods, or otherwise coming in contact with TNT or TNT-contaminated media. Environmental Protection Agency (EPA) has assigned TNT a weight-of-evidence carcinogenic classification of (possible human carcinogen)[3,4].

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Currently, TNT contaminated water is treated by various method, including activated carbon adsorption, oxidation with hydrogen peroxide/ozone, supercritical water oxidation, Fenton reagent oxidation and photo catalytic oxidation. These methods are all useful for the degradation of TNT. However, the residual products after treatments with these methods are still potentially harmful.

Ever increasing needs for a secure society and green environment essentially require the detection of TNT with rapidity, high sensitivity and low cost. The use of ionic liquid is an alternative that has been demonstrated to be effective for the extraction of many organic compounds at room temperature[5,6]. The room temperature ionic liquid, a kind of environmentally friendly solvent and catalyst, has gained wide attention of scholars from various fields such as synthesis, catalysis, separation and electrochemistry due to its adjustable physical and chemical properties[7-10]. Ionic liquids are non-flammable, thermally stable, exhibit negligible vapor pressure, and offer the potential for recyclability. For these reasons, It is interested to study the degradation TNT using ionic liquids[11].

There is a continuing interest in application of ionic liquids in extractive separations documented[2,5-7]. ionic liquids are composed of an organic cation and either an organic or an inorganic anion. They remain liquid over a wide range of temperatures, including room temperature[8,9]. Ionic liquids are a new group of solvents of great interest, which have been recently studied as potential "green solvents". Practically, zero vapour pressure of the most ILs and temperature stability make them attractive catalytic solvents in many applications. Therefore, the aim of this paper was to study the effect of reaction time, concentration and the pH of mixed solution of IL on the degradation of TNT by using IL (1-butyl-3-methylimidazolium chloride) and its modified MIL (1-butyl-3-methylimidazolium tetrachloroferrate).

EXPERIMENTAL

Materials and chemicals

All the chemicals used in this study were analytical reagent grade and utilized without further purification. Chemicals used are 1-butyl 3-methyl imdazolium chloride [BMIM][Cl], iron (III) chloride , Sodium hydroxide and hydrochloric acid were purchased from Aldrich. TNT used in this experiment was supplied by military Factory-18. The TNT concentration of the sample was 148 ppm.

A solution containing TNT was prepared by dissolving various amounts of TNT with deionized water to the desired initial concentrations.

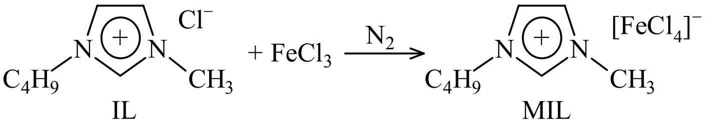
Stock solution of TNT was prepared by weighing out 100 mg of TNT and transferring each to a 1000 mL measuring flask. The flask was filled with distilled water, and the resulting heterogeneous solution was stirred for 3 days to effect complete solution. This procedure gave a 100 ppm TNT standard stock solution. These standards were then injected into the HPLC for each TNT kinetic run, and a calibration curve was thus obtained.

High performance liquid chromatography (HPLC)

The instrument used in the analysis of the samples was HPLC (P202460865) made in 2010, model Jasco The HPLC consisted of a LC Shimadzu pump 10AT equipped with a UV detector selected at $\lambda = 254$ nm and fitted with a LiChrosphere RP-8 column 250 mm* 4.6 mm. 5 µm particle size (merck). The system was operated in isocratic mode (methanol/water; 70/30,v/v) at a flow rate of 1.3 mL min^{-1}.

Preparation of [BMIM][$FeCl_4$] based ionic liquids

Under the protection of nitrogen, the modified ionic liquid (MIL) (dual-functionalized ionic liquid) was prepared by simple addition of metal chloride to imidazolium cations (imidazolium chloride) (molar ratio 1 : 1). Imidazolium cations was placed in the three-necked glass flask with a magnetic stirrer and metal chloride was then very slowly added under stirring Eq. (1). The reaction of metal chloride and imidazolium cations was highly exothermic and care had to be taken not to permit the temperature of the mixture to rise above 60°C; otherwise, thermal decomposition occurred. The resulting melt was used for testing in the reactions[12].



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Catalyst characterization

Fourier transform infrared (FTIR) spectroscopy

To obtain detailed information about the molecular structure of the supported catalysts, the IR transmission spectroscopic investigation was carried out at room temperature on Mattson 8100. spectrometer using KBr disc method. IR data were collected by averaging 32 scans with a spectral resolution of 4 cm^{-1} over the wave number range of 400-1200 cm^{-1}. Fourier transform infrared spectroscopic (FTIR) analysis was carried out by using an ATI Mattson Genessis Ser FTIR Tm infrared spectrophotometric.

Differential thermal analysis (DTA) and thermal gravimetric analysis (TGA)

Differential thermal analysis (DTA) and Thermogravimetric analysis (TGA), were performed to trace the structure changes accompanying the thermal treatment. This technique was recorded simultaneously on an apparatus manufactured by TGA-50 shimadzu instrument, in the range from 40 to 600°C. The heating rate was 10 K/min under nitrogen atmosphere.

RESULTS AND DISCUSSION

Infrared spectroscopy (FTIR)

As illustrated in Fig. 1, much broader band was observed for IL (sample a), which is assigned to N-H stretch at wave number 3600-3180, this peak is disappeared in modified ionic liquid MIL (sample b) but observed bands in the region 3750-3400 cm^{-1}, indicate the presence of Lewis and brönshated acid sites. This peak is the main character to indicate the activity of the catalyst.

Various bands in Fig. 1 the spectrum were identified from which corresponding to alkenes asymmetric stretching bands of CH and C=C at wave number 3081 and 1629 cm^{-1} for sample (a), which were shifted to bands at wave number 3103 and 1721 (sample b) due to interaction with iron salt $FeCl_3$.

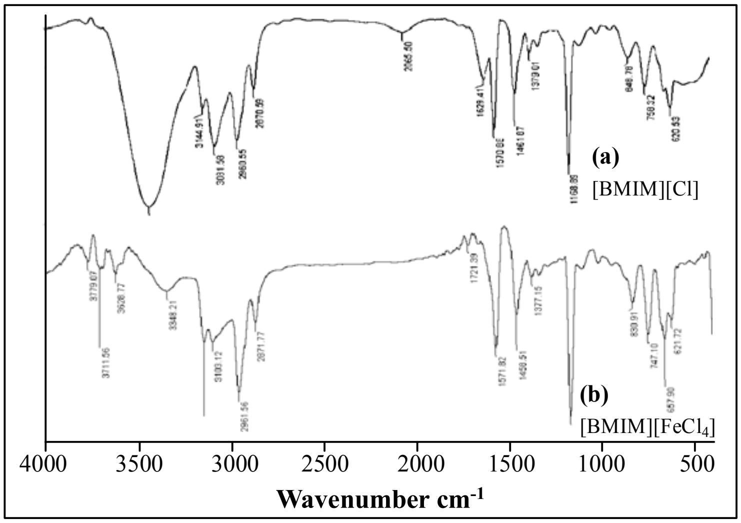

Fig. 1: FTIR Spectra of (a) ionic liquids [BMIM][Cl] and (b) modified ionic liquids [BMIM][$FeCl_4$] based ionic liquids

The very sharp bands in samples (a & b) at wave number 1186 cm^{-1} could be due to the presence of C-N stretch band related to imidazolium ring. The peak at 1570 cm^{-1} that corresponds to imidazole ring stretching in pure IL, the occurrence of complexation between [$FeCl_3$] and pure [BMIM]Cl can be further proved by the formation of a shoulder at 1571 cm^{-1} in [BMIM][$FeCl_4$].

Thermal decomposition temperatures thermal gravimetric analysis (TGA)

Fig. 2 shows the DTA curves of the thermal decomposition of ILs. Several endothermic peaks were observed in the DTA curve. The 1st peak is a relatively located at about 70.61°C, indicating the loss of water of crystallization (H_2O) for [BMIM] $FeCl_4$ (MIL).

The increase of temperature was accompanied by successive appearance of other endothermic peaks, their maxima are located at 380.26° for [BMIM] $FeCl_4$, based ionic liquid, respectively. These peak are related to the successive decomposition of the produced type of imidazolium chloride based ionic liquids, which slightly affected by the alkyl chain on the ionic liquid and the variation of anions, i.e. the thermal stability is seen to vary with the cation-anion combination under study.

The result from TGA curves (Fig. 2) for [BMIM] $FeCl_4$ based ionic liquid. From this figure, it can be seen that the sample started to decompose gradually at 270.15°, 380.26°C with a total loss of 19.62 and 58.95 wt %. This showed that the stability of [BMIM] $FeCl_4$ based ionic liquid is attained upto 380°C.

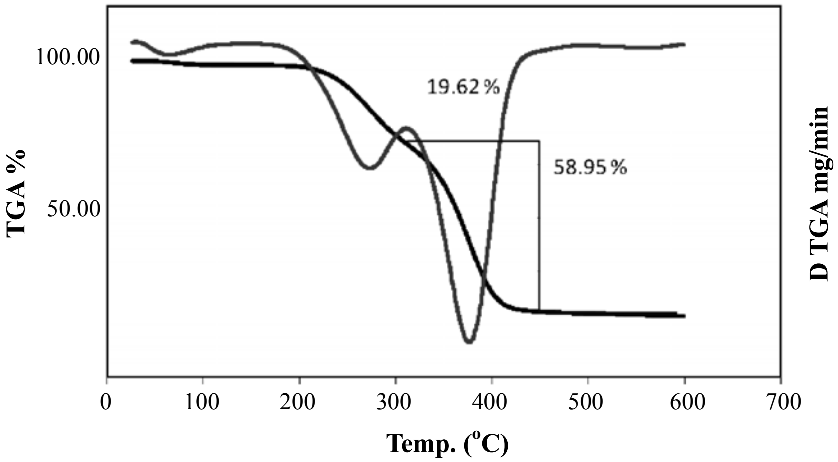

Fig. 2: DTGA & TGA results of [BMIM] $FeCl_4$ based ionic liquid

Kinetics of TNT degradation by imidazolium chloride and imidazolium tetracholoferrate based ionic liquid

Typically, batch tests were undertaken by adding 0.1 g of ILs into 100 mL Erlenmeyer flasks, in which each bottle included 100 mL of TNT stock solution with an initial TNT concentration at 100 mg/L. Then the Erlenmeyer flasks were capped and processed with magnetic stirrer at room temperature. At certain time intervals of this reaction, different samples were taken and separated from the solution, then TNT residual concentration was determined after reacting with ILs. As shown in Fig. 3, the rate of degradation of TNT on MIL was very fast, and the residual concentration of TNT in solution decreased sharply in the first 1 h. As MIL has relatively large magnetic property and strong adsorption capacity[13], TNT from aqueous solution was adsorbed mainly on the surface of MIL and adsorption rate is faster than the degradation rate of TNT by IL, which means that the adsorption phenomenon of TNT is dominating at this stage. It was observed that TNT residual concentration was about 3.5% by reduction with MIL Table 1.

Table 1: Effect of time on TNT concentration using different IL

Time (min)	0	15	30	45	60	75	90	105	120
([BMIM][Cl]) (IL)	100	85.92	83.42	82.57	81.62	81.44	80.6	80.28	80.18
([BMIM][FeCl$_4$]) (MIL)	100	49.56	37.30	28.90	23.20	16.12	8.13	5.24	3.52

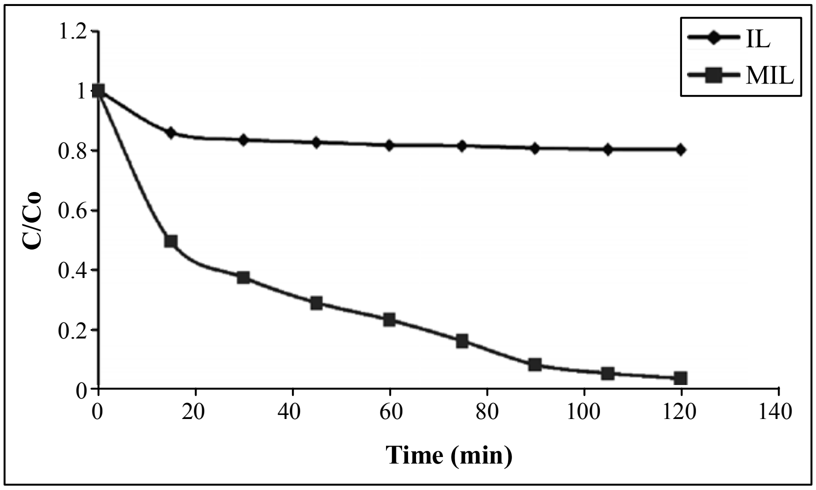

Fig. 3: Concentration variation of TNT with time

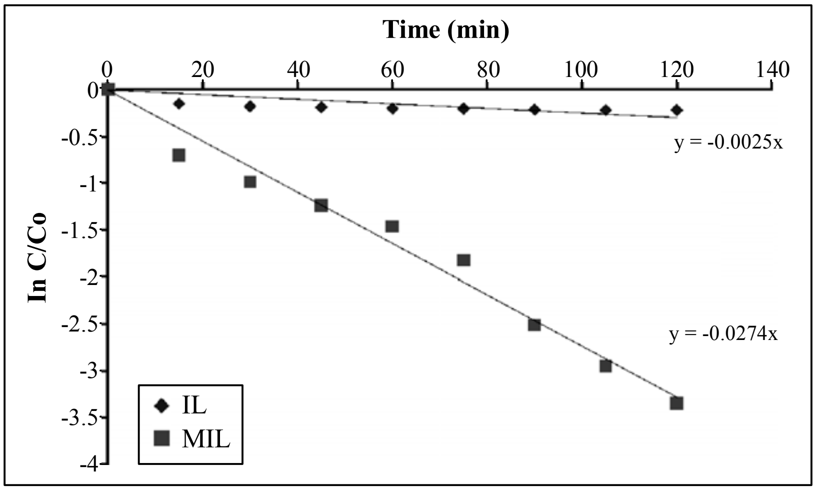

Fig. 4: Relationship between logarithmic plots of TNT concentration versus time

After 2 h of reaction and there after the residual concentration of TNT in solution was below the detection limit. The logarithmic plots of residual concentration of TNT in solutions versus time are shown in Fig. 4, Showing good linear relationship and the correlation coefficient (R^2) is larger than 0.97. As illustrate from Fig. 4, it may be concluded that the rate of TNT reduction by MIL can be described by the pseudo first-order reaction and can be expressed as follows[11]:

$$v = -dc_{TNT}/dt = k_{SA}\ a_s\ \rho_m \qquad \ldots(2)$$

Where C_{TNT} is the TNT concentration (mg L^{-1}) at time t (min), k_{SA} is the specific reaction rate constant based on the IL and ρ_m is the mass concentration of the IL. For a specific reaction, k_{SA}, as, and ρ_m are fixed, so Eq. 2 can be reduced to:

$$k_{obs} = k_{SA}\ a_s\ \rho_m \qquad \ldots(3)$$

Where k_{obs} is the observed pseudo-first rate constant (min^{-1}). From Eqs. (2) and (3), Eq. (4) can be obtained based on the relationship of ln(C/C_o) and time, can be detected:

$$\ln C_t/C_o = -\ kt \qquad \ldots(4)$$

Where C_o and C_t are the TNT content at time zero and time t (min), respectively, and k is the first-order rate constant (min^{-1}).

Half-lives ($t_{1/2}$ (min)) are calculated using Eq. (5), which is derived from Eq. (4) by replacing Ct with $C_o/2$.

$$t_{1/2} = \ln_2/k \qquad \ldots(5)$$

Eq. 5 is the expression of Langmuir–Hinshelwood kinetics model, which is also called the pseudo first-order model. This formula can be obtained based on the linear relationship between ln(C/C_o) and time, it is illustrated that the reduction of TNT by ILs is in accordance with the pseudo first-order kinetics model. The observed reaction rate constant (k) and half-lives ($t_{1/2}$) accordingly calculated for each concentration are listed in Table 2. This phenomenon has been attributed to the favorable role of IL to continue absorption TNT, at higher concentration of IL, the reduction process takes place by absorption process of the TNT on the surface of IL which causes the degradation of TNT. Therefore, the TNT were retained in the ILs, and then the water will become lower-TNT[12], i.e. the strong affinity of the ILs for the TNT is related to the high polarity of the IL.

Table 2: Comparison between IL and MIL as TNT reduction (at 2 h and 303 K)

	Reduction ratio of TNT	**k_{obs} (h^{-1})**	**$t_{1/2}$ (min)**
[BMIM][Cl]	19.82	0.0025	277.2
[BMIM][$FeCl_4$]	96.82	0.0274	25.29

Effects of different initial MIL concentration on the reduction rate of TNT

The effect of MIL concentration on TNT degradation is shown in Fig. 5, Table 3, suggested that the degradation efficiency of TNT by MIL was increased as MIL concentration increased. When the concentration of MIL increased, the acidity increased (from FTIR spectra Fig. 1), hence catalytic activity increase, that is modification Imidazolium chloride with $FeCl_3$, favored degradation of TNT. For example, when the concentration of MIL was at 1.2, 0.6, 0.4 and 0.1, the percentage of TNT degradation was 96.89, 93.15, 89.12 and 87.00 % respectively, over 120 min. As illustrate in Table 3, shows that the concentration of residual TNT in solution was < 4 mgL^{-1} when the concentrations of MIL 1.2 gL^{-1}, hence, an MIL concentration of 1.2 g L^{-1} was used for the remainder of this study.[14,15]

Table 3: Residual TNT concentration with effect of MIL concentration

Time, min **IL conc.**	**0**	**15**	**30**	**45**	**60**	**75**	**90**	**105**	**120**
1.2	100	49.56	37.30	28.90	23.20	16.12	8.13	5.24	3.52
0.6	100	52.31	42.00	32.65	27.40	22.31	12.31	8.80	6.85
0.4	100	54.20	45.10	36.25	32.59	26.55	16.70	12.32	10.88
0.1	100	57.00	46.50	39.25	34.60	29.18	20.70	16.14	13.25

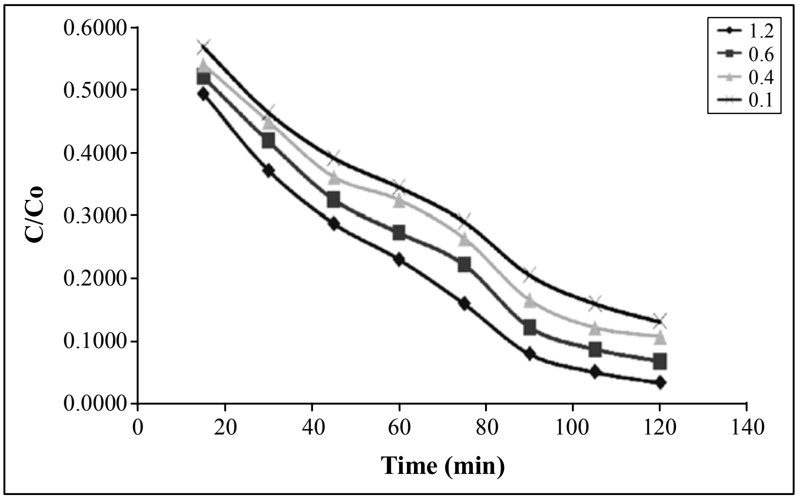

Fig. 5: Residual TNT concentration with effect of MIL concentration

As illustrated in Fig. 6, it shows the TNT reduction at different MIL concentrations, which demonstrates that all followed the pseudo first-order kinetics model when the reductions of TNT were at different MIL initial concentrations. When MIL added was at 0.1 g/L, 0.4 g/L, 0.6 g/L and 1.2 g/L respectively, the observed pseudo-first rate constant of TNT is at 0.0175 min^{-1}, 0.0194 min^{-1}, .0.0227 min^{-1} and 0.0274 min^{-1}, respectively, where it can be concluded that the pseudo first-order kinetics constants increased with increasing of MIL concentration.

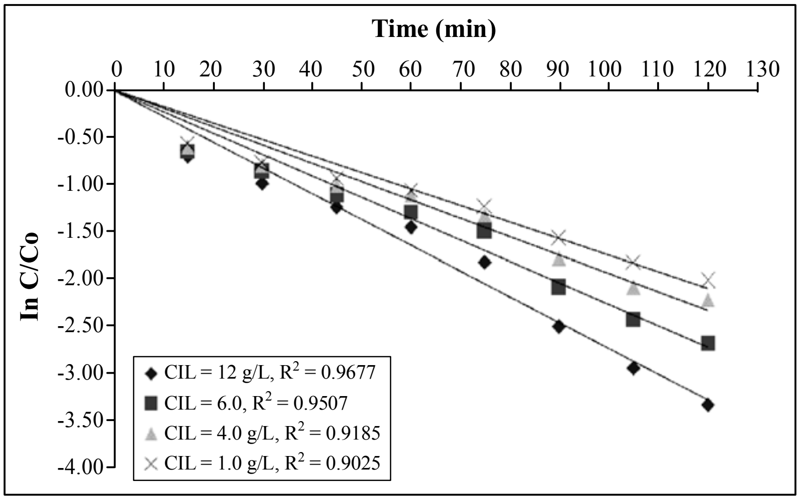

Fig. 6: Effects of concentration of IL of mixed solution on the rate of TNT reduction

This phenomenon can be explained by the increased adsorption and reaction with MIL, where the TNT reduction was thus accelerated when the concentration was increased. When the data were plotted as the observed rate constant (K_{obs}) against the initial concentration of MIL (CIL), a strong linear regression equation can be obtained as shown in Fig. 7, and the correlation coefficient (R^2) of this line is > 0.98, which indicates the observed rate constant (K_{obs}) is proportional to the concentration of MIL and K_{obs} can be improved by increasing the acidity of IL[16,17].

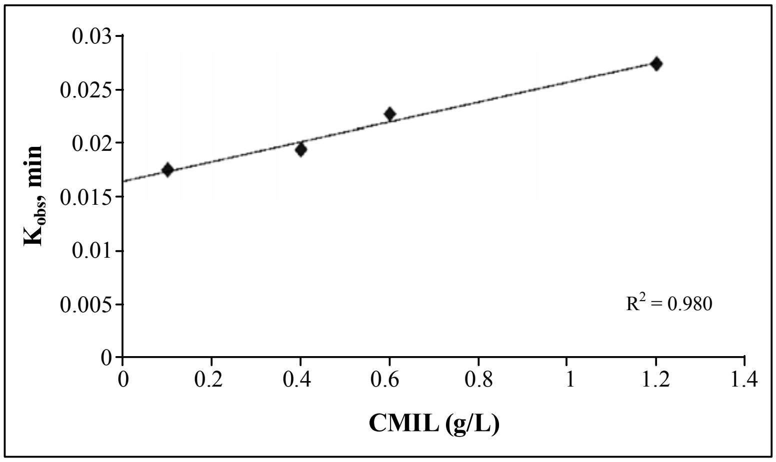

Fig. 7: Relationship of observed rate constant and concentration of IL

Stock solution of TNT was prepared by weighing out 100 mg of TNT and transferring each to a 1000 mL measuring flask.

Effects of pH value on reaction rate of TNT reduced by IL

Batch experiments of 100 mg/L TNT reduced using 1.2 g/L IL were undertaken in different pH values, the initial solution pH was adjusted to 2.0, 5.0, 7.0, 9.0 and 11.0 using 0.1 M HCl or NaOH, and 1.2 g/L of IL was added to each solution. Fig. 8 shows the relationship between correlation coefficients and rate constants at different Ph values. It can be concluded that the correlation coefficient of each regression line is larger than 0.90, which indicates the reduction of TNT on IL also follows the pseudo-first kinetics model when the pH value of mixed solutions was changed. In addition, the reduction rate increased when the pH was increased. The degradation of TNT by IL was conducted at an initial pH value of 2,5,7,9 and 11 and is presented in Fig. 8, where the k_{obs} were 0.0028, 0.0064, 0.0077, 0.135 and 0.0233 respectively. It can be seen that the TNT removal rate increased as pH increased, and maximum removal efficiency was observed at initial pH 11. Finaly, the rate of TNT degradation varied with pH and was faster under alkaline condition[18].

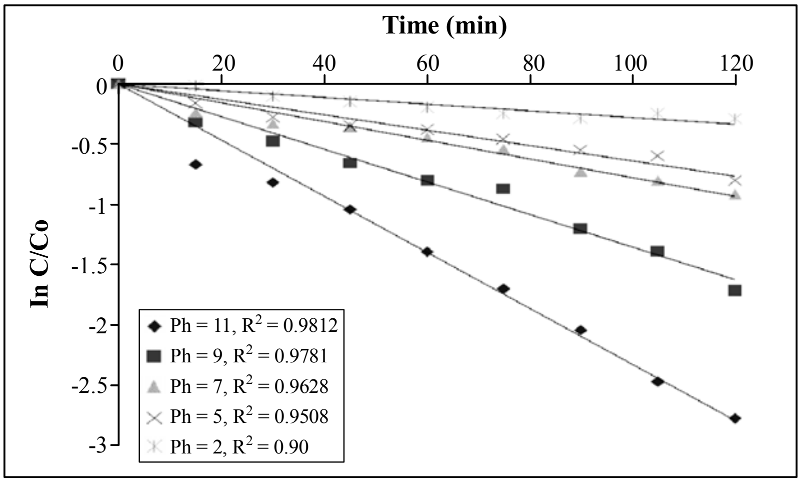

Fig. 8: Effects of pH value of mixed solution on the rate of TNT reduction

CONCLUSION

From the above investigation, it may be concluded that TNT in solution can be reduced by IL and MIL, where the TNT reduction can be influenced by a number of factors, including the initial concentration of TNT of mixed solution, the reaction time and the pH of mixed solution. In addition, the reaction rate of TNT reduction on IL and MIL were in accordance with the pseudo first-order reaction and the observed rate constant (K_{obs}) is proportional to the concentration of ILs added. Compared with 1-butyl-3-methylimidazolium chloride based IL, reaction rate of TNT reduction on 1-butyl-3-methylimidazolium tetrachloroferrate based IL is 11 times faster than reduction on 1-butyl-3-methylimidazolium chloride.

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