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Reduction of *p*-nitrotoluene by aqueous ammonium sulfide: Anion exchange resin as a triphasic catalyst

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Abstract

The reduction of *p*-nitrotoluene (PNT) by aqueous ammonium sulfide was carried out using a triphasic (liquid–liquid–solid) catalyst, anion exchange resin (AER). The maximum enhancement factor of about 57 was observed with 20% (w/v) loading of AER. The reaction was observed to be kinetically controlled with apparent activation energy of 49.8 kJ/mol. The rate of reduction of PNT was established to be proportional to the square of the concentration of sulfide and to the cube of the concentration of PNT. Based on the detailed kinetic study, an empirical kinetic model was developed to correlate the experimentally obtained conversion versus time data. The developed model predicted the PNT conversions reasonably well.

1. Introduction

The reactions between organic soluble substrates and inorganic reagents cannot proceed to an appreciable extent regardless of the amount of energy, external agitation, or time of exposure unless some catalyst is used to bring the reactants in contact with each other. Phase transfer catalyst (PTC) has now-a-days become very popular in bringing the inorganic reagents either dissolved in water (liquid–liquid PTC) or present in solid state (solid–liquid PTC) to the organic soluble substrates [1]. Several varieties of such kinds of heterogeneous reactions, such as nucleophilic substitutions [2–7], and some oxidation [7,8], and reduction reactions [9–11], have been intensified using PTCs.

Catalyst recovery is usually difficult in the case of soluble phase transfer catalysts and is seldom reused [12,13]. This affects the cost and purity of product and poses disposal problems as quaternary ammonium compounds are harmful in liquid effluents and are toxic to certain aquatic species. This leads to the development of the PTC immobilized on a solid support such as insoluble polymer or inorganic solids [14,15]. Despite the advantages of ease of separation of the catalyst and isolation

of the product, the insoluble PTCs are not widely used because of their reduced catalytic activity compared with their soluble analogs and high cost of immobilization. This is attributed to the difficulty of commercial synthesis of catalysts with specific concentrations of PTC in them.

The present work deals with a detailed study of the commercially important reaction of *p*-nitrotoluene (PNT) with aqueous ammonium sulfide in the presence of un-impregnated inorganic solid, anion exchange resin (Seralite SRA-400 (Cl⁻ form)), to explore its catalytic activity in enhancing the rates of reduction of PNT. The reaction rates in the case of un-impregnated inorganic solid are expected to be slower than those obtained with impregnated supports. However, the former strategy is inherently simpler and reagent losses can be minimized.

The catalytic activity of commercial anion exchange resigns (AER) was tested by several workers for varieties of reactions, such as oxidation of alcohols [12,16], aldol condensation [17,18], hydration of ethylene oxide [19], nucleophilic substitutions [12,13], alkylations [12,20], oxidation of organic pollutants [21], transesterification reactions for biodiesel production [22]. However, intensification of the commercially important reduction of nitroarenes by aqueous ammonium sulfide using AER was never reported earlier. The commercial importance of this reaction was discussed elsewhere [23].

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2. Experimental

2.1. Chemicals

Toluene (≥99%) and liquor ammonia (∼26%) of analytical grade were procured from Merck (India) Ltd., Mumbai, India. *p*-nitrotoluene (>99%) of synthesis grade were purchased from Loba Chemie Pvt. Ltd., Mumbai, India. Anion exchange resin-Seralite SRA-400 (Cl⁻ form) having functional group of quaternary ammonium ion (Equivalent to Amberlite IRA-400) (particle size: 20–50 mesh; ion exchange capacity = 3–3.5 meq/g dry resin) was obtained from SISCO Research Laboratories Pvt. Ltd., Mumbai, India.

2.2. Equipment

The reactions of PNT with aqueous ammonium sulfide were carried out batch-wise in a fully baffled mechanically agitated glass reactor of capacity $250\,cm^3$ (6.5 cm i.d.). A 2.0 cm-diameter six-bladed glass disk turbine impeller with the provision of speed regulation, located at a height of 1.5 cm from the bottom, was used for stirring the reaction mixture. The reactor assembly was kept in a constant temperature water bath whose temperature could be controlled within ±1 K.

2.3. Preparation of aqueous ammonium sulfide

For the preparation of aqueous ammonium sulfide, around 15 wt% aqueous ammonia was prepared first by adding suitable quantity of LIQR ammonia in distilled water. Then H_2S gas was bubbled through this aqueous ammonia in a $250\,cm^3$ standard gas-bubbler. The gas bubbling was continued until the desired sulfide concentration was obtained in the aqueous ammonia.

2.4. Experimental procedure

In a typical run, a known amount of AER was taken into the reactor and then $50\,cm^3$ of the aqueous phase containing a known concentration of sulfide was charged into the reactor and kept well agitated until the steady-state temperature was reached. Then the organic phase containing measured amount of PNT and solvent (toluene), kept separately at the reaction temperature, was charged into the reactor. The reaction mixture was then agitated at a constant speed. About $1.0\,cm^3$ of the organic layer was withdrawn at a regular interval after stopping the agitation and allowing the phases to separate.

2.5. Analysis

All samples from the organic phase were analyzed by gas–liquid chromatography (GLC) using a $2\,m \times 3\,mm$ stainless steel column packed with 10% OV-17 on Chromosorb W (80/100). A Chemito Model 8610 GC interfaced with Shimadzu C-R6A Chromatopac data processor was used for the analysis. Initial sulfide concentrations were determined by the standard iodometric titration method [24].
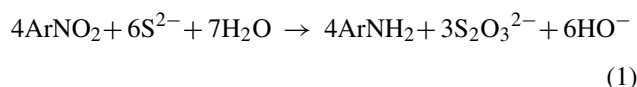
3. Results and discussion

3.1. Zinin reduction: stoichiometry and mechanism

The reduction reaction of nitroarenes by negative divalent sulfur (sulfide, hydrosulfide and polysulfides) (aqueous ammonium sulfide was used in this work) is called Zinin reduction [25]. Sodium sulfide (Na_2S), sodium disulfide (Na_2S_2), sodium hydrosulfide (NaSH), or alcoholic or aqueous ammonium sulfide (used in the present work) are commonly used to carry out this reaction. The sulfide reduction has considerable practical value as it enables chemoselective reduction of nitro group in the presence of C=C, azo, other nitro groups, or any other functional group that is harmed by acid media (e.g., some ethers and thioethers). The use of aqueous ammonium sulfide as a reducing agent especially have considerable commercial significance as this process has enormous potential to remove and utilize the hydrogen sulfide and ammonia simultaneously from the industrial gas stream and thereby solving the sulfur disposal problem [23].

The stoichiometry of the zinin reduction using Na_2S (reaction of Eq. (1)) [9–11,26] and Na_2S_2 (reaction of Eq. (2)) [26,27] is now well established. However, there is hardly any information on the stoichiometry of the same reaction using aqueous ammonium sulfide.
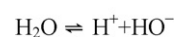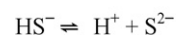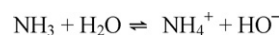
(a) Reduction by sulfide ions:

$$4ArNO_2 + 6S^{2-} + 7H_2O \rightarrow 4ArNH_2 + 3S_2O_3^{2-} + 6HO^- \tag{1}$$

(b) Reduction by disulfide ions:

$$ArNO_2 + S_2^{2-} + H_2O \rightarrow ArNH_2 + S_2O_3^{2-} \tag{2}$$

(c) Reduction by hydrosulfide ions:

$$ArNO_2 + 3HS^- + H_2O \rightarrow ArNH_2 + 3S + 3HO^- \tag{3}$$

In aqueous ammonium sulfide, the sulfide ions (S^{2-}) and the hydrosulfide ions (HS^-) remain in equilibrium [28,29] as shown by Scheme 1. For the reduction of nitro compounds by aqueous ammonium sulfide, it has been established in our earlier publication [23] that the sulfide ions present in the aqueous phase reduces the nitroarenes according to the reaction of Eq. (1), whereas the course of reduction follows the reaction of Eq. (3) in case of hydrosulfide ions. Since the concentration of the sulfide ions relative to hydrosulfide ions in the aqueous phase remains very small, the course of the reduction proceeded through the reaction of Eq. (3) predominately. The reaction of

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + HO^-$$

$$H_2S \rightleftharpoons H^+ + HS^-$$

$$HS^- \rightleftharpoons H^+ + S^{2-}$$

$$H_2O \rightleftharpoons H^+ + HO^-$$

Scheme 1.

Eq. (3) was also observed to be enhanced by the factors that increase the concentration of hydrosulfide ions relative to sulfide ions like ammonia and sulfide concentration in the aqueous phase.

The elemental sulfur formed according to the reaction of Eq. (3) reacts with ammonium sulfide to form ammonium polysulfides $(NH_4)_2S_n$ where $2 \leq n \leq 6$ [30]. Among the various polysulfides, only the disulfide ions are reported to be transferred to the organic phase and reduce the nitrotoluenes following the reaction of Eq. (2) [23].

Although many published works on Zinin reduction exist, the exact mechanism of this important reaction is still not clear. The first product probably is a nitroso compound, which is rapidly reduced to hydroxylamine and then to amine [25]. The rate-determining step is considered to be the attack of negative divalent sulfur on the nitro group, because no intermediate compounds are observed to be formed during the reaction.

3.2. Effect of stirring speed

For any kinetic study, it is important that the mass transfer resistances be negligible during the reaction. To determine the role of mass transfer resistances, the effect of stirring speed on the rate of reaction of PNT was studied in the range 1000–3000 rev/min under otherwise identical experimental conditions in presence of AER catalyst as shown in Fig. 1. The reaction rate was found to be increased with stirring speed up to about 2000 rev/min; above this stirring speed, the variation of reaction rate with the stirring speed was found to be negligibly small as shown in the figure. The reaction may therefore be considered as free from mass transfer resistance above the stirring speed of 2000 rev/min. All other experiments were performed at a safe stirring speed of 2500 rev/min to ensure the absence of mass transfer resistance in the reaction system.
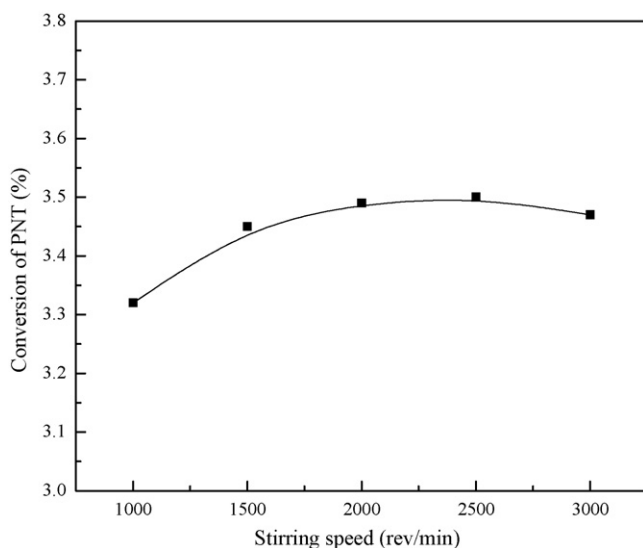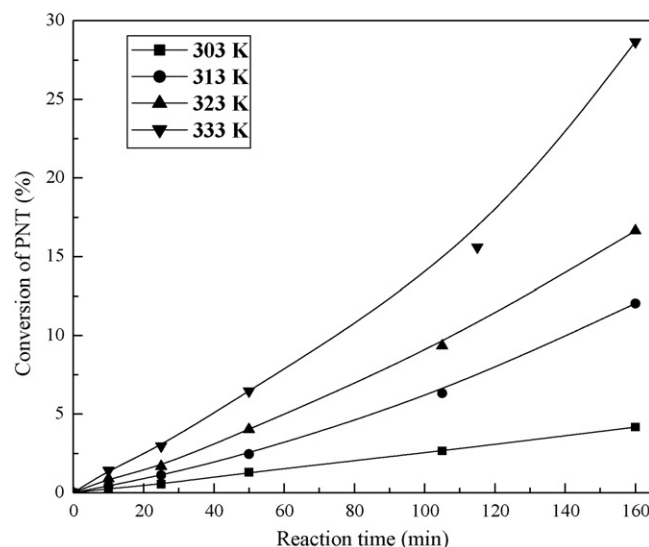

Fig. 2. Effect of temperature on conversion of PNT. Volume of organic phase $= 5 \times 10^{-5}$ m^3; PNT concentration $= 1.75$ kmol/m^3; AER $= 20\%$ (w/v); volume of aqueous phase $= 5 \times 10^{-5}$ m^3; sulfide concentration $= 2.08$ kmol/m^3; NH$_3$ concentration $= 7.76$ kmol/m^3; stirring speed $= 2500$ rev/min.

3.3. Effect of temperature

The effect of temperature on the conversion of PNT was studied in the range of 303–333 K under otherwise identical experimental conditions in the presence of AER catalyst as shown in Fig. 2. The conversion of PNT increased with temperature as expected. The initial rates were calculated at different temperatures and Arrhenius plot of ln (initial rate) against $1/T$ was made (Fig. 3). The apparent activation energy was calculated from the slope of the best-fitted straight line as 49.8 kJ/mol. The high value of apparent activation energy again confirms that the reaction system is kinetically controlled.
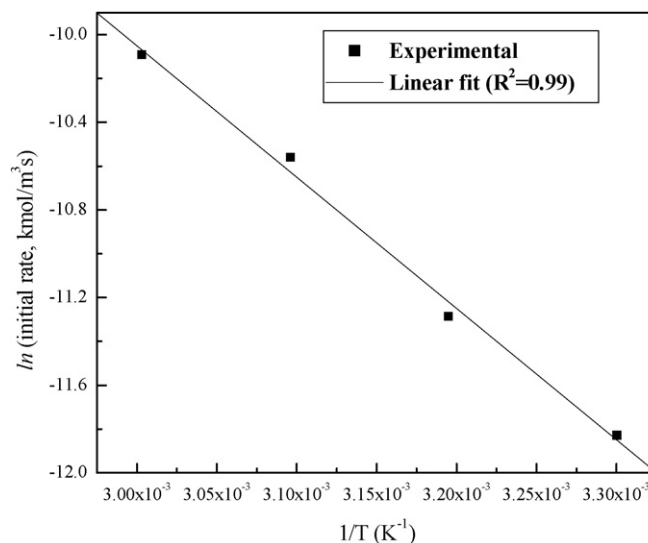

Fig. 1. Effect of stirring speed. Volume of organic phase $= 5 \times 10^{-5}$ m^3; PNT concentration $= 1.75$ kmol/m^3; AER $= 20\%$ (w/v); volume of aqueous phase $= 5 \times 10^{-5}$ m^3; sulfide concentration $= 2.34$ kmol/m^3; concentration of NH$_3$ $= 7.75$ kmol/m^3; temperature $= 323$ K; matching PNT conversion $= 5\%$.

Fig. 3. Arrhenius plot of ln (initial rate) versus $1/T$. All conditions are same as in Fig. 2.

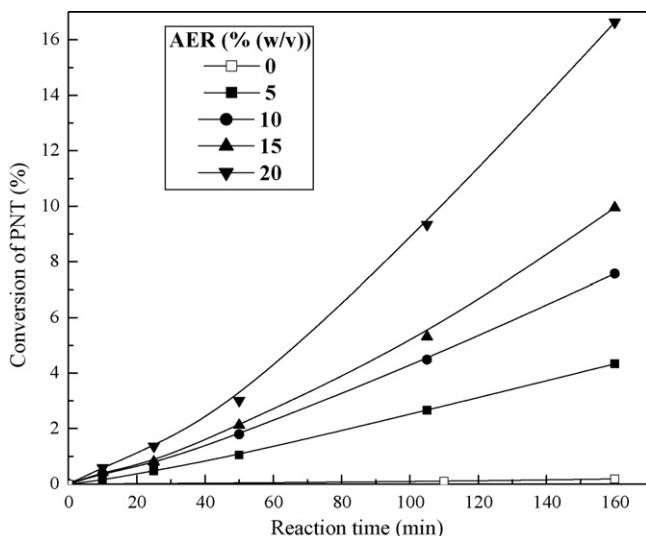Fig. 4. Effect of AER loading on conversion of PNT. Volume of organic phase = 5×10^{-5} m^3; PNT concentration = 1.75 kmol/m^3; volume of aqueous phase = 5×10^{-5} m^3; sulfide concentration = 2.08 kmol/m^3; NH$_3$ concentration = 7.76 kmol/m^3; temperature = 323 K; stirring speed = 2500 rev/min.
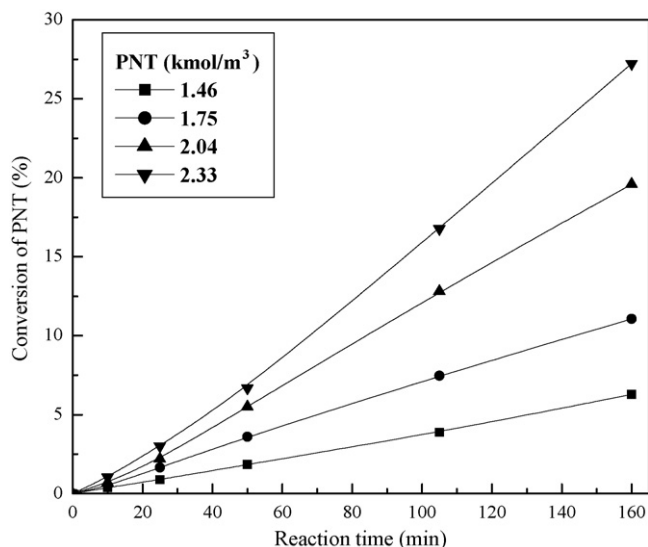

Fig. 5. Effect of PNT concentration on conversion of PNT. Volume of organic phase = 5×10^{-5} m^3; AER = 20% (w/v); volume of aqueous phase = 5×10^{-5} m^3; sulfide concentration = 2.34 kmol/m^3; NH$_3$ concentration = 7.75 kmol/m^3; temperature = 323 K; stirring speed = 2500 rev/min.

3.4. Effect of AER loading

The effect of AER loading on conversion of PNT is shown in the Fig. 4. The study was also conducted in the absence of catalyst as shown in the same figure. With increase in AER loading the conversion of PNT increases as observed from the figure. It is also observed from the figure that the conversion of PNT is only about 0.2% in absence of catalyst whereas it is around 16.6% with 20% (w/v) AER loading after 160 min of reaction under otherwise identical experimental conditions.

The enhancement factor, which is the ratio of the rates of reaction in the presence of catalyst to that in the absence of catalyst, was calculated for different AER loadings. Table 1 shows the variation of enhancement factor with AER loading. The maximum enhancement factor of about 57 was observed with 20% (w/v) AER loading. However, for the same reaction, the enhancement factor of 250 was observed using only 1.5% (w/v) of a phase transfer catalyst (PTC), tetrabutylammonium bromide (TBAB) [23]. Therefore, the PTC is superior over AER catalyst for this reaction in terms of enhancement factor only. However, repeated re-usability of the AER catalyst may surpass this advantage of PTC.

3.5. Effect of concentration of p-nitrotoluene

The effect of concentration of PNT on the conversion was studied at four different concentrations in the range of 1.46–2.33 kmol/m^3 in the presence of AER under otherwise identical experimental conditions as shown in Fig. 5. The conversion of PNT increases with increase in concentration of the PNT.

In order to determine the order of the reaction with respect to PNT concentration, the initial reaction rate was calculated at different PNT concentrations and the plot of *ln* (initial rate) against *ln* (PNT concentration) was made (Fig. 6). From the slope of the linearly fitted line, the order of the reaction with respect to PNT concentration was obtained as 3.09. Since this value is close to three, the reaction can be considered as third order
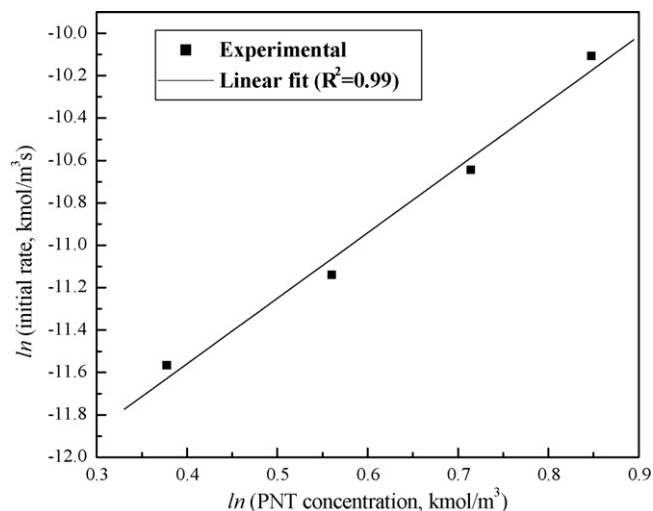
Table 1
Effect of AER loading on enhancement factor[a]

AER loading (gm)	Rate of reaction × 10^5 (kmol/m^3 s)	Enhancement factor
0.0	0.05	–
5.0	0.89	17.8
10.0	1.33	26.6
15.0	1.91	38.2
20.0	2.86	57.2

[a] Matching PNT conversion = 4%; all other conditions are same as in Fig. 4.

Fig. 6. Plot of *ln* (initial rate) versus *ln* (PNT concentration). All conditions are same as in Fig. 5.
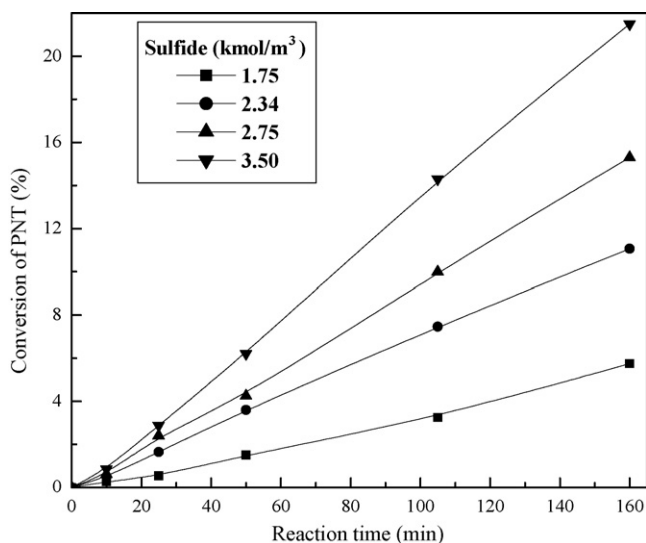
Fig. 7. Effect of sulfide concentration on conversion of PNT. Volume of organic phase = 5×10^{-5} m^3; PNT concentration = 1.75 kmol/m^3; AER = 20% (w/v); volume of aqueous phase = 5×10^{-5} m^3; NH$_3$ concentration = 7.75 kmol/m^3; temperature = 323 K; stirring speed = 2500 rev/min.

Fig. 8. Plot of *ln* (initial rate) versus *ln* (sulfide concentration). All conditions are same as in Fig. 7.

with respect to PNT concentration. However, for the reduction of nitroaromatics by sodium sulfide under two-phase conditions [26], and reduction of *p*-nitroanisole by sodium sulfide in presence of PTC (TBAB) [11], the rate of reaction was reported to be proportional to the concentration of nitroarenes. The rate was also reported as proportional to the concentration of nitrobenzene for its reduction with sodium disulfide under two-phase conditions [27].

3.6. Effect of sulfide concentration

The effect of sulfide concentration in the aqueous phase on the conversion of PNT was studied in the range of 1.75–3.5 kmol/m^3 under otherwise identical experimental conditions in the presence of AER catalyst as shown in Fig. 7. With increase in the concentration of sulfide, the conversion of PNT increases, as it is evident from the figure. From the plot of *ln* (initial rate) against *ln* (initial sulfide concentration) (Fig. 8), the order of the reaction with respect to the sulfide concentration was obtained as 1.64. Since this value is closer to integer 2, the reaction was, therefore, considered as 2nd order with respect to sulfide concentration. However, for the reduction of nitroarenes with aqueous sodium sulfide, the reaction rate was reported to be first order with the sulfide concentration [11,26]. The rate was also reported to be proportional to the square of the concentration of sodium disulfide [27].

3.7. Reusability of catalyst

In this experiment, the once used AER catalyst was first separated from the reaction mixture by filtration, and then repeatedly washed with distilled water and dried and used again to carry out the same reaction. The catalytic activity of the once used AER catalyst was compared with that of the fresh one under
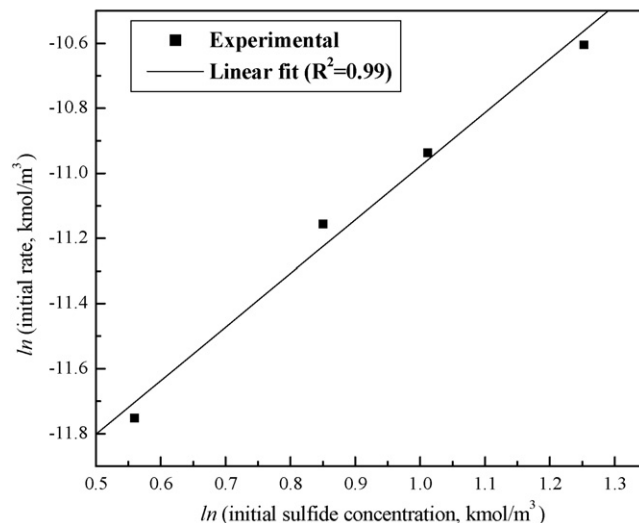
otherwise identical experimental conditions as shown in Fig. 9. The conversion of PNT (so also reaction rate) in presence of once used AER catalyst was found to be more compared to that of fresh catalyst as observed from the figure.

It was established in our earlier publication [23] that the elemental sulfur is formed in this reaction and it reacts with ammonia and hydrogen sulfide resulting in the formation of ammonium disulfide, which reduces the nitro compounds at a faster rate. The enhancement of the rate of reaction in case of once used catalyst compared to that of fresh catalyst may be due to the presence of elemental sulfur on the surface of the once used catalyst.
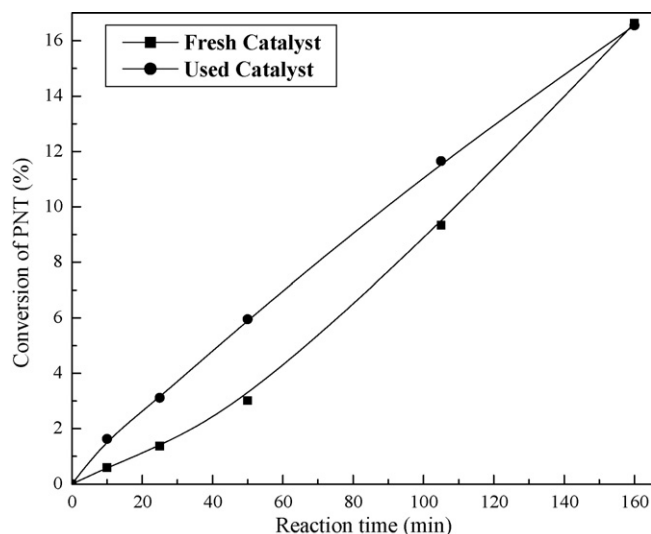

Fig. 9. Reusability of the catalyst. Volume of organic phase = 5×10^{-5} m^3; PNT concentration = 1.75 kmol/m^3; AER = 20% (w/v); volume of aqueous phase = 5×10^{-5} m^3; sulfide concentration = 2.08 kmol/m^3; NH$_3$ concentration = 7.76 kmol/m^3; temperature = 323 K; stirring speed = 2500 rev/min.

3.8. Kinetic modeling

The reaction was shown to follow a complex reaction mechanism involving three different reactions (Eqs. (1–3)) with Eq. (3) being predominating one. The elemental sulfur formed in this reaction (Eq. (3)) enhanced the reaction rate resulting in 'S' nature of conversion versus time curve [23]. In the present study, curves of similar nature are also observed (see Figs. 2, 4, 5 and 7). For such a complex reaction, an empirical kinetic model was therefore developed to correlate the experimentally obtained conversion versus time data.

As discussed earlier, the rate of reduction of PNT is proportional to the square of the concentration of sulfide and to the cube of the concentration of PNT. Therefore, the rate of reduction of PNT $(-r_A)$ for a fixed AER loading can be expressed by the following equation:

$$-r_A = k_1 C_A^3 C_S^2 + k_2 C_A^3 C_S^2 C_B \qquad (4)$$

where C_A is the concentrations of PNT in the organic phase. The second term in the above rate expression takes care of 'S' nature of curves due to the formation of elemental sulfur during the reaction as discussed previously. Since the concentration of NH_3 in the aqueous phase was kept around 15 wt%, its effect was not incorporated in this kinetic model.

Since, the course of the reduction follows the stoichiometry of Eq. (3) predominantly, the concentration of sulfide (C_S) and elemental sulfur (C_B) in the aqueous phase are obtained from the overall mass balance based on the same stoichiometry as given by the following expressions:

$$C_S = C_{SO} - 3f(C_{AO} - C_A) \qquad (5)$$

$$C_B = 3f(C_{AO} - C_A) \qquad (6)$$

where C_{SO} and C_{AO} represent the initial concentrations of sulfide and PNT, respectively. The factor "f" is the ratio of the volume of organic phase to that of the aqueous phase and is assumed to be independent of conversion.

A non-linear regression algorithm was used for parameter estimation. The optimum values of the rate constants, k_1 and k_2, for the PNT were estimated by minimizing the objective function (E) as given by the following equation:

$$E = \sum_{i=1}^{n} [\{(-r_A)_{pred}\}_i - \{(-r_A)_{expt}\}_i]^2 \qquad (7)$$

The optimum values of the rate constants, k_1 and k_2, at different temperatures are estimated as listed in Table 2. Both the rate constants increase with increase in temperature as expected. An Arrhenius plot of $ln(k)$ against $1/T$ was made as shown in
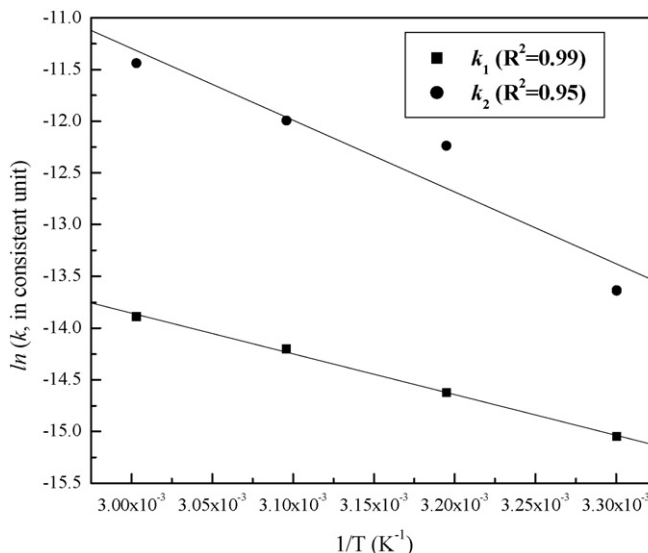

Fig. 10. Arrhenius plot of $ln (k)$ versus $1/T$.

Table 3
Activation energies and pre-exponential factors of the rate constants

$k_1 = A_{10}\mathrm{Exp}\left(-\frac{AE_1}{RT}\right)$		$k_2 = A_{20}\mathrm{Exp}\left(-\frac{AE_2}{RT}\right)$	
A_{10} [(kmol/m^3)$^{-4}$s^{-1}]	AE_1 (kJ/mol)	A_{20} [(kmol/m^3)$^{-5}$s^{-1}]	AE_2 (kJ/mol)
0.13	32.7	1.41×10^4	57.7

Fig. 10. The activation energy and pre-exponential factor of the rate constants were evaluated from the slope and intercept of the Arrhenius plot respectively, as shown in Table 3. Based on the estimated rate constants, the conversions of PNT were calculated at different temperatures and compared with the experimentally obtained conversions. As can be seen from Fig. 11, a good agreement was observed between the predicted and experimental conversions.
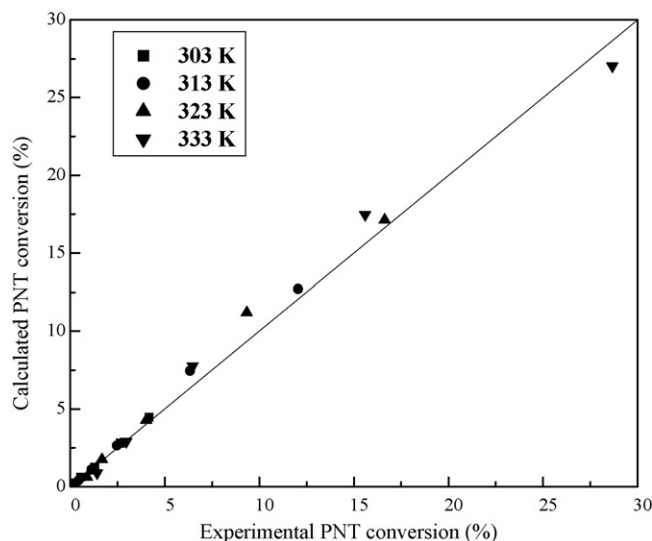

Fig. 11. Comparison of calculated and experimental PNT conversions. All conditions are the same as in Fig. 2.

Table 2
Rate constants of the model Eq. (4)

Rate constants	Temperatures (K)			
	303	313	323	333
$k_1 \times 10^7$ (kmol/m^3)$^{-4}$ s^{-1}	2.92	4.46	6.81	9.30
$k_2 \times 10^5$ (kmol/m^3)$^{-5}$ s^{-1}	0.12	0.48	0.62	1.07

4. Conclusions

Anion exchange resin (Seralite SRA-400 (Cl-form)) was successfully used as a triphasic (liquid–liquid–solid) catalyst to carry out the reduction of PNT by aqueous ammonium sulfide. The maximum enhancement factor of about 57 was observed with 20% (w/v) of AER. The reaction was observed to be kinetically controlled with apparent activation energy of 49.8 kJ/mol. The rate of reduction of PNT was established to be proportional to the square of the concentration of sulfide and to the cube of the concentration of PNT. The rate enhancement was also observed with the once used catalyst due to the presence of elemental sulfur on the surface of the catalyst. Based on the detailed kinetic study, an empirical kinetic model was developed to correlate the experimentally obtained conversion versus time data. The developed model predicted the PNT conversions reasonably well.

Acknowledgment

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