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Journal of Hazardous Materials B98 (2003) 117–126

Journal of Hazardous Materials

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Adsorption of ammonium dinitramide (ADN) from aqueous solutions 1. Adsorption on powdered activated charcoal

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Received 28 June 2002; received in revised form 7 October 2002; accepted 8 October 2002

Abstract

Investigations on the adsorption of ammonium dinitramide ($NH_4N(NO_2)_2$) (ADN) from aqueous solutions on powdered activated charcoal (PAC) were carried out in order to find out an effective and easier method of separating ADN from aqueous solutions. The effectiveness of PAC in the selective adsorption of ADN from aqueous solutions of ADN (ADN-F) and ADN in presence of sulfate (SO_4^{2-}) and nitrate (NO_3^-) ions (ADN-PS) was examined and compared using batch and column methods. The adsorption process follows both Langmuir and Freundlich adsorption isotherms and the isotherm parameters for the models were determined. The observed data favor the formation of monolayer adsorption. The adsorption capacities were found to be 63.3, 119, 105.3 and 82 mg of ADN per g of PAC for ADN-F (batch), ADN-PS (batch), ADN-F (column) and ADN-PS (column), respectively. Break-through curves for ADN-F and ADN-PS were obtained for the optimization of separation of ADN from aqueous solutions. Elution curves were generated for the desorption of ADN from PAC using hot water as eluent.

Keywords: Adsorption; Ammonium dinitramide (ADN); Langmuir and Freundlich isotherms; Powdered activated charcoal

1. Introduction

Ammonium dinitramide ($NH_4N(NO_2)_2$) (ADN) is a powerful, environmental-friendly oxidizer developed in 1990s for use in composite solid rocket propellants [1,2]. It is an

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PII: S0304-3894(02)00289-3

ionic compound containing the ammonium ion and a new oxide of nitrogen, the dinitramide anion ($-N(NO_2)_2$). ADN is envisaged as an attractive alternative to ammonium perchlorate ($NH_4 \cdot ClO_4$) (AP) in composite solid propellants because of its higher energetics and halogen free exhaust products during burning. Much of the work is published on the synthesis of ADN and its analogues [3–7]. Most of the methods make use of exotic nitrating agents such as N_2O_5 or NO_2BF_4 [7]. A recent literature reports the synthesis of ADN using conventional nitrating agents such as HNO_3/H_2SO_4 [8]. This process results in ADN along with ammonium sulfate ($(NH_4)_2SO_4$) and ammonium nitrate (NH_4NO_3) in water. The separation of ADN from aqueous solution involves precipitation, drying, extraction and recrystallization from different solvents and is a time consuming and costly process. The adsorption technique is proven to be an effective method of separation at relatively lower cost in comparison to solvent extraction procedure for many materials. ADN can be adsorbed on a variety of adsorbents like molecular sieves, activated alumina, silica gel, activated charcoal etc. The adsorbed ADN is then eluted with a suitable eluting solvent.

In the first phase of our present work, powdered activated charcoal (PAC) was used as adsorbent for the separation of ADN from aqueous solutions. The adsorption behavior of ADN by PAC was investigated using Langmuir and Freundlich isotherms. The Langmuir and Freundlich isotherm constants were determined and the amount of PAC to be used for the adsorption of ADN was also worked out. Breakthrough curves were generated for predicting the column efficiency in the recovery of ADN. Adsorbed ADN was desorbed using hot water as eluent.

2. Experimental

2.1. Materials

Ammonium dinitramide was synthesized in our laboratory [9]. It is a pale yellow hygroscopic powder soluble in polar solvents including water. The compound was characterized by UV, IR and thermal methods. ADN solution has a strong absorption maximum at 284 nm in UV. IR spectrum shows characteristic peaks at 3136 cm^{-1} (ν N–H of NH_4^+), 1531 cm^{-1} (asymmetric in phase of NO_2 group), 1344 cm^{-1} (symmetric in phase of NO_2 group).

The reaction mixture containing ammonium sulfate (3900 mg l^{-1}) and ammonium nitrate (3000 mg l^{-1}) along with ADN (600 mg l^{-1}) was the process solution (ADN-PS).

Activated charcoal powder (Sarabhai M. Chemicals Limited, Mumbai, India) with a specific surface area (BET method) of 400–450 $m^2\,g^{-1}$ and a particle size (Fischer method) of 17 μm was dried at 110 °C for 10–12 h and stored in a desiccator prior to use.

2.2. Instruments

A CARY 5e UV-Vis-NIR spectrometer was used for the measurement of ADN concentration before and after adsorption.

2.3. Adsorption experiments

Experiments were conducted by batch and continuous methods at room temperature (30 °C). Batch adsorption experiments were carried out by stirring 3 g of PAC with 100 ml of an aqueous solution of ADN-F or ADN-PS of the desired concentration (0.01–0.1 M) in different glass-stoppered erlenmeyer flasks using a magnetic stirrer for predetermined time intervals (30–60 min) till equilibrium was achieved. Column adsorption experiments were carried out on a 20 mm diameter glass column with a sintered disc at the bottom by placing 4 g of PAC and 100 ml solution of ADN-F or ADN-PS of varying concentrations (0.01–0.1 M) at a constant flow rate of 3 ml min^{-1}, and the solution after adsorption was collected for different periods of time (30 min intervals).

The equilibrium concentration, C_e of the solution was determined by UV spectrophotometer by taking weighed quantities of aliquots of the collected solution. The concentration of ADN adsorbed was obtained by calculating the difference of the concentration of ADN in solution before and after adsorption using the experimentally determined molar extinction co-efficient at 284 nm, ε_{284} 5248 l mol^{-1} cm^{-1} [9].

3. Results and discussion

3.1. Effect of adsorption time

The amount of ADN adsorbed per unit weight of adsorbent as a function of time is given in Fig. 1. The quantity of ADN adsorbed increases with the increase of the adsorption

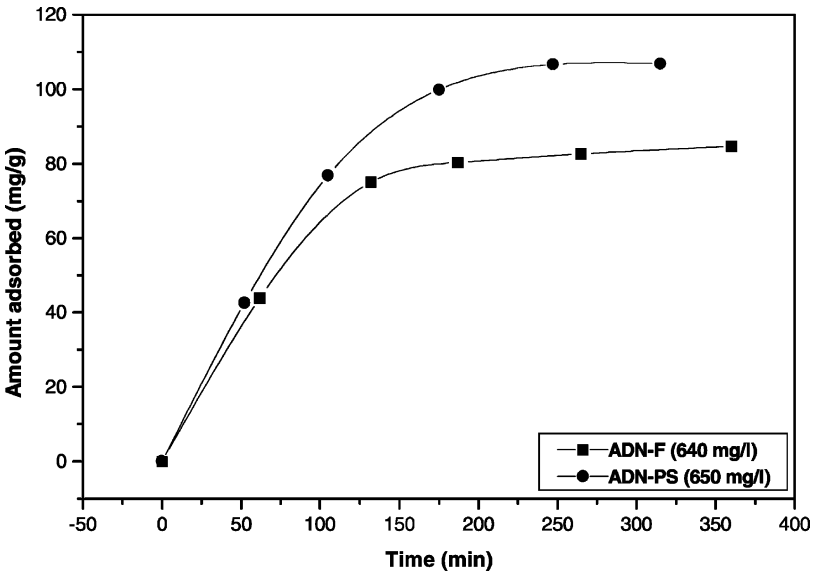

Fig. 1. The amount of ADN adsorbed per unit weight of PAC as a function of time with 4 g of adsorbent at 30 °C.

time for ADN-F and ADN-PS. However, it remains constant after an equilibrium time of 175 min for ADN-F and 200 min for ADN-PS, which indicates that the adsorption tends toward saturation at the above mentioned time.

3.2. Adsorption isotherms

Various isotherm models are available for expressing the adsorption process [10,11]. The adsorption isotherm for the adsorbed ADN on PAC can be analyzed by Langmuir and Freundlich isotherms.

3.2.1. Langmuir isotherm

The linear representation of the Langmuir isotherm [12] can be expressed as

$$\frac{C_e}{Y_e} = \frac{1}{Qb} + \frac{C_e}{Q} \tag{1}$$

Where C_e is the equilibrium concentration of ADN in solution (mg l^{-1}), Y_e the milligrams of adsorbed ADN per gram of adsorbent (mg g^{-1}), Q the maximum amount of adsorbed ADN per gram of adsorbent (mg g^{-1}) and b the Langmuir constant (l mg^{-1}). Thus, a plot of C_e/Y_e versus C_e should yield a straight line with a slope of $1/Q$ and an intercept of $1/Qb$ from which the values of Q and b can be readily obtained. Fig. 2 shows the plot of C_e/Y_e versus C_e, which is a straight line with relatively good correlation coefficient (Table 1), showing that all the data correctly fit the Langmuir relation and indicating that the adsorption of ADN from aqueous solution on PAC follows the monolayer adsorption.

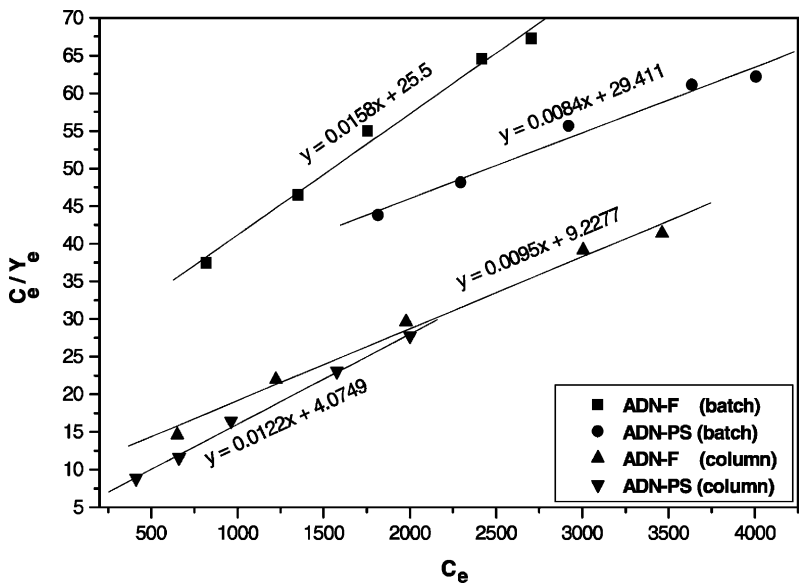

Fig. 2. Langmuir plots for the adsorption of ADN on PAC at 30 °C.

Table 1
Langmuir constants from Eq. (1) at 30 °C

System	Langmuir constants			Correlation coefficient (r)
	Q (mg g^{-1})	b (l mg^{-1})	$K = Qb$ (l g^{-1})	
ADN-F (batch)	63.3	0.00062	0.0392	0.9884
ADN-PS (batch)	119.0	0.00029	0.0345	0.9739
ADN-F (column)	105.3	0.00103	0.1084	0.9894
ADN-PS (column)	82.0	0.0030	0.2455	0.9949

The Langmuir constants obtained from Fig. 2 are given in Table 1. The Langmuir equilibrium constant $K = Qb$ was also measured and given in Table 1. As it is seen in Table 1. the amount of ADN adsorbed per gram of charcoal is higher for ADN-PS compared to ADN-F performed in batch, and the amount of ADN adsorbed is lower for ADN-PS compared to ADN-F performed in column. Langmuir theory is restricted to cases where only one layer of molecules can be adsorbed at the surface [13], and hence the adsorption of ADN from aqueous solutions on PAC follows monolayer adsorption as evident from the observed data fit in Langmuir isotherm.

3.2.2. *Freundlich isotherm*

The Freundlich adsorption equation [14] is expressed as

$$Y_e = PC_e^{1/n} \tag{2}$$

or the linearized form of the equation

$$\log Y_e = \log P + \frac{1}{n}\log C_e \tag{3}$$

where P and $1/n$ are empirical constants (Freundlich parameters), the values of which are equal to the intercept and slope of the plot of $\log Y_e$ versus $\log C_e$. Freundlich plots for the adsorption of ADN on PAC are shown in Fig. 3.

The adsorption of ADN on powdered activated charcoal was found to correspond with the Freundlich adsorption isotherm. The Freundlich constants deduced from the straight lines in Fig. 3 are given in Table 2 along with correlation coefficients.

For all the experiments, the exponent 'n' is greater than 1 which indicates good adsorption of ADN on PAC. The adsorption of ADN from aqueous solutions on PAC fit well

Table 2
Freundlich constants from Eq. (3) for adsorption of ADN on PAC at 30 °C

System	Freundlich constants		Correlation coefficient (r)
	$\log P$	n	
ADN-F (batch)	0.15	1.96	0.9996
ADN-PS (batch)	0.18	1.81	0.9941
ADN-F (column)	0.60	2.67	0.9993
ADN-PS (column)	0.93	3.56	0.9981

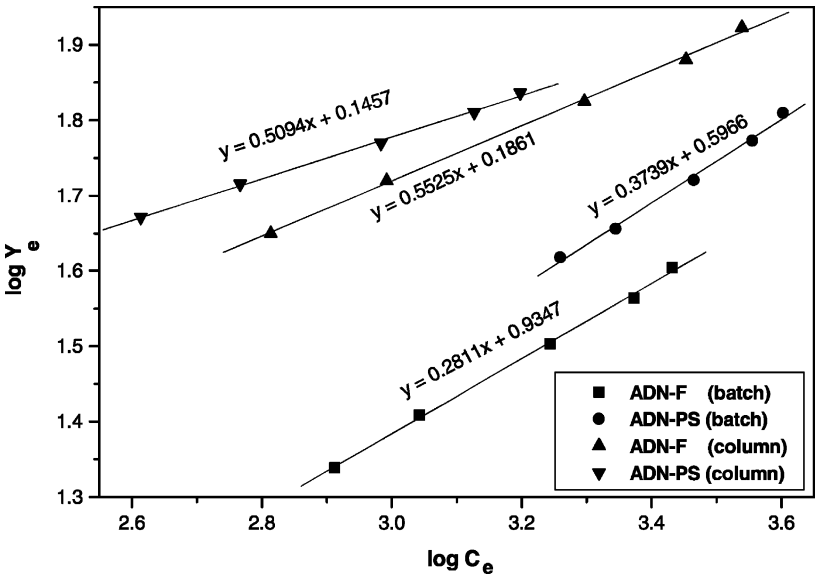

Fig. 3. Freundlich plots for the adsorption of ADN on PAC at 30 °C.

for both Freundlich and Langmuir isotherms with correlation co-efficient >0.98 (Tables 1 and 2).

3.3. Results of column adsorption model

A reported theoretical model was adapted in the present study for measuring the change in ADN concentration at the column exit. In a column, the fraction of ADN that is being adsorbed is denoted as A and the fraction of that is remaining in the aqueous solution and passing through the stationary adsorbent is denoted as P. It is assumed that the rate of decrease in the adsorption fraction (A) is proportional to A and P as shown in Eqs. (4) and (5).

$$-\frac{\mathrm{d}A}{\mathrm{d}t}\alpha AP \tag{4}$$

or

$$-\frac{\mathrm{d}A}{\mathrm{d}t} = kAP \tag{5}$$

the final form of the Eq. (5) becomes

$$P = \frac{1}{1+\exp[k(\tau - t)]} \tag{6}$$

$$t = \tau + \frac{1}{k}\ln\left(\frac{P}{1-P}\right) \tag{7}$$

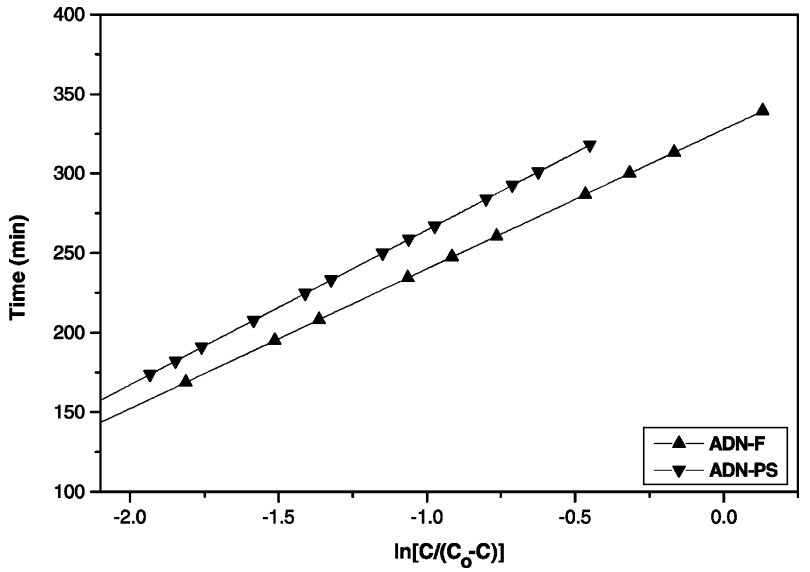

Fig. 4. Linear plots of time, t vs. $\ln[C/(C_0 - C)]$ for ADN-F and ADN-PS.

The detailed derivation of Eq. (7) is reported elsewhere [15]. The derivation of Eq. (7) is based on the definition that 50% breakthrough of the adsorption process occurs at time τ. Due to the sigmoid nature of the breakthrough curve, the adsorbent bed should be completely saturated at 2τ. ADN fraction (P) passing through the adsorbent column is equal to C/C_0, where C is the ADN concentration of the exiting aqueous solution at time t and C_0 the inlet ADN concentration. Fig. 4 shows the plot of adsorption time t versus $\ln[C/(C_0 - C)]$ for ADN-F and ADN-PS on PAC. It is a straight line with τ as intercept and $1/k$ as slope, respectively. k and τ (model parameters) thus determined are used to construct the breakthrough curve using Eq. (7). Reasonable linear fit of the data was obtained and the model parameters of the breakthrough curves derived from Fig. 4 are listed in Table 3.

The breakthrough curves for ADN-F and ADN-PS were constructed using the model parameters τ and k listed in Table 3 and are given in Fig. 5. The calculated breakthrough time for 0.1 mg l^{-1} of ADN exiting from the column is 75 min for ADN-F and 69 min for ADN-PS. The presence of nitrate and sulfate ions have little effect on the adsorption of ADN on PAC, this is evident from the close breakthrough times observed for ADN-F and ADN-PS.

Table 3
Model parameters of the breakthrough curves from Fig. 4

System	k (l min^{-1})	τ (min)
ADN-F	0.1027	97
ADN-PS	0.1140	88

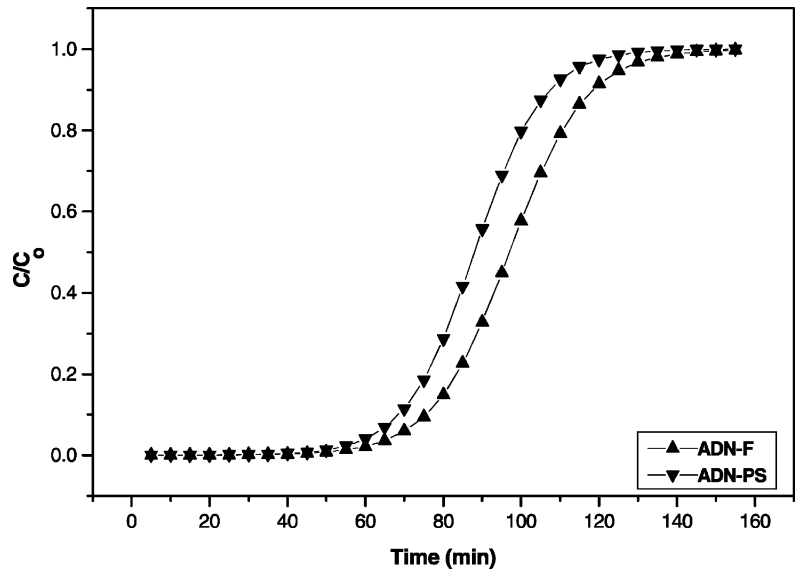

Fig. 5. Predicted breakthrough curves for ADN-F and ADN-PS on PAC with a flow rate of 3 ml min^{-1} and an initial ADN concentration of 6500 mg l^{-1}.

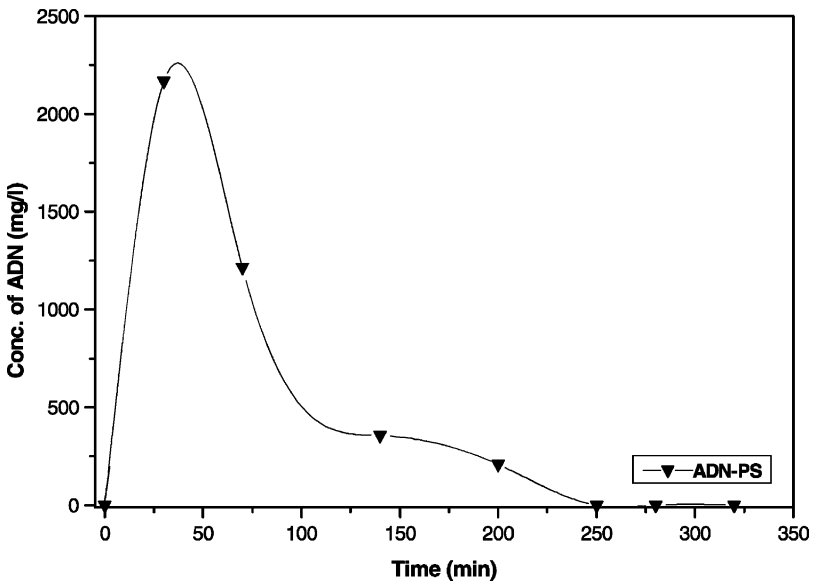

Fig. 6. Desorption of ADN from PAC with hot water as a function of time with 3.5 ml min^{-1} flow rate.

3.4. Desorption of ADN from PAC

Desorption studies were performed on ADN-PS adsorbed on PAC using a column under similar conditions by placing 4 g of PAC and an ADN-PS solution containing 6500 mg l^{-1} of ADN. The solution passing through the column was collected and refed two to three times. The exit solution was analyzed by UV and the amount of ADN adsorbed in the column was calculated. The adsorbed ADN was then eluted with hot water (50°C) at a flow rate of 3 ml min^{-1}. A plot of the amount of ADN in eluted samples at different time intervals was made and is shown in Fig. 6. In a typical run, the amount of ADN adsorbed on PAC for an initial concentration of 6500 mg l^{-1} is 4300 mg, which is about 66%. The amount of ADN recovered using hot water as eluent is 3850 mg, which is about 89%. These results show higher efficiency of the removal and recovery of ADN on PAC using hot water as eluent. Ion chromatographic analysis of the eluent shows 60 ppm nitrate and 0 ppm sulfate ions. Hence, PAC is proved to be efficient in the adsorption of ADN and allows recovery of ADN with hot water.

4. Conclusions

In the present study, the separation of ADN from aqueous solutions was evaluated in batch and continuous methods using powdered activated charcoal. The equilibrium concentrations were established for ADN-F and ADN-PS. Langmuir and Freundlich adsorption isotherms were generated for these systems and the equilibrium concentrations were determined. Adsorptive capacities observed were 63.3, 119, 105.3, 82 mg of ADN per g of PAC for ADN-F (batch), ADN-PS (batch), ADN-F (column) and ADN-PS (column), respectively. The results revealed that monolayer adsorption isotherms were sufficient to describe the equilibrium adsorption of ADN from aqueous solutions. Theoretical column adsorption model was applied for the prediction of ADN concentration in the exit aqueous solution. The determination of the two model parameters τ and k helps in establishing the complete breakthrough curve and is a convenient measure for determining the accurate breakthrough times for separation of ADN from ADN-PS. Elution of ADN was achieved by using hot water as eluent.

Acknowledgements

The authors would like to thank Mr. A.J. Raghavan of Propellant Engineering Division for helpful discussions and comments in preparing this manuscript. One of the authors G. Santhosh wishes to thank the Indian Space Research Organization (ISRO) for award of a research fellowship.

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