

Full Length Research Paper

A study on removal characteristics of para-nitrophenol from aqueous solution by fly ash

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The removal characteristics of para-nitrophenol from aqueous solution by fly ash were investigated under various conditions of contact time, pH and temperature. The influence of pH on the para-nitrophenol uptake by the fly ash was carried out between pH4 and pH 10. The level of uptake of para-nitrophenol by fly ash increased at higher pH values. The effect of temperature on the uptake of para-nitrophenol was investigated between 30 and 60°C; the adsorption increased at lower temperature. Rate constants were evaluated in terms of first-order kinetics. The rate constants k for uptake of different concentrations of para-nitrophenol was $1.10 \times 10^{-2} \text{ s}^{-1}$ and $1.14 \times 10^{-2} \text{ s}^{-1}$, respectively. The experimental results underlined the potential of coal fly ash for recovery of para-nitrophenol from waste water. The main mechanisms involved in the removal of para-nitrophenol from solution by fly ash were electron – withdrawing effect of NO_2 group of benzene ring and adsorption at the surface of the fly ash.

Key words: Fly ash, para-nitrophenol, adsorption, kinetics, mechanism.

INTRODUCTION

Fly ash is a waste product obtained from burning of coal. Given the large amount of fly ash generated in coal-burn power plants and large dumping sites required for the safe disposal, any means of reuse, recycling and recovery of fly ash will be a welcome development. Reports have shown that fly ash has been used as a binding reagent for the fixation of heavy metal and nutrients contained in hazardous wastes and organic wastes (Lin and Hsin, 1996; Vincini et al., 1994; Shende et al., 1994; Parsa et al., 1996). It has been reported that many researchers have reused fly ashes as adsorbents for waste water or air pollutants control (Rivatti et al., 1988; Sell et al., 1994). Alinnor (2007) reported the use of fly ash for the removal of heavy metal ions from aqueous solution.

The removal of toxic solvent from polluted environment has received much attention in recent years, especially in Nigeria. Removal of toxic solvent from polluted

environment can be done by several techniques but the adsorption technique is widely used due to its high rate, high uptake capacity, effective treatment in dilute solution, low cost and regeneration (Saleem et al., 1993). Adsorption is a reliable technique that achieves rapid results. Adsorption of organic compounds on the surface of carbon has been studied extensively (Uranowski, 1998; Tanju and James, 1999; Lin and Liu, 2000; Yu and Chou, 2000; Wiessner et al., 1998).

The role of granular activated carbon surface chemistry in the adsorption of trichloroethylene and trichlorobenzene has been reported (Tanju and James, 1999). In fact, a number of studies were conducted to show the effectiveness of fly ash in the removal of organic materials from aqueous solutions (Nollet et al., 2003; Wang et al., 2005; Kumar et al., 2005; Gupta et al., 1990). Khalid et al. (2004) have reported the use of zeolites for the removal of para-nitrophenol from waste water by adsorption technique. Iqbal et al. (2005) have studied adsorption of phenol on activated charcoal from aqueous solution. The most important characteristics of fly ash are calcium content that provides alkalinity in the

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Table 1. Chemical composition of the fly ash.

Constituent	Wt. %
SiO ₂	57.25
Al ₂ O ₃	22.03
Fe ₂ O ₃	8.36
CaO	2.97
MgO	0.97
SO ₃	0.76
TiO ₂	0.68
K ₂ O	0.52
Others	6.49

system raising pH to strongly alkaline value (~ 12) and the (SiO₂ + Al₂O₃ + Fe₂O₃) content (Komnitas et al., 2004).

Research efforts on fly ash to date have been focused on the study of mechanisms involved in contaminant uptake. A lot of research works have been carried out on the removal of toxic solvents from aqueous solution by activated charcoal and other adsorbents. But work on the removal characteristics of para-nitrophenol by fly ash is very scanty. In view of this, para-nitrophenol was chosen. The aim of present study was to investigate the use of fly ash as a low – cost adsorbent for the removal of toxic solvent such as para-nitrophenol from aqueous solutions. The kinetics and mechanism of para-nitrophenol uptake by the fly ash was investigated.

MATERIALS AND METHODS

The fly ash used as the adsorbent in this present investigation was obtained from Nigeria Coal Corporation, Enugu. The fly ash samples were dried at 105 ± 1°C for 2 h before tests. The fly ash samples were ground and sieved to a particle size of 250 µm before use (Alinnor, 2007). Table 1 shows the chemical composition of the fly ash samples used in this study, SiO₂ and Al₂O₃ contents make up about 79% of the fly ash, while Fe₂O₃ and CaO compose about 11%

About 1g portions of fly ash were taken in different Erlenmeyer flasks. 100cm³ of para-nitrophenol solution was added to each flask having different concentrations (2.0x10⁻³ – 5.x10⁻³ m). The content of the flasks was stirred in a water bath for different durations of time at 30°C using magnetic stirrer. The pH was noted before and after stirring with pH meter. The slurries were then filtered through ordinary filter paper. The clear filtrate was then analyzed for para –nitrophenol (PNP) content by Spectrophotometer (Spectronic 21D) at wavelength 400 nm.

Blank determinations were performed under similar experimental conditions. The amount of para-nitrophenol adsorbed by the fly ash was then calculated from the difference in concentration of blank and sample. The reported values of PNP adsorbed by fly ash in each test were the average of at least three measurements (Iqbal et al., 2005).

The effects of pH on the uptake of para–nitrophenol by fly ash were determined by adjusting the pH of the slurry in the range of pH4 to pH10. At the end of agitation period, the PNP uptake by fly ash was determined as earlier described. The influence of

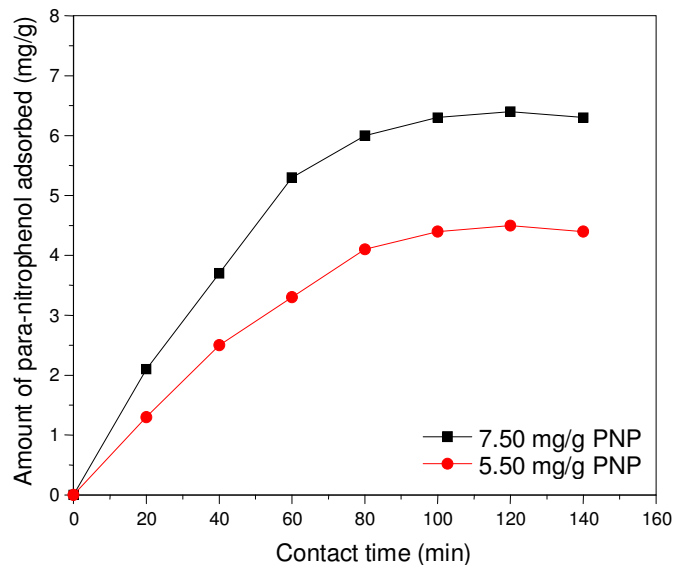


Figure 1. Effect of contact time on the adsorption of para-nitrophenol on fly ash at pH 6.8.

temperature on the adsorption of PNP on fly ash was carried out between 30 and 60°C using thermostated water bath. Also, at the end of agitation period, the para – nitrophenol adsorbed by fly ash was determined as described above. All the chemicals used were of analytical reagent grade.

RESULTS AND DISCUSSION

Reaction kinetics

The effect of contact time on adsorption of 5.50 and 7.50 mg/g para-nitrophenol is shown in Figure 1. The rate of uptake of PNP by fly ash increases with time initially. The PNP removal in the first 20 min was 1.3 and 2.1 mg/g, respectively for the two concentrations studied. Figure 1 indicates that equilibrium was established within 2 h in both concentrations of PNP. At equilibrium, 4.1 mg/g or 74.55% and 6.1 mg/g or 81.33% were removed from the initial concentrations of PNP by the fly ash. The results indicated that level of removal of PNP by fly ash depends on the initial concentration of para-nitrophenol.

The rate constants for adsorption of PNP on fly ash were determined using first-order kinetics (Eligwe and Okolue, 1994; Alinnor, 2007):

$$\ln (C_0/C_t) = kt \quad \dots\dots\dots(1)$$

Where C₀ is the initial PNP solution concentration, C_t is the concentration at time t, and k is the rate constant.

Figure 2 shows that the initial rate of PNP uptake conforms to first-order kinetics as shown in Equation (1). A plot of $\ln C_0/C_t$ versus t should yield a straight line

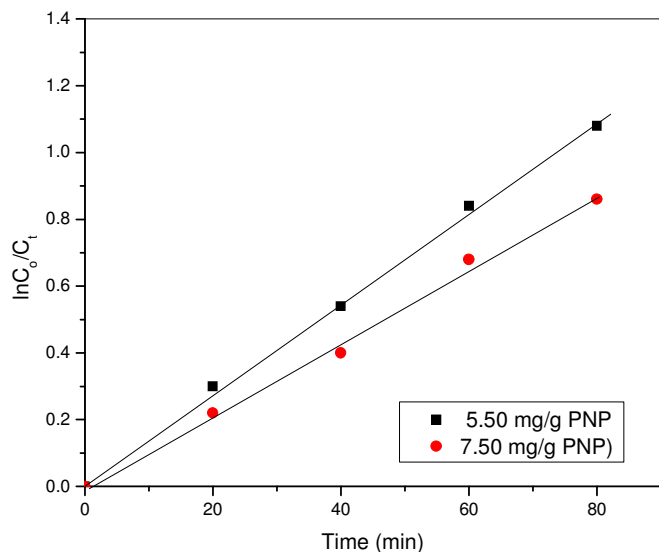


Figure 2. First-order kinetic plot for para-nitrophenol adsorption on fly ash.

from the slope of which the rate constant k was calculated to be $1.10 \times 10^{-2} \text{ s}^{-1}$ and $1.14 \times 10^{-2} \text{ s}^{-1}$ for PNP concentrations, 7.50 and 5.50 mg/g, respectively.

Effect of pH

The adsorption isotherms of para-nitrophenol at different pH ranges are shown in Figure 3. The range of concentration varied from 3.0×10^{-3} to 5.0×10^{-3} M and the pH ranges were pH 4 to 10. Figure 3 shows that the amount of para-nitrophenol adsorbed from aqueous solution is significantly high at pH9 when compared to pH10, pH6 and pH4 respectively. At low pH4 the adsorption of para-nitrophenol on fly ash increases rapidly. This may be attributed to substitution of nitro (NO_2) group, an electron-withdrawing group in the benzene ring. This NO_2 group substitution will enable the ring to withdraw more electrons from the oxygen atom thereby increasing the acid strength of para-nitrophenol. In view of the increase in acidic strength of PNP, the PNP will rapidly adsorb on the negatively charged surface of fly ash. Bhatgava and Sheldarkar (1993) working on adsorption of para-nitrophenol on clay reported an increase in adsorption of para-nitrophenol on clay due to presence of nitro group in the benzene ring. At intermediate pH6 there was a gradual increase on the removal of PNP from aqueous solution onto fly ash. This reduction of adsorption of PNP onto fly ash at intermediate pH6 may be attributed to the reduction in acidic strength of PNP at pH6 when compared to pH4.

Figure 3 shows that the removal of PNP from aqueous solution was more at pH9 when compared to pH 10. At pH 9 the surfaces of the adsorbent were negative and

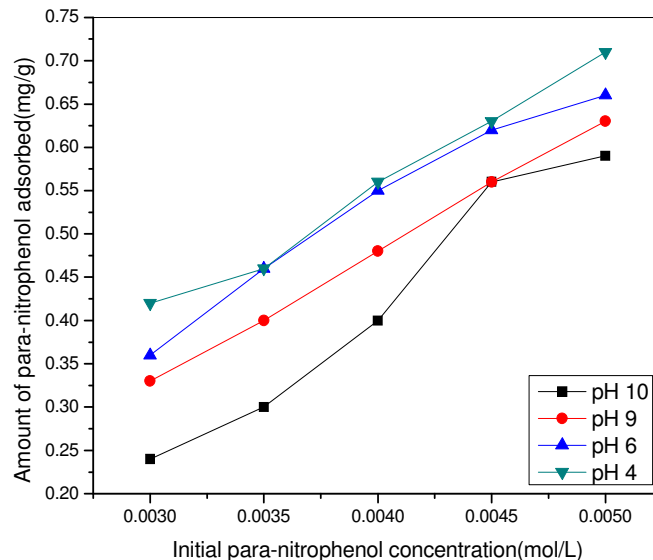


Figure 3. Effect of pH on adsorption of para-nitrophenol on fly ash.

there was an increase on the uptake of PNP by the fly ash. The increase in PNP uptake by fly ash may be explained in terms of electrostatic interaction. This can be seen by the sharp increase on the amount of PNP uptake at pH9. The increase in PNP uptake by fly ash at higher pH values may also be attributed to calcium content and ($\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$) content of fly ash that provides alkalinity in the system raising the pH to strongly alkaline values, thereby facilitating the adsorption of PNP by the fly ash.

However, the decrease in PNP uptake by fly ash at pH10 compared to pH9 may be attributed to dissociation of PNP into phenolate anions. At pH 10 fly ash surface acquires more negative charge due to presence of OH^- ions on the surface of fly ash. The more negatively charged fly ash surface would have repulsed the resultant PNP phenolate anion with each other, which would have resulted in lower adsorption of para-nitrophenol onto fly ash at pH10 when compared to pH9

A schematic representation of the electrostatic repulsion between the PNP phenolate anion and the negatively charged fly ash surface is depicted in Figure 4.

Moreover, PNP phenolate ions have more affinity for an aqueous solution than neutral PNP and thus provide another contributing factor to low adsorption rates. Solubility is another factor, which can affect the adsorption of PNP. Solubility of PNP changes with changes in the pH of the medium and thus would have its own contributing role in adsorption.

Effect of temperature

The removal of para-nitrophenol from aqueous solution

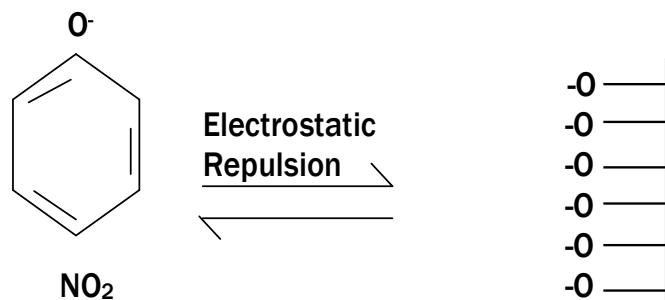


Figure 4. Electrostatic repulsion mechanism between phenolate ion and charged fly ash surface.

is temperature dependent. Figure 5 shows the amount of PNP removed from aqueous solution as a function of temperature at PNP concentrations of 26.0 and 31.0 mg/g, respectively. There was a gradual decrease on the uptake of PNP by fly ash from 30 to 60°C. At initial concentration 26.0 mg/g of PNP at 30°C the amount of PNP adsorbed was 21.0 mg/g or 80.72%. As the temperature increased, the amount of PNP adsorbed decreased. At 40°C the amount of PNP uptake by fly ash was 15.0 mg/g or 57.69%. As temperature increased to 60°C, the amount of PNP removed from aqueous solution was 4.5 mg/g or 17.31%

At initial concentration 31.0 mg/g of PNP, at 30°C, the amount of PNP removed from aqueous solution was 26.5 mg/g or 85.48%. At 40°C the amount of PNP removed by fly ash decreased to 19.8 mg/g or 63.87%. From 40 to 60°C there was a progressive decrease in the amount of PNP removed by fly ash. At 60°C the amount of PNP removed was 11.5 mg/g or 37.10%.

It can be seen that the PNP adsorption follows a similar pattern in the two concentrations studied, but the amount adsorbed at a particular temperature differs. These results indicate that the uptake of PNP increases at lower temperature. The decrease on the uptake of PNP with the increase in temperature may be explained as a result of the increase in the average kinetic energy of the PNP phenolate anions; thus increasing the repulsive forces between the phenolate anions and negatively charged fly ash surface. This could lead to desorption or cause the PNP to bounce off the surface of the fly ash instead of colliding and combining with it. Therefore, the increase in temperature may be associated with the decrease in the stability of PNP phenolate anion-adsorbent complex. Jain et al. (2004) reported a decrease in adsorption of phenol onto fly ash as temperature increases from 30 to 50°C.

Conclusion

This study revealed the application of coal fly ash as an adsorbent for removal of toxic solvents from waste water. The kinetic study shows that PNP was adsorbed onto the

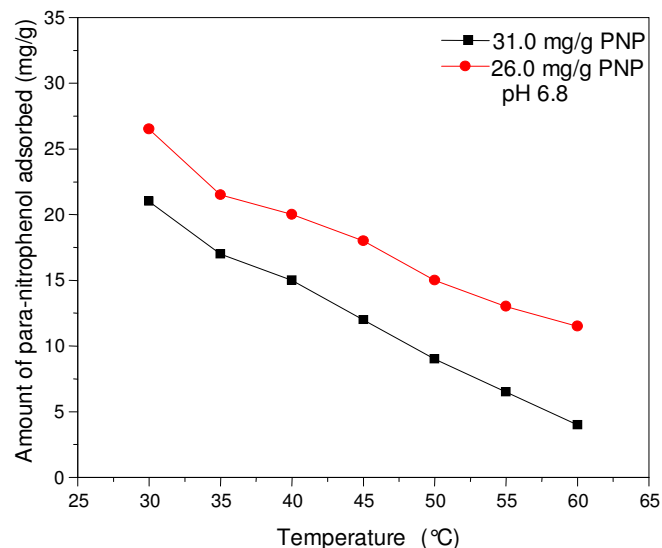


Figure 5. Effect of temperature on adsorption of para-nitrophenol on fly ash.

fly ash very rapidly within the first 20 min, while equilibrium was attained within 2 h for both concentrations of PNP studied. This investigation revealed that PNP uptake was high at pH9 due to the increase of negatively charged fly ash surface, which enhances adsorption. Also the substitution of NO₂ group in benzene ring enhances adsorption. This study revealed that the increase in temperature decreases uptake of PNP by the fly ash.

RECOMMENDATION

Fly ash could be used by industries for the treatment of waste water to remove heavy metal ions and organic materials. Using of fly ash for waste water treatment will reduce cost since it is a waste product from coal. Also treatment of soil with fly ash will reduce the population of plant parasites. Reduction of plant parasite will increase agricultural yield. Fly ash could also be used to neutralize soil acidity, thereby increasing agricultural yield. It could be used in the manufacture of cement. This will reduce the cost of reduction of cement since it is a waste product from coal. Reduction in price of cement will enhance development of any country.

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