

STUDIES ON THE EFFICIENCY OF A LOCAL FERTILIZER  
WASTE AS A LOW COST ADSORBENT

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**Abstract**—Waste slurry, generated in local fertilizer plants, is converted into activated carbon in air, steam and nitrogen atmospheres. Products so obtained have been characterized and utilized for the removal of phenols, especially 2,4-dinitrophenol. Investigations include the effect of pH, kinetics of adsorption and the effect of salts on the uptake of DNP. Carbon prepared in air exhibits good sorption capacity for DNP and the adsorption data follows both Langmuir and Freundlich models. Some experiments have also been performed with a view to recover phenols and have *in situ* regeneration of spent carbon column. It is observed that 5% NaOH removes almost 96% of phenol loaded on the carbon column and a treatment with 1 M HNO<sub>3</sub> reactivates the adsorbent particles which can be used for 6–10 cycles at a stretch.

**Key words**—activated carbon systems, carbon, adsorbent, activated carbon columns

### INTRODUCTION

In waste water treatment, the process of adsorption has an edge over other methods, due to its sludge free clean operation. In an ever increasing search for low cost adsorbents various substances like fly ash, coal dust, soil, bark, peat moss and straw have been tried from time to time as reported by Randall *et al.* (1974), Chaney and Hundermann (1979) and Larsen and Schierup (1981). Activated carbon is being universally used in spite of its higher production cost and regeneration difficulty. In India all the fertilizer plants produce a waste slurry (consisting of carbon particles) which is generated after liquid fuel combustion and causes a disposal problem. Currently this is being used as filler etc. in various industrial plants. Efforts have been made to prepare activated carbon from the waste slurry and this paper reports the properties and sorption characteristics of the product.

### EXPERIMENTAL

The fertilizer waste slurry was initially treated with hydrogen peroxide to oxidize the adhering organic material and then heated at 200°C till the evolution of black soot stopped. The heated product was cooled and activated in air, steam and nitrogen atmospheres.

Activation, in the presence of air, was performed in an ordinary furnace at 450°C for 1 h. On laboratory scale about 1.0 kg of the material could be activated at one time. No activation agents were used. Temperature and time were optimized by observing the surface properties of carbon obtained by activating the raw material for different intervals of time and at varying temperatures. Products obtained at temperatures higher than 450°C possess poor adsorption

capacity. The finished product is 60% of the original waste material.

For activation in different environment 50 g of the product was heated in a tubular furnace (30 × 2 cm) in a steam or nitrogen environment. A continuous supply of steam or nitrogen was maintained and activation was done for about 1 h at 700°C. Activation temperature is optimized on the basis that the evolution of hydrocarbons (from raw material) start at 500°C and is complete at 700°C. Initial heating and treatment of the raw material (as reported in activation in the presence of air) was not done in this case. The yield of the finished product is 55% of the original waste slurry.

Material so obtained was treated with 1.0 M HCl solution to remove the ash content and washed with distilled water. The washed product was dried at 100°C and stored in a desiccator. Adsorbent was broken into smaller particles and a 250–300 BSS mesh fraction was used in subsequent investigations.

In order to achieve reproducibility from batch to batch, the conditions for activation were carefully controlled.

### Analysis

Samples were analysed for carbon, iron plus aluminium oxides, silica and ash contents. A known amount was heated at 900°C in a furnace to a constant weight. Residue was dissolved in concentrated HCl and filtered and the solution was analysed for iron and aluminium gravimetrically. C, Al and Fe contents in the three samples range between 90 and 92% carbon, 0.4 and 0.6% Al and 0.6 and 0.8% Fe. The amount of silica and ash was found to be negligibly small.

Infrared spectra of the samples were recorded by Beckman IR-20 spectrophotometer while the scanning electron microscopy was done in Philips SEM 501 electron microscope and the X-ray measurements were done by Philips X-ray diffractometer employing nickel filtered Cu-K<sub>α</sub> radiations. Surface area of the samples was measured by methylene blue adsorption and confirmed by BET method.

### Adsorption studies

Preliminary investigations exhibit a high uptake of phenols on this adsorbent material in comparison to metal ions. Results obtained with 2,4-dinitrophenol (DNP) are

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discussed in this report. DNP can be easily and directly estimated spectrophotometrically at 360 nm.

Initially isotherms were run by taking different concentrations of DNP ( $0.0184$ – $0.184$  mg ml<sup>-1</sup>) at pH 2, 4 and 10. Experiments were performed in stoppered glass flasks containing 100 ml of adsorbate solutions and a definite amount of the adsorbent (10 mg). Solutions were continuously stirred for 12 h and left for equilibration for 18 h at 30°C. Biological degradation of phenols was also taken into account by running blank determinations.

DNP adsorption in the presence of NaCl, BaCl<sub>2</sub> and AlCl<sub>3</sub> was also observed as a function of pH.

#### *Kinetic measurements*

The kinetics of DNP adsorption on the carbon sample activated in air, was observed by bath technique (finite bath system). A number of stoppered Pyrex glass flasks containing a definite volume (100 ml in each case) of solutions of DNP of known concentrations were placed in a thermostat-shaking assembly. After attaining the desired temperature, a known amount of adsorbent was added into each flask and the solutions were mechanically agitated. At predecided intervals of time, solutions in various flasks were separated from the sorbent material and analysed to determine the uptake of DNP. Equilibrium was attained in about 8 h.

The influence of concentration of DNP on the rate of adsorption was observed by taking  $3.0$ – $7.0 \times 10^{-4}$  M solutions of the same, while  $1.5$ – $5.0$  g l<sup>-1</sup> of adsorbent was used to study the variation in rate of uptake as a function of the amount of activated carbon. Similarly the influence of pH was observed in the range 2.0–10.0.

#### *Regeneration*

Chemical regeneration of the adsorbent was also tried with a variety of chemicals.

## RESULTS AND DISCUSSION

### *Characterization of the adsorbent material*

All the three samples of activated carbon are quite stable in water, salt solutions, acids and bases.

One gram of each sample was stirred with 100 ml of deionized water (pH 6.8) for 2 h and left for 24 h in an air tight stoppered conical flask. A lowering of pH was observed in each case but it was maximum in the sample activated in air and minimum in the one activated in steam.

According to Steenberg's (1971) classification, the material under investigation may be treated as "L" carbon.

The infrared spectra of the sample activated in air shows weak and broad peaks in the region of  $1800$ – $1600$  cm<sup>-1</sup>. The band at  $1710$  corresponds to a normal carbonyl group (Szymanski and Alpert, 1964), while the one at  $1605$  cm<sup>-1</sup> may be attributed to conjugated hydrogen bonded carbonyl groups as suggested by Hallum and Drushel (1958). Sample activated in steam is almost transparent while the one activated in N<sub>2</sub> is completely transparent in the infrared. Although some inference can be drawn about the surface functional groups from i.r. spectra, the weak and broad bands do not provide any authentic information about the nature of surface oxides but this data definitely indicates the presence

of some surface groups in the adsorbent material activated in air, as compared to the other two samples.

X-ray spectra also does not show any peak thereby indicating the amorphous nature of the product.

Surface area of the samples activated in air, N<sub>2</sub> and steam are  $629$ ,  $391$  and  $195$  m<sup>2</sup> g<sup>-1</sup> respectively (measurements made by BET method). These values are consistent with the adsorptive behaviour of the three varieties of carbon which have been activated in different environments.

SEM photographs (Fig. 1) of the three samples clearly reveal the different nature of the flocs and the porosity of the sample activated in air.

Adsorption isotherms of DNP on the two activated carbon samples are given in Fig. 2. It is interesting to observe that the sample activated in steam does not exhibit any uptake of the adsorbate while the one prepared in nitrogen atmosphere also exhibits poor

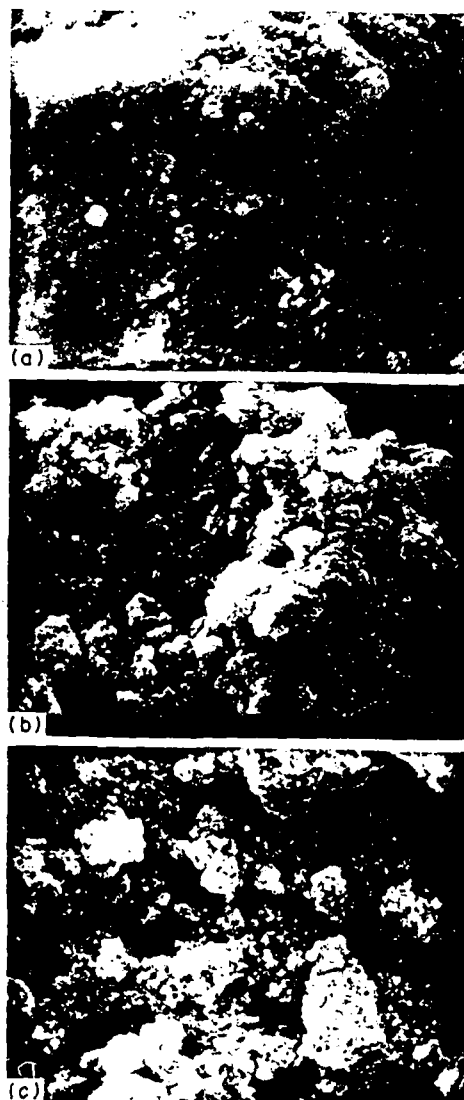


Fig. 1. Scanning electron micrographs of carbon activated in (a) air, (b) nitrogen and (c) steam atmospheres.

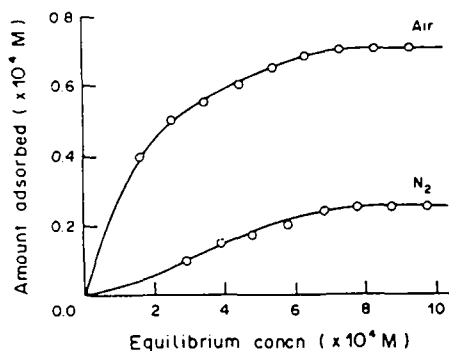


Fig. 2. Adsorption of DNP on activated carbon activated in different atmospheres.

adsorption capacity in comparison to the air activated sample. As such the subsequent investigations with DNP were made only on the sample activated in air.

The removal of DNP (Fig. 3) at different concentrations of adsorbent takes place in two phases. First phase of solute uptake the "immediate solute removal", obtained within a few minutes, is followed by "subsequent removal of solute" and this continues for a longer period of time. The logarithmic plot for the same data [Fig. 5(a)] shows a linear variation and can be expressed as:

$$\Delta S = K_i \cdot t^m$$

where  $\Delta S$  is the percent solute removal,  $t$  the contact time in hours,  $m$  the slope of linear plot and  $K_i$  is a constant coefficient. Slope " $m$ " depicts the adsorption mechanism and the term " $K_i$ " may be taken as rate factor [i.e. percent solute removed per ( $t = 1$ ) hour, Cooney *et al.*, 1983]. It is observed that an increase in the amount of activated carbon ( $1.5$ – $5.0$   $\text{g l}^{-1}$ ) results in a decrease in slope values (Table 1) with corresponding increase in the factor " $K_i$ ". Higher values of rate factor, " $K_i$ ", indicate an enhancement in the rate of solute removal with

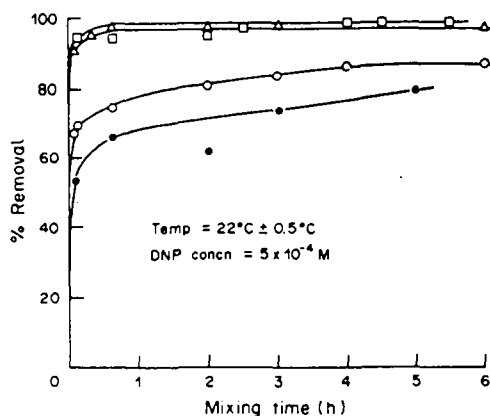


Fig. 3. Variation of rate of removal of DNP on adsorbent at different adsorbent concentrations. Adsorbent concentration ( $\text{g l}^{-1}$ ): ●—1.5; ○—2.5; △—4.0; □—5.0.

Table 1. Variations of log (time) vs log (percent removal) plot constants at different adsorbent concentrations. DNP concn =  $5.0 \times 10^{-4}$  M; volume of solution = 100 ml; temperature =  $22 \pm 0.5^\circ\text{C}$

Concentration of adsorbent ( $\text{g l}^{-1}$ )	Slope " $m$ " $\times 10^2$	Intercept log " $K_i$ "
1.5	7.86	4.30
2.5	6.73	4.35
4.0	1.99	4.57
5.0	1.35	4.56

increase in carbon concentration whereas larger slope ( $m$ ) values at smaller adsorbent concentrations indicate a better sorption mechanism, which may be due to an improved bonding between solute molecules and adsorbent particles. Although solute removal (%) increases with increasing adsorbent concentrations, the adsorption efficiency under identical conditions goes down. It is observed that after 4 h of equilibration, 98.8% of DNP (concn  $5 \times 10^{-4}$  M, pH  $\sim 4$ ) is removed with  $5.0$   $\text{g l}^{-1}$  of adsorbent whereas with  $2.5$   $\text{g l}^{-1}$  of adsorbent, the removal is 86.4% (Fig. 3) at the same concentration and pH of DNP. As such the enhanced quantity of adsorbent ( $2.5$ – $5.0$   $\text{g l}^{-1}$ ) is able to remove only an additional 12.4% amount of adsorbent. Taking into account the handling problems associated with large quantities of carbon and also considering a relatively smaller solute removal with smaller amounts of adsorbent,  $2.5$   $\text{g C l}^{-1}$  has been taken as optimum adsorbent concentration and 7–8 h time is quite sufficient for complete equilibrium attainment.

The relationship between "percent removal" and "initial adsorbate concentration" (Fig. 4) depicts that the removal of adsorbate decrease with increasing DNP concentration and so the removal of even trace quantities of the pollutant, from the solution, is not expected to pose any special problem in the system under investigation.

The linearized logarithmic plots [Fig. 5(b)] of the data shown in Fig. 4 can also be mathematically expressed as  $\Delta S = K_i \cdot t^m$ . The plots [Fig. 5(b)] reveal

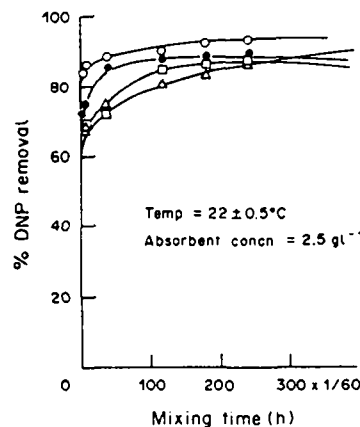


Fig. 4. Variation of rate of removal of DNP on adsorbent at different DNP concentrations. DNP concentration ( $\times 10^{-4}$  M): ○—3.0; ●—4.0; △—5.0; □—7.0.

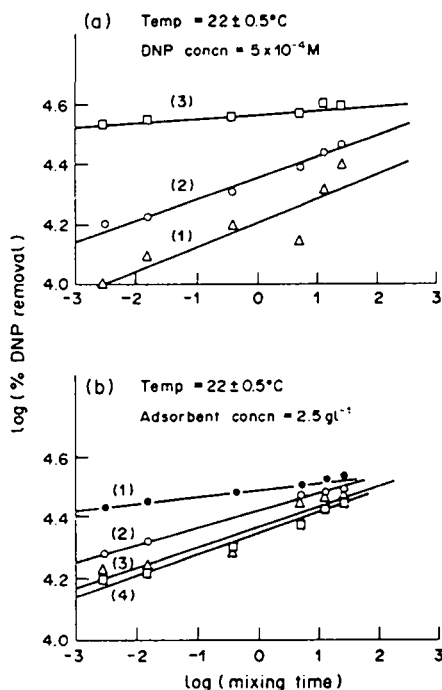


Fig. 5. Logarithmic rate of solute uptake. (a) Adsorbent concentration ( $\text{g l}^{-1}$ ):  $\circ$ —2.5;  $\square$ —5.0;  $\triangle$ —1.5. (b) DNP concentration ( $\times 10^{-4} \text{M}$ ):  $\bullet$ —3.0;  $\circ$ —4.0;  $\triangle$ —7.0;  $\square$ —5.0.

that increase in DNP concentration causes an increase in slope " $m$ " and a decrease in constant " $K_i$ " (Table 2). The large values of " $m$ " for larger DNP concentrations indicate a better adsorption mechanism or stronger bonds between adsorbate and adsorbent. This justifies subsequent removal of solute by diffusion through carbon particles, when concentration gradient is larger at solid-liquid interface. Smaller values of " $K_i$ ", for comparatively larger DNP concentration, result in smaller values of adsorbate removed in the first phase (immediate solute removal), and this may be due to comparatively lesser "active sites" available on carbon particles for the adsorption of solute molecules.

According to Weber and Moris (1963) a value of  $m = 0.5$  reflects "intraparticle diffusion" as the rate determining step. The uptake of solute on adsorbents like activated carbon involves two processes. One is the transport of adsorbate from solution to particle solution interface and the second is the adsorption on the accessible surface of adsorbent particle. If intra-

Table 2. Variation of log (time) vs log (percent removal) plot constants at different DNP concentrations. Adsorbent concn =  $2.5 \text{ g l}^{-1}$ ; volume of solution =  $100 \text{ ml}$ ; temperature =  $22 \pm 0.5^\circ \text{C}$

DNP concentration ( $\text{ml}^{-1}$ ) $\times 10^4$	Slope " $m$ " $\times 10^2$	Intercept $\log "K_i"$
3.0	2.46	4.49
4.0	5.88	4.43
5.0	6.73	4.35
7.0	7.12	4.37

particle diffusion is the rate determining step, the value of " $m$ " in the kinetic plots should be 0.5, while smaller values indicate the involvement of both the processes to almost an equal extent. In these investigations the value of  $m$  is much less than 0.5 and the sorption rate seems to be equally dependent on both and neither of these appear to be sufficiently slow as to be the rate determining step. This is in conformity with the findings of Di Giano and Weber (1973) who report that the uptake of smaller and more compact molecules, such as 2,4-dinitrophenol, is not governed solely by intraparticle diffusion.

The variation in kinetics of adsorption with hydroxyl ion concentrations has been determined by observing the solute removal at different pH values (Fig. 6). Increasing  $\text{H}^+$  ion concentration does not influence the kinetics of adsorption of DNP and the uptake almost remains constant from pH 2 to 5, but at pH 8 and beyond it decreases significantly. A similar decrease in the uptake of DNP with increasing pH has been reported by Di Giano and Weber (1973), Weber and Moris (1963) and Zogorski *et al.* (1976). This effect is obvious if one considers the acidic nature of adsorbate, its  $\text{p}K_a$  value (3.96) and the fact that adsorption of nondissociated species is more favoured on carbon-adsorbent.

The kinetic studies, on the system under experiment, show that the carbon obtained from fertilizer waste is a good scavenger of DNP at low concentrations of adsorbate and removes it at a faster rate when pH of the solution is below 5.

#### Langmuir and Freundlich plots

The sorption data seems to follow both Langmuir as well as Freundlich adsorption models (Figs 7 and 8). Freundlich parameters [ $(1/n) = 0.40$  and  $k = 0.75$ ;  $(x/m) = kC^{1/n}$ ] reflect the suitability of the system under investigation. Langmuir plot reveals a maximum uptake of  $147 \text{ mg DNP g}^{-1}$  of adsorbent while in practice the maximum adsorption observed is  $128 \text{ mg g}^{-1}$  adsorbent. Normally in batch process a

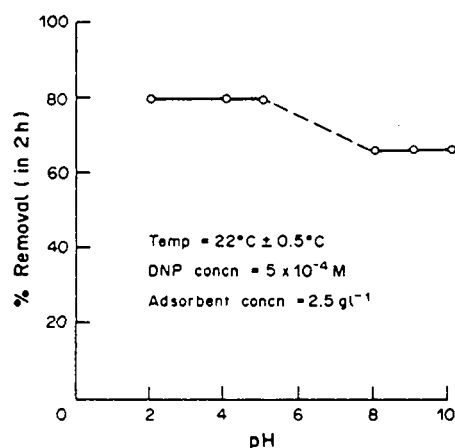


Fig. 6. pH effect on rate of DNP removal.

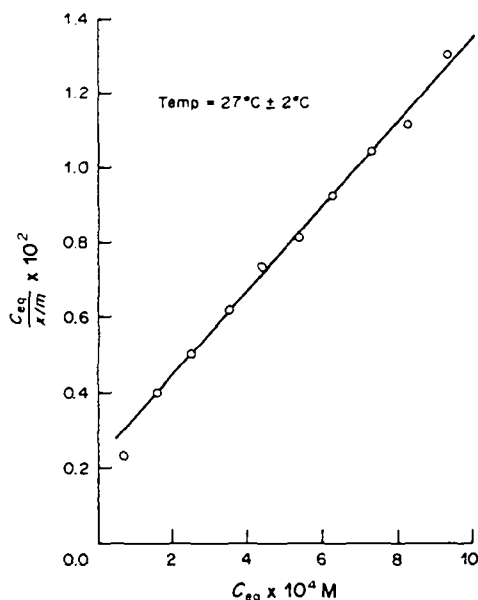


Fig. 7. Plot of Langmuir adsorption isotherm.

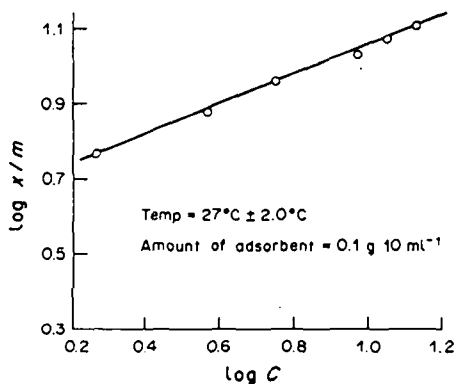


Fig. 8. Plot of Freundlich adsorption isotherm.

complete utilization of the sorption capacity of adsorbent is not possible.

Weber and Chakravarti (1974) expressed the feasibility of the process in terms of a dimensionless constant separating factor or equilibrium parameter "R", defined by:  $R = (1/1 + dCo)$  where  $d$  and  $C$  are the terms appearing in Langmuir isotherm:  $q = (Qm \cdot dC/1 + dC)$ . The value of  $R$  denotes an unfavourable ( $R > 1$ ), linear ( $R = 1$ ) or favourable ( $R < 1$ ) process. In these investigations the value of  $R$  is 0.32 and this, further, exhibits the efficacy of the material under consideration.

Weber (1981) has given the uptake of phenols on various commercially available activated carbons. Maximum uptake on carbonaceous carbon (trade name XE-348) with a surface area of  $500 \text{ m}^2 \text{ g}^{-1}$  is  $105 \text{ mg g}^{-1}$  while that on XE-340 with an area of  $400 \text{ m}^2 \text{ g}^{-1}$  is  $80 \text{ mg g}^{-1}$ . The sample BACM (trade name) with an area of  $1000 \text{ m}^2 \text{ g}^{-1}$  is capable of

removing  $210 \text{ mg phenol g}^{-1}$  adsorbent. In comparison to these, the sample under investigation has a surface area of  $629 \text{ m}^2 \text{ g}^{-1}$  and does adsorb  $128 \text{ mg phenol g}^{-1}$  of activated carbon.

#### Salt effect

Sometimes dissolved salts may also be present in waste water along with organic contaminants. Presence of these salts may affect the removal of organics. As such the uptake of 2,4-dinitrophenol (fixed  $6 \times 10^{-4} \text{ M}$  concentration) has been studied in the presence of varying concentrations ( $2-6 \times 10^{-4} \text{ M}$ ) of inorganic salts e.g. NaCl,  $\text{BaCl}_2$  and  $\text{AlCl}_3$  at a fixed adsorbent concentration. There is no effect of NaCl on the uptake of DNP between pH 2 and 4. Even higher concentrations of NaCl do not cause any effect in the specific pH range (2-4) but at pH 10, adsorption increases by 66%. The presence of  $\text{BaCl}_2$  and  $\text{AlCl}_3$  do not effect the uptake of DNP to a significant extent ( $< 2\%$ ). Plots have not been shown here.

The influence of anions on the uptake of phenols has also been investigated with salts having a common cation ( $\text{Na}^+$  ion). Studies reveal that anions cause very little influence on the sorption of DNP by activated carbon.

The enhancement in the uptake of DNP, in the presence of sodium salt at pH 10, may be attributed to some change in the distribution of organic species present thereby influencing the rate or the extent of adsorption. Besides this the possibility of some alteration in the alignment of adsorbed molecules and neutralization of repulsive forces between adsorbate and adsorbent perhaps to create new or particularly favourable adsorption sites cannot be ruled out. Weber *et al.* (1969) have also reported a parallel observation for *p*-nitrophenol.

#### Recovery of adsorbed material and regeneration of column

This is an important process in waste water treatment. In order to achieve this and to assess the practical utility of the adsorbent, studies were undertaken by column operations as well. A glass column  $40 \times 0.5 \text{ cm}$  was filled with  $0.500 \text{ g}$  (size 200 mesh) of activated carbon. The column was loaded with DNP and the solutions percolated downwards at a flow rate of  $0.2 \text{ ml min}^{-1}$ . Desorption was tried with a number of eluting agents, viz., acids, NaOH, ethanol, methanol etc. With acids the elution of phenol was quite small while the recovery with methanol or ethanol was only 60% of the amount loaded. Almost complete (96%) desorption of DNP could be achieved with only 5% NaOH. This is due to the formation of sodium salt of DNP which could be readily removed.

It is further observed that the column loses about 2-5% of its adsorption efficiency, after the first run. A good deal of experimentation with various reagents have shown that a treatment with 1 M  $\text{HNO}_3$  solution

at a flow rate of  $0.5 \text{ ml min}^{-1}$  restores the lost sorption capacity to almost the original value. No loss is however observed in subsequent runs and a column can be used for 8–10 cycles without further regeneration. It is quite interesting to observe that a decrease in sorption efficiency takes place only after first run in a virgin column and at this point a treatment with  $1 \text{ M HNO}_3$  is essential. After running the same for a number of cycles the column can again be chemically regenerated without dismantling it.

#### Cost factor

As mentioned earlier the uptake of DNP on the carbon generated from fertilizer waste slurry is comparable to other commercially available varieties. The cheapest variety of commercially available carbon (of surface area specified earlier) in this country is  $\$1.0 \text{ kg}^{-1}$  ( $\$100 \text{ ton}^{-1}$ ). The waste slurry is available for  $\$1.00 \text{ ton}^{-1}$  and considering the cost of transport, electrical energy etc. the cost of the finished product is  $\$50 \text{ ton}^{-1}$ . The recovery of phenols and the chemical regeneration of column without dismantling the same, further bring down the cost factor.

#### Treatment of effluent

Waste waters obtained from a coal gasification plant (data given below) were successfully treated on the columns of this adsorbent material. The analysis of coal gasification plant effluent is: pH—8.2; SS—250; phenols—2800; COD—1600;  $\text{SCN}^-$ —130;  $\text{CN}^-$ —0.5; ammonia—7200; TOC—6305 ( $\text{mg l}^{-1}$ ). The effluent was just treated with a mild acid (to bring down the pH), allowed to settle down for some time in a tank and then fed to carbon columns. Phenols mentioned in the analysis are a mixture of various substituted compounds of the same class and the entire amount could be eluted with NaOH.

#### CONCLUSION

Waste slurry generated in fertilizer plants has been converted to a cheap carbonaceous adsorbent. The product, activated in air, exhibits promising ad-

sorption characteristics for phenols and can be used as a suitable adsorbent for phenolic wastes from various industries. The cost of production of material is almost half as compared to other commercially available samples and the activity is quite comparable. Phenols adsorbed on the columns of this material can be eluted quantitatively with 5% NaOH. Exhausted columns can be chemically regenerated by treating with  $1 \text{ M HNO}_3$  and no dismantling is required. Other salts present in phenolic effluents do not cause any disturbing affect.

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