

# Simultaneous Adsorptive Removal of Cyanide and Phenol from Industrial Wastewater: Optimization of Process Parameters

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## Abstract

Cyanide and phenol are found extensively in the effluents of refinery, coke plant, electroplating industries and are extremely dangerous to environment. Commercial granular activated carbon (GAC) was used as an adsorbent for the simultaneous removal of cyanide and phenol in the present study. The effect of process parameters such as pH, temperature ( $T_c$ ), adsorbent dose ( $D_c$ ) and contact time ( $t_c$ ) on the performance of adsorption was investigated. Optimum pH was found to be 8 for simultaneous removal of cyanide and phenol. Temperature did not have any significant on cyanide removal, but phenol removal was observed to increase with the increase in temperature. Both compounds were optimally removed at 35<sup>o</sup> C. The percentage removal of compounds increased with an increase in the concentration of GAC. However the specific uptake did not increase on GAC concentration's greater than 30 g/L, which was considered as the optimum dose of adsorbent. Removal of cyanide was slightly higher than that of phenol, but the difference is not significant, at optimum conditions.

**Key words:** Simultaneous removal, cyanide, phenol, optimization; process parameters, GAC

## Introduction:

Cyanide and phenol compounds are the strictly regulated compounds worldwide because of their extreme toxicity<sup>1,2</sup>. Although these compounds are present in small concentrations in a number of daily items like plants, microorganisms, foods, cosmetics etc. their large-scale presence in the environment is attributed to the various human activities as these compounds are extensively used in various industries<sup>3,4</sup>. While bulk of cyanide occurs in environment due to metal finishing and mining industries, phenol occurs mainly in refineries, pharmaceuticals and coal processing industries<sup>3,4</sup>. Cyanide and phenol compounds are utilized and also found in the effluents of industries like

coke plant, paint and dye formation, automobile manufacturing, explosive manufacturing, chemicals, pesticides industries, synthetic fiber and resin manufacture etc. Generally cyanide compounds are present in the environmental matrices and waste streams as simple and complex cyanides, cyanates and nitriles while the phenol compounds exist as various substituted derivatives of phenol<sup>3, 4</sup>. The stability of these compounds (cyanides and phenols) is pH dependant and therefore their potential environmental impacts and interactions can vary depending on the system. Of these compounds, simple cyanides, which refer to the simple salts of cyanide such as KCN and NaCN

are most dangerous forms of cyanide<sup>5</sup>. They can dissociate rapidly in acidic environment and produce HCN which is very poisonous. This form of cyanide is highly unstable even in the slightest of acidic conditions<sup>3</sup>. Phenol and its derivatives then to photo oxidize in the environment and thus form a wide range of primary and secondary pollutants and thus have a huge impact on environment<sup>4</sup>.

Due to their toxic effects, effluents containing compounds of cyanide, phenol of both cannot be discharged without detoxification into the environment. Regulations on the discharge of the effluents containing cyanides and phenols have been imposed by various environmental agencies and boards. The maximum permissible limit of cyanide in discharge effluents defined by the United States

Environmental Protection Agency (USEPA), disposal standard in Mexico and the Minimum national standard (MINAS) of Central Pollution Control Board (CPCB) India is 0.2 mg/L<sup>6</sup>. Swiss and German regulation standards for cyanides are 0.01 mg/L for surface water and 0.5 mg/L for sewers<sup>7</sup>. For phenol the maximum permissible limit in industrial effluents defined by USEPA, the disposal standards in European Union and MINAS of CPCB India is 0.5 mg/L<sup>4,8</sup>. Cyanide and phenol compounds in wastewater can be treated by many physical, chemical and biological methods like anodic oxidation, ozonation, copper catalyzed hydrogen peroxide, electrical attenuation, distillation, activated carbon and resin adsorption, and biological treatment etc.<sup>3,4</sup>. Most of these methods are not expensive and so not readily applicable.

**Background of Adsorption Process:** Activated carbon adsorption is a very successful and widely

utilized technique<sup>9</sup>. Several reports on the treatment of water containing cyanide and phenol on plain, treated and metal impregnated activated carbons of different origins are available. Dash et al. studied the removal of various cyanide forms on GAC. GAC was found to be feasible to treat concentrations of cyanide up to 300 mg/L<sup>10</sup>. Huff et al. studied the feasibility of treating refinery wastewater using powdered activated carbon<sup>11</sup>. Guo et al. studied removal of low levels of cyanide, till 1 mg/L, to define the working conditions required to reduce the residual levels of cyanide<sup>12</sup>. Adsorption was observed to be a slow process and uptake continued to take place till 30 h. Adhoum and Monser studied removal of cyanide by metal impregnated activated carbon and found that Ag-impregnated activated carbon had higher cyanide removal efficiency than Ni-impregnated activated carbon<sup>13</sup>. Srivastava et al. studied the removal of phenol by granular activated carbon and found it effective for removal up to 50 mg/L and the contact time for equilibrium was established at 5 h<sup>14</sup>. El-Naas et al. studied removal of phenol on date-pit activated carbon and found it to be effective for removal. The regeneration efficiency was also found to be quite high<sup>15</sup>. Girods et al. studied the removal of phenol on wood particle board waste based activated carbon and found that the removal capacity was as high as 500 mg/g<sup>16</sup>. Activated carbon has a very high surface area and also a good cyanide and phenol adsorption capacity. Though effective, high cost and 10-15% loss in conventional regeneration techniques are some problems encountered in the usage of activated carbon<sup>6</sup>.

There are many reports on adsorptive removal of various cyanide and phenol forms but no report mention's the simultaneous removal of cyanide and phenol. Also not many reports mention the

usage of plain granular activated carbon for adsorption. So the behavior of process parameters for simultaneous adsorption of cyanide and phenol is not clear. In this study an attempt has been made to analyze the efficiency of activated carbon for removal of cyanide (NaCN) and phenol simultaneously in batch reactors and to optimize the process parameters for simultaneous removal.

## Materials and Methods

All the chemicals were of analytical grade and prepared by distilled water. The cyanide solution was prepared by dissolving 1.89 g of NaCN in 1 L of distilled water, whose pH was pre-adjusted to 10, to yield a stock sodium cyanide solution of 1000 mg (CN<sup>-</sup>)/L. Phenol solution was prepared by dissolving 1 g of pure phenol crystal in 1 L of distilled water to obtain phenol stock solution of concentration 1000 mg (Phenol)/ L. The stock solutions were diluted respectively to obtain the compound solution comprising of 50-350 mg/L of cyanide and phenol. The commercial GAC of apparent density and particle sizes of 400 g/L and 4-5 mm respectively was used in batch experiments after being treated with 0.5 M H<sub>2</sub>SO<sub>4</sub> in 1:2 ratio, washed with distilled water and dried at 110<sup>0</sup> C for 24 h. GAC dose of 10-50 g/L were used for the adsorption of cyanide and phenol and optimum dose was decided. Effects of pH and temperature on adsorption were studied for pH 4-12 and temperature 20-45<sup>0</sup> C for the compound solution with initial concentration of 100 mg/L of both cyanide and phenol. All adsorption studies were conducted in 250 mL conical flasks containing equal initial concentration of cyanide and phenol with optimum adsorbent dosage of 30 g/L. The concentration of cyanide and phenol in the flasks varied in the range of 50-350 mg/L with a 1:1

ratio of cyanide and phenol. All the adsorption studies were carried out in a rotary incubator shaker at agitation speeds of 120 rpm and agitation period of 48-72 h. The effects of the process parameters such as pH, temperature, adsorbent dose and agitation time on cyanide and phenol were investigated on the combined solution. Total cyanide was determined by picric acid colourimetric method at 520 nm as described by standard methods with a precision up to 0.001 mg/L<sup>17</sup>. Total phenol was determined by colourimetric 4-aminoantipyrine method at 510 nm as described by standard methods<sup>17</sup>. pH was measured using pH meter as specified by standard methods by WTW<sup>®</sup> Germany (makes pH 720). All spectrometric measurements were carried out using DR-4000 UV-VIS spectrophotometer (Hach<sup>®</sup> USA).

## Results and Discussions

The experiments were conducted to investigate the effects of various process parameters on simultaneous adsorptive removal of cyanide and phenol from the compound synthetic solution containing both. The results observed from the investigations have been discussed below.

**pH:** pH of the solution affects the surface charge of the adsorbent, degree of ionization along with speciation of different pollutants<sup>18</sup>. The influence of pH on the extent of adsorption of cyanide and phenol from their mixture is shown in figure 1. A steady increase in the adsorption of cyanide was seen above pH of 7. Maximum adsorption occurred in the pH 8 to 9. Slight decrease was observed at higher pH. For phenol, maximum pH was observed in acidic region. Adsorption was almost constant till pH 8 but showed a steep reduction on higher values. Thus

we could conclude that pH of 8 is optimum for simultaneous adsorption of cyanide and phenol.

In the alkaline conditions free cyanide is present predominantly in neutral HCN form<sup>19</sup>. Equilibrium adsorption between GAC and cyanide indicates that extent of adsorption is not dependant on pH in ranges of 7-10. Dash et al. studied the adsorption of cyanide on activated carbon and showed that maximum adsorption occurs at pH 9.2 for NaCN<sup>10</sup>. Guo et al. studied the effects of pH on dilute cyanide solutions and observed that effect of pH was very less pronounced in adsorption but had a marked effect on the stability of cyanide<sup>12</sup>. At low pH values cyanide exists as HCN which is a weak acid and highly soluble in water. This affinity of water at low pH prevents its adsorption onto GAC<sup>12,20</sup>. Also at a higher pH the de-protonation on GAC surface provides functional groups, for chemisorptions, on its surface that can undergo ion exchange type of interaction with cyanide ions<sup>12</sup>. Blanco-Martinez et al. studied the effect of pH on adsorption of mono-hydroxylated phenol on activated carbon<sup>21</sup>. At pH less than 9.8 the surface is positively loaded and at pH near 7 phenol molecules are more protonated than at higher values. Thus they are attracted to the positive charged surface of activated carbon. At pH of 11 the surface is negatively loaded and thus repulses the phenol molecules<sup>21,22,23</sup>. Thus from literature and the present study it was observed that the optimum pH for removal of cyanide and phenol from combined effluent is 8.

**Effect of Temperature:** The influence of temperature on cyanide and phenol adsorption was examined at the optimum conditions for 24 h. figure 2 shows the effect of temperature on adsorption by GAC. The effect of temperature on removal of cyanide was not great but it was

observed that for phenol, the adsorptivity increases with the increase in temperature. In case of cyanide it was seen that equilibrium adsorption increased slightly up to 25<sup>0</sup>C and optimum conditions were established in 30 – 35<sup>0</sup>C. At higher temperature there is a possibility of desorption of cyanide from the activated carbon. It was observed that there was no increase in the adsorption beyond 35 <sup>0</sup>C which could be explained by the phenomenon of desorption that takes place as temperature increases<sup>10, 24</sup>.

For phenol the adsorptivity increases with the increase in temperature. This could be established by the fact that if adsorption process is controlled by diffusion, the sorption capacity will increase with increase in temperature, since diffusion is an endothermic process<sup>14</sup>. Though highest removal has been observed at 45<sup>0</sup>C, optimum temperature was established in range of 35-40<sup>0</sup>C. Also with the increase in temperature, the solubility of phenol decreases and thus more readily adsorbed<sup>24</sup>. Thus, optimum temperature for the equilibrium adsorption of cyanide and phenol was established as 35 (±1) <sup>0</sup>C.

**Effect of Adsorbent Concentration:** From the experimental results it was found at various concentrations, the percent removal of cyanide and phenol from the mixture increased with the increase in the adsorbent dose. Figures 3 and 4 present the specific uptake of cyanide and phenol for various concentrations of GAC on varying cyanide and phenol concentrations. From the figures it is evident that the specific uptake was decreased beyond GAC dose of 20 g/L for low concentrations of compounds. However for higher initial concentrations, there was reduction in rate of decrease of specific uptake. It was

observed from the graphs that at higher concentrations the specific uptake remained constant even at higher concentrations.

The maximum specific uptakes for adsorption of cyanide and phenol for GAC under the given experimental conditions were 6.38 and 6.33 mg/g, respectively. Increase in the adsorbent dose results in the increase in the number of active sites, which lead to increase in the percentage removal of cyanide and phenol. However no significant increase in the percentage removal was observed with the increase in adsorbent concentration beyond 30 g/L. This may be due to the two stages of cyanide and phenol adsorption (i.e. fast formation of monolayer followed by slow plateau stage)<sup>24</sup>. Also it was observed that the specific uptake of cyanide and phenol was not much higher after minimum GAC dosage of 30 g/L. Hence, the optimum dose of GAC for removal of cyanide and phenol from mixture could be taken as 30 g/L GAC. It was also observed that the specific uptake of cyanide on GAC surface was slightly higher than that of phenol but the difference was negligible.

**Effect of Time of contact:** The contact time between the adsorbent and the pollutants is of significant importance in the treatment of effluent by adsorption. An establishment of equilibrium in short period by rapid uptake of the pollutants signifies the efficiency of the adsorbent being used in the effluent treatment. Figures 5 and 6 present the plots of percentage cyanide and phenol removal against contact time of GAC at an adsorbent concentration of 30 g/L at various initial cyanide and phenol concentrations at optimum pH and temperature conditions. It was observed from figure 5 that

cyanide removal is a slow process and equilibrium was achieved only after 36 h. For phenol, from figure 6, it was observed that equilibrium condition was reached at about 18-24 h.

Generally in physical adsorption most of the adsorbate species are adsorbed within a short time of exposure<sup>23</sup>. However chemisorption requires a longer contact time for achieving a strong chemical bond and hence attaining equilibrium. The adsorption results show that the uptakes of both adsorbate species were fast at the initial stage of contact time and there after became slower near the equilibrium. In between these two stages of uptake, the rate of adsorption was found to be nearly constant. This phenomenon is because of availability of large number of vacant sites in the initial stages of adsorption and competition for the remaining active surfaces in the later stages<sup>25</sup>. The repulsive forces between the solute matter of solid and bulk phase also hinders the remaining vacant sites from being occupied. The resistance to mass transfer between the bulk phase and solid is overcome by the energy provided by agitation to bring the cyanide and phenol species from bulk of solutions to active sites of adsorbent<sup>12</sup>. However, at the initial stage, percent removal of cyanide and phenol increased very fast with increase in contact period due to combination of all the above effects. From all these plots it was found that the adsorptive removal of cyanide and phenol ceases after 36 h and 24 h respectively with an adsorbent concentration of 30 g/L.

Dash et al. studied the adsorption of various cyanides on GAC and observed that NaCN achieved equilibrium only after 42 h<sup>10</sup>. Srivastava et al. studied the adsorption of phenol on GAC. Equilibrium adsorption was reported in

about 5 h<sup>14</sup>. Thus we could conclude that the presence of phenol did not bring any significant change in the contact time of adsorption of cyanide but the presence of cyanide provided competition for phenol adsorption increasing the time before equilibrium is achieved.

## Conclusion

Cyanide (NaCN) adsorbed in alkaline conditions and phenol adsorbed in acidic conditions. The optimum pH for simultaneous adsorption of cyanide and phenol is 8. Temperature does not have significant effect on the adsorption of cyanide but in case of phenol, adsorption increases with the increase in temperature. Optimum temperature conditions for adsorption of cyanide and phenol are in range of 35 (±1) °C. Though the percentage removal of pollutant increases with the increase in adsorbent dose, the specific uptake decreased considerably on adsorbent dose greater than 30 g/L. Equilibrium adsorption time for cyanide and phenol are 36 h and 24 h respectively. Presence of cyanide increases the contact time before which equilibrium adsorption of phenol is achieved. No significant removal is shown beyond 300 mg/L of cyanide and phenol. Thus GAC could be utilized for treatment of dilute solutions of cyanide and phenol.

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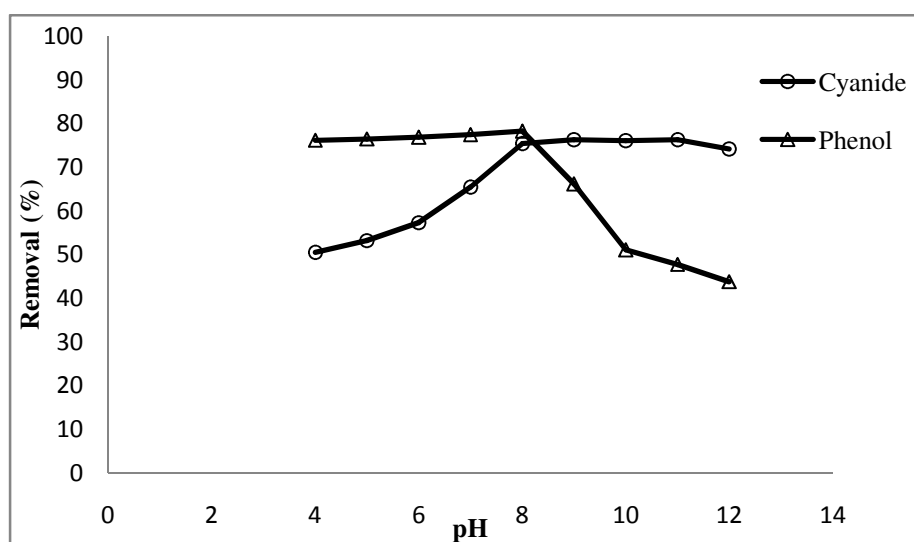


Figure 1: Effect of pH on adsorption of Cyanide and Phenol ( $C_{i, CN} = 100$  mg/L,  $C_{i, Phenol} = 100$  mg/L,  $P_c = 4-5$  mm,  $D_c = 30$  g/L,  $t_c = 72$  h)

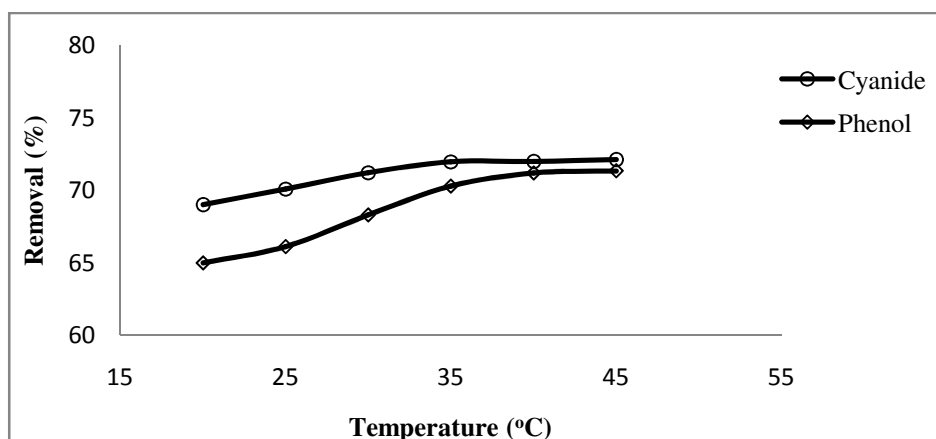


Figure 2: Effect of temperature on adsorption of Cyanide and Phenol ( $C_{i, CN} = 100$  mg/L,  $C_{i, Phenol} = 100$  mg/L,  $P_c = 4-5$  mm,  $D_c = 30$  g/L,  $t_c = 72$  h)



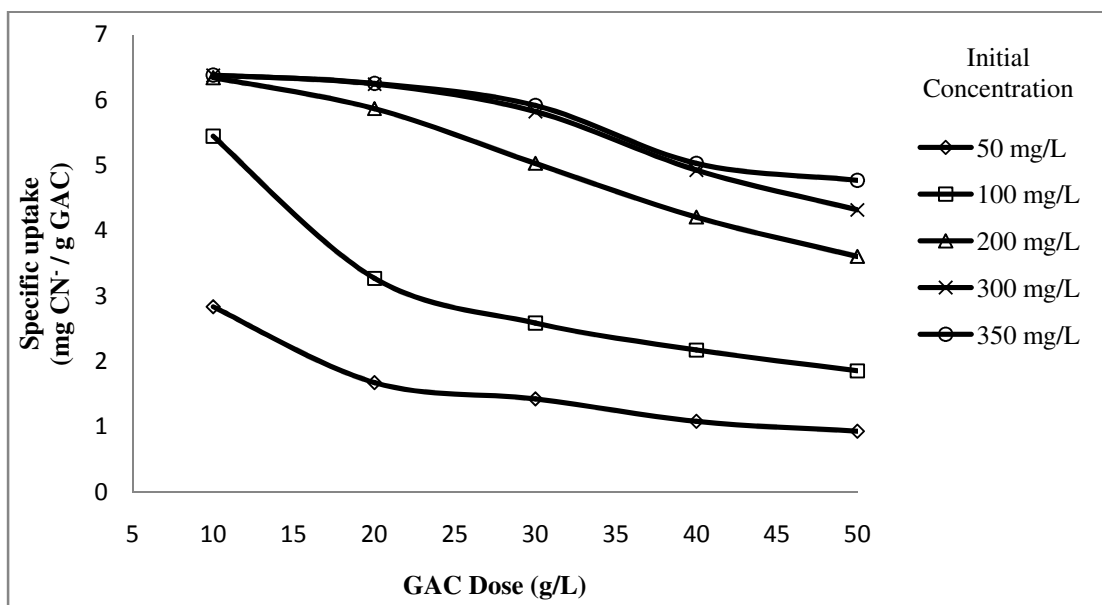


Figure 3: Specific uptake of cyanide (NaCN) on GAC (  $P_c = 4-5$  mm,  $t_c = 72$  h)

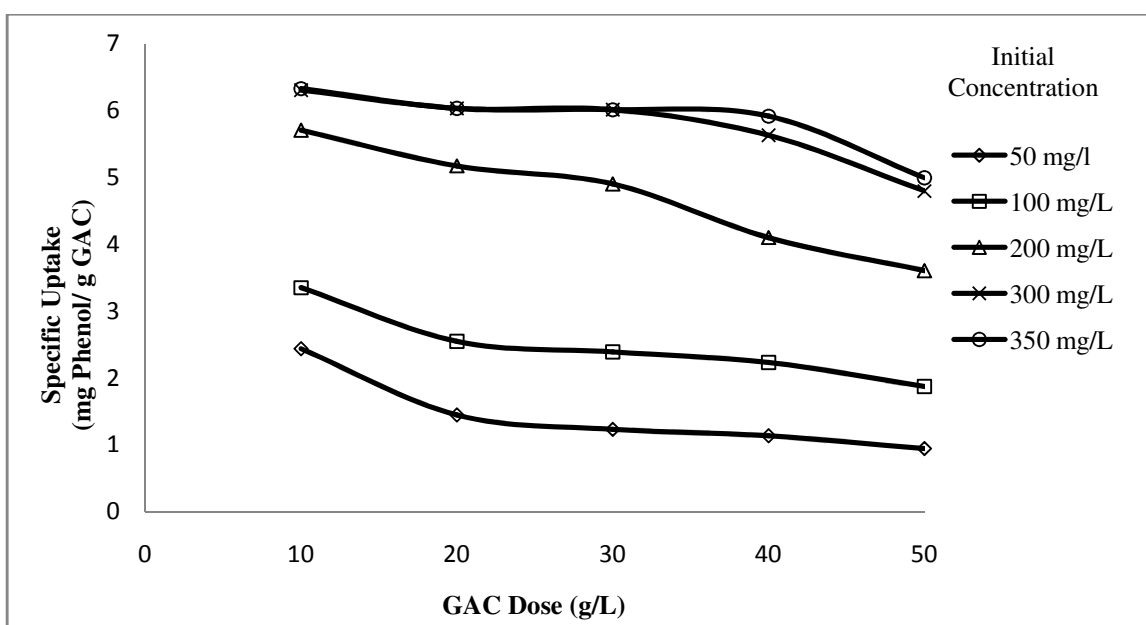


Figure 4: Specific uptake of Phenol on GAC (  $P_c = 4-5$  mm,  $t_c = 72$  h)

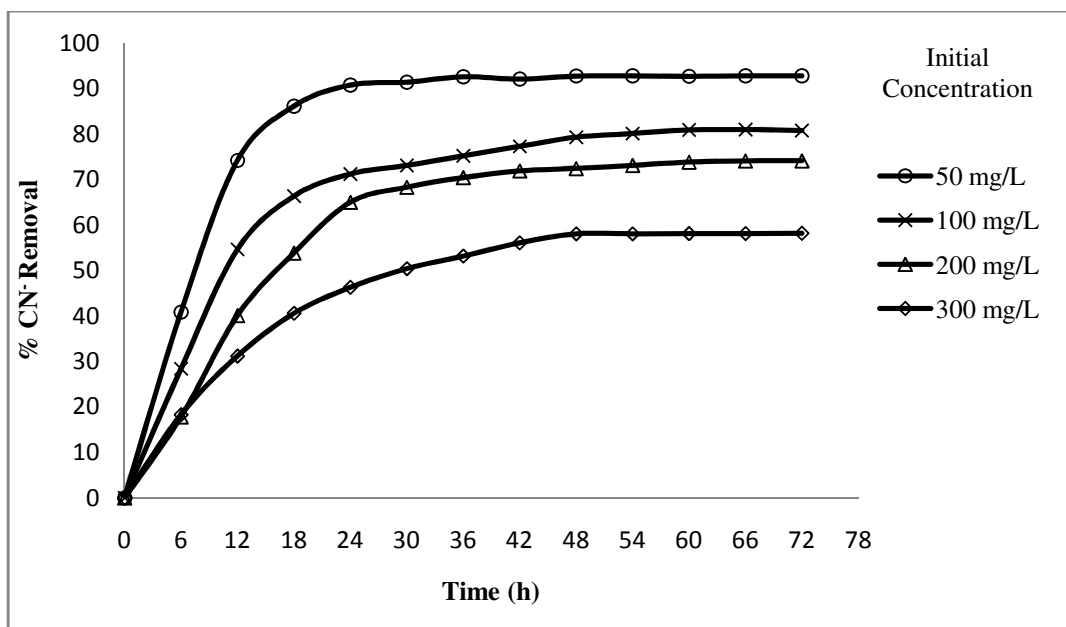


Figure 5: Effect of contact time on adsorption of cyanide (NaCN) on GAC ( $P_c = 4-5$  mm,  $D_c = 30$  g/L)

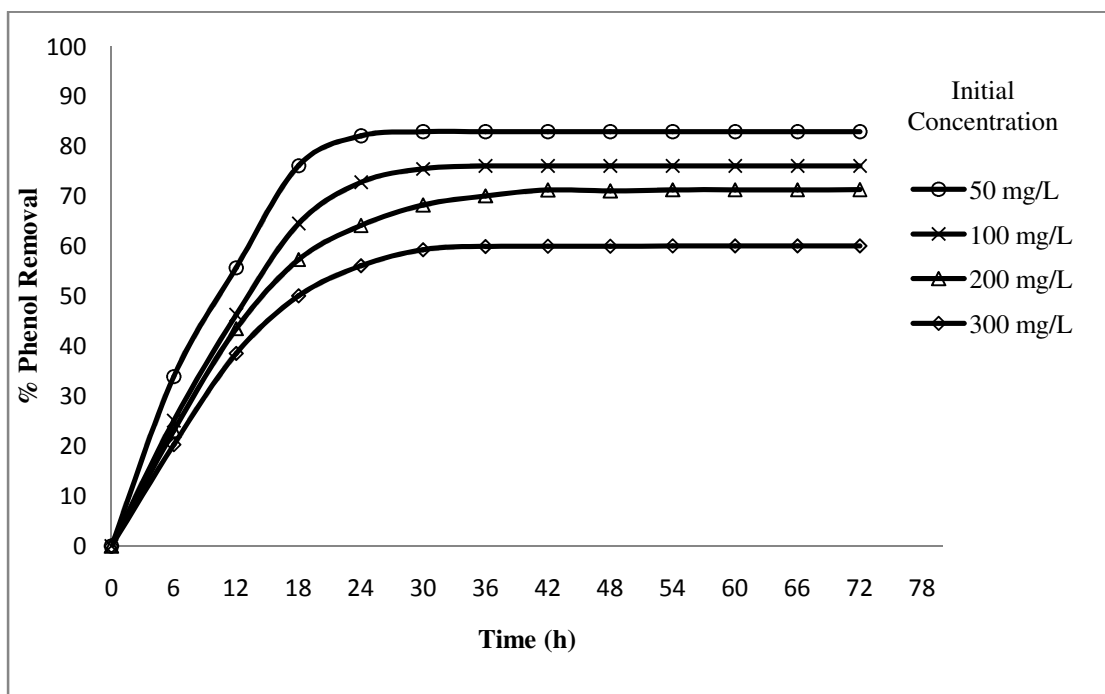


Figure 6: Effect of contact time on adsorption of Phenol on GAC ( $P_c = 4-5$  mm,  $D_c = 30$  g/L)