

# Physico-chemical Treatment of Tar-Containing Wastewater Generated from Biomass Gasification Plants

Vrajesh Mehta, and Anal Chavan

**Abstract**—Treatment of tar-containing wastewater is necessary for the successful operation of biomass gasification plants (BGPs). In the present study, tar-containing wastewater was treated using lime and alum for the removal of in-organics, followed by adsorption on powdered activated carbon (PAC) for the removal of organics. Lime-alum experiments were performed in a jar apparatus and activated carbon studies were performed in an orbital shaker. At optimum concentrations, both lime and alum individually proved to be capable of removing color, total suspended solids (TSS) and total dissolved solids (TDS), but in both cases, pH adjustment had to be carried out after treatment. The combination of lime and alum at the dose ratio of 0.8:0.8 g/L was found to be optimum for the removal of in-organics. The removal efficiency achieved at optimum concentrations were 78.6, 62.0, 62.5 and 52.8% for color, alkalinity, TSS and TDS, respectively. The major advantages of the lime-alum combination were observed to be as follows: no requirement of pH adjustment before and after treatment and good settleability of sludge. Coagulation-precipitation followed by adsorption on PAC resulted in 92.3% chemical oxygen demand (COD) removal and 100% phenol removal at equilibrium. Ammonia removal efficiency was found to be 11.7% during coagulation-flocculation and 36.2% during adsorption on PAC. Adsorption of organics on PAC in terms of COD and phenol followed Freundlich isotherm with  $K_f = 0.55$  &  $18.47$  mg/g and  $n = 1.01$  &  $1.45$ , respectively. This technology may prove to be one of the fastest and most techno-economically feasible methods for the treatment of tar-containing wastewater generated from BGPs.

**Keywords**—Activated carbon, Alum, Biomass gasification, Coagulation-flocculation, Lime, Tar-containing wastewater.

## I. INTRODUCTION

WITH the gradual depletion of fossil fuels, biomass based energy generation (biomass gasification) is receiving global attention. Biomass gasification holds huge potential for rural electrification projects, especially in third world countries like India and China, where biomass supplies are abundant (agricultural products) and where electricity supply from the grid is not available.

The process of biomass gasification converts biomass into a gaseous fuel called producer gas having calorific value in the range of 4.7-5.0 MJ/Nm<sup>3</sup> [1]. Producer gas produced from

different fuels (wood, coconut shell, rice husk etc.) in different gasifier types (up-draft, down-draft etc.) may considerably vary in composition. Producer gas in its raw form tends to be extremely polluted, containing significant quantities of tars, soot and ash. These contaminants must be removed from the producer gas before it enters the internal combustion engine or gas engine, so that engine damage and high degree of engine maintenance may be avoided [2,3]. Thus, gas cleaning is an important component of any biomass gasification plant (BGP). Gas cleaning is performed in different systems, including water scrubbers & wet electrostatic precipitators. These systems use water for cleaning these contaminants; this, in turn, leads to the generation of wastewater. This wastewater is typically loaded with various contaminants and must be treated before being released into the environment. Thus, study on wastewater treatment from BGPs is very important and needs attention.

Wastewater generated from BGPs consists of organic as well as inorganic compounds. The main component of organic contaminants is tar. Tar can be considered as a mixture of several acidic, basic and neutral compounds. The acidic components include acids and phenols, basic include nitrogen containing compounds and neutral components include poly-aromatic compounds (PAHs) [4]. The main component of inorganic residues is ammonia and small concentrations of H<sub>2</sub>S and chlorides [5]. Many of these compounds of concern resist biological degradation and may exert significant toxicity towards micro-organisms in biological treatment. The same characteristics which render these target compounds resistant to biological treatment make them amenable to removal through physical or chemical methods [6].

Physical treatment involving the use of UV light-induced wet oxidation or adsorption on various coke sorbents was recommended to treat this type of wastewater. However, electric energy consumption is relatively high for the UV light-induced wet oxidation, and adsorption has certain limitations due to the presence of non-adsorbable compounds [7].

Chemical precipitation using various salts of Fe and Al promote formation of flocs and reduce the concentration of colloidal and particulate matter in the wastewater. In spite of its short retention times and low capital costs, chemical treatment for effluents from BGPs has received less attention. This can be attributed to three major factors: high cost of chemicals for precipitation as well as pH adjustment; insufficient proof of efficiency of the treatment technique;

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generation of chemical sludge that must be treated before disposal. Chemical oxidation of tars by  $H_2O_2$  was investigated in lab-scale units. However, due to the high operating costs, these processes have not yet been accepted [8].

The goal of this study is to demonstrate the efficiency of the physico-chemical treatment system (coagulation-flocculation followed by adsorption) for tar-containing wastewater generated from BGPs. The efficiency of the treatment system was measured in terms of maintenance of neutral pH, and removal of total suspended solids (TSS), total dissolved solids (TDS), color, alkalinity, ammonia, chemical oxygen demand (COD) and phenol. These parameters are very important, as most of the BGPs carry out recirculation of treated wastewater for gas cleaning [9]. If these constituents are not removed at the treatment plants efficiently, it can result in poor efficiency of both the gas cleaning system and the gasification process. The specific technical objectives of this study are:

1. Identify the optimum individual doses of lime and alum (coagulant) required to achieve the best treatment efficiency.
2. Identify the optimum and minimum dose of the coagulant-combination (lime and alum) required to achieve good treatment efficiency without having to conduct final pH adjustment.
3. Determine the efficiency of the coagulation-flocculation process at optimum coagulant dosage followed by adsorption on powdered activated carbon (PAC).

According to our knowledge, this is the first paper reporting lime-alum treatment followed by adsorption on PAC as the complete treatment for tar-containing wastewater generated from BGPs. Moreover, most of the studies use either lime alone or alum alone for precipitating pollutants present in wastewater. However, this study shows the efficiency of wastewater treatment when alum and lime are combined, which avoids the requirement of pH adjustment after the treatment.

## II. MATERIALS AND METHODS

### A. Source and Characteristics of Wastewater

All the experiments were performed on the wastewater collected from a BGP installed in Bangalore, India. The organics present in wastewater were determined using Gas Chromatography-Mass Spectrometry (GC-MS) (GC-17A. MS-QP 5000, Shimadzu, Japan) at Shiva Analyticals (India) Ltd., Bangalore. The sample was extracted in dichloromethane and was injected (1  $\mu$ L) into GC-MS without concentrating it by evaporation. GC-MS was equipped with Electron Impact Detector (EID). The injector temperature was set at 250 $^{\circ}$ C and interface temperature was set at 300 $^{\circ}$ C. The oven temperature program was as follows: initial temperature 40 $^{\circ}$ C with hold time 5 min, ramping at 5 $^{\circ}$ C/min up to 280 $^{\circ}$ C with hold time 0 min. MS analytical conditions were maintained at scan interval of 0.2, scan speed of 2000 amu/sec and mass range of 20-400.

### B. Coagulation-flocculation Experiments

A jar apparatus was utilized for performing all coagulation-flocculation experiments. Two sets of experiments were performed in this study. First, lime and alum were individually used as coagulants at various concentrations: 0.1, 0.2, 0.4, 0.6, 0.8, 1, 2, 3, 4 and 5 g/L. The concentrations were within the range reported in the literature [10,11]. Secondly, at optimum dosage of lime and alum, combined treatment using lime and alum was performed at various dose ratios.

In all these experiments, initial pH adjustment was not performed. All the experiments were performed at the initial pH of 7.4-7.6 and at ambient temperatures. The wastewater was first mixed to ensure a homogeneous sample. One liter sample was drawn into a beaker and placed on a Jar apparatus. Appropriate amount of coagulant (lime/alum) was added and allowed to mix rapidly at 140 rpm for 5 min. In the lime-alum combination, lime was added first and rapid mixing was performed at 140 rpm for 5 min, followed by addition of alum and rapid mixing at 140 rpm for 5 min. In both the experiments, rapid mixing was followed by slow mixing for flocculation at 30 rpm for 30 min. The flocs formed after these coagulation-flocculation processes were allowed to settle down for 30 min. The supernatant was analyzed for various parameters.

### C. Adsorption Experiments

The effluent was treated with the optimum dose of the combination of lime and alum followed by adsorption on PAC. The iodine value of PAC was 1050 mg/g. Pretreated wastewater (100 mL) was added into a series of Erlenmeyer flasks for adsorption experiments. About 2.0 g of PAC was added into the flasks and shaken at 120 rpm in an orbital shaker. Every 10 min, a known amount of solution was taken from the mixtures and analyzed to obtain various parameters. The flasks were shaken at 120 rpm till equilibrium was attained. Adsorbent (0.25–2.0 g) was added to a series of Erlenmeyer flasks (each of which contained 100 mL of pretreated wastewater) and treated for equilibrium time. After equilibrium was reached, the solutions were later centrifuged at 7800 rpm for 10 min to separate the adsorbent. The supernatant was analyzed for various parameters.

### D. Sample Analysis

All the effluent parameters were measured as per standard methods for examination of water and wastewater [12]. The instruments used for measuring pH, TDS, conductivity were pH probe (Eutech Instruments, CyberScan, Singapore), TDS meter (Eutech Instruments, TDS Testr, Singapore) and conductivity meter (Eutech Instruments, EC Testr 11+, Singapore), respectively. Color was analyzed at 456 nm with a visible spectrophotometer (Thermo Scientific, Genesys 20, USA) and calibrated against platinum-cobalt standards. Phenol was analyzed using the amino-antipyrine method [12].

## III. RESULTS AND DISCUSSION

### A. Characteristics of Wastewater

Effluents from BGPs are typically grayish-black in color, with fine particles and exert more oxygen demand. The

wastewater characteristic is reported in Table I. High  $COD_{soluble}/COD_{total}$  shows that a major part of the organics was present in the dissolved form. The total ion chromatogram (TIC) profile of the sample is demonstrated in Fig. 1. The TIC revealed the presence of o-cresol (RT: 5.31 min), m-cresol (RT: 5.89 min), 2,6-xyleneol (RT: 7.13 min), 2,4-xyleneol (RT: 7.17 min), 4-Ethyl Phenol (RT: 7.56 min), o-tolualdehyde (RT: 8.46 min), p-tolualdehyde (RT: 8.65 min) and ethyl benzaldehyde (RT: 9.78 min). The integration of the GC-MS profile with the library revealed the dominance of three organics: m-cresol, o-cresol and 2-ethyl benzaldehyde. Presence of isomers of phenols is in agreement with the results reported by Jayamurthy et al. [4]. However, presence of 2-ethyl benzaldehyde in this wastewater was not reported by Jayamurthy et al. [4].

### B. Qualitative Description

The characteristics and appearance of the sludge and effluent were found to be different for different treatment methods. During lime treatment, yellowish white precipitates formed immediately and settled very rapidly. However, at high concentrations of lime (2 g/L and above), a slimy layer was found in the supernatant of the treated effluent. During alum treatment, sludge settleability was found to be poor. At high concentrations of alum, aggregates that formed settled after 1 hr of sedimentation time; at low concentrations, the aggregates required 10-12 hrs for settling. After sludge settlement, the supernatant was cloudy in appearance. While the supernatant from lime treatment was found to be yellowish in color, the supernatant from alum treatment was found to be grayish in color. In lime-alum treatment, supernatant was found to be yellowish in color and the flocs formed were compact.

### C. Optimum Coagulant Dosage

The optimum dose of coagulant depends upon the type of wastewater, pH, coagulant, as well as the criteria chosen to determine the optimum dose. The optimum dose of lime was found to be 0.8 g/L, with maximum removal efficiency for color, TSS and TDS, and minimum amount of sludge generation. The optimum dose of alum was observed to be 0.8 g/L with maximum TSS, TDS and minimum amount of sludge generation. However, the optimum dose of alum for maximum color removal was found to be 1.0 g/L. Lime was found to remove ammonia more efficiently than alum. In the lime-alum combination, lime:alum dose of 0.8:0.8 g/L was found to demonstrate maximum removal of TSS, TDS, alkalinity, and minimum amount of sludge generation. However, the lime:alum dose of 0.9:1.0 g/L provided maximum removal of color and ammonia. The coagulation-flocculation process was found to be more efficient for the removal of color, TDS, TSS and alkalinity than for the removal of COD and phenol.

**pH and Alkalinity:** Generally, in coagulation-flocculation experiments, pH adjustment is performed before treatment [10, 11]. However, the present study did not follow a similar

Parameter	Unit	Values
pH	--	7.49 ( $\pm 0.015$ )
Color	Co-Pt unit	1076.5 ( $\pm 38.5$ )
TDS	mg/L	1875 ( $\pm 75$ )
TSS	mg/L	82.5 ( $\pm 2.5$ )
Alkalinity (as $CaCO_3$ )	mg/L	537.5 ( $\pm 12.5$ )
Ammonical Nitrogen	mg/L	242.55 ( $\pm 12.45$ )
Nitrate nitrogen	mg/L	0.62 ( $\pm 0.02$ )
Phosphate (as $PO_4^{3-}$ )	mg/L	0.12 ( $\pm 0.03$ )
$COD_{total}$	mg/L	3599.5 ( $\pm 57.5$ )
$COD_{soluble}$	mg/L	3499.5 ( $\pm 57.5$ )
Phenol	mg/L	465 ( $\pm 10$ )
Oil and Grease	mg/L	36 ( $\pm 4.0$ )

Note: Values in parenthesis are standard deviation

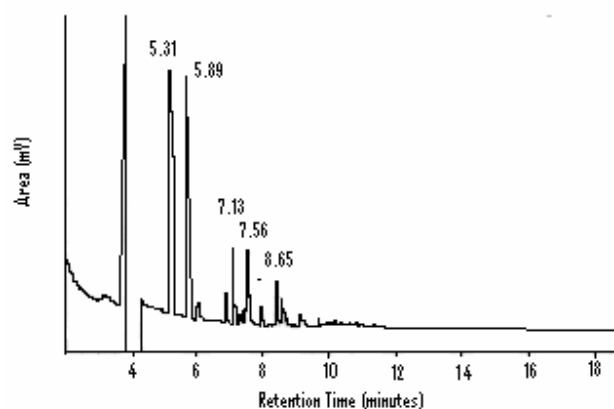


Fig. 1 TIC profile of effluent from biomass gasification plant

procedure since the objective of this study was to obtain the best treatment efficiency for the removal of color, TSS, TDS, alkalinity, ammonia, phenol and COD while minimizing the usage of chemicals. The initial pH of the raw wastewater was 7.49. Generally, pH of the wastewater increases with increase in lime concentration and decreases with increase in alum concentration. An increase in the concentrations of lime and alum from 0.2 to 3.0 g/L caused the pH of the wastewater to respectively increase from 8.18 to 11.85 and decrease from 7.25 to 4.40 (Fig. 2 a). At optimum individual concentrations of lime (0.8 g/L) and alum (0.8 & 1 g/L), the final pH of the effluent was not found to be in the neutral range (6.5-8.5).

When the combination of lime and alum was used for treatment, for the lime: alum (g/L) doses of 0.8:0.8, 0.8:1.0 and 0.9:1.0, the wastewater pH was found to be in the neutral range (Fig. 3). At all these ratios, high removal efficiencies in terms of alkalinity (60-62%) were observed. This indicates that at these ratios, most of the hydroxide alkalinity got precipitated resulting in low alkalinity in the supernatant. For all other dose ratios, pH was found to be above 8.5, resulting in high alkalinity in the effluent. Alkalinity removal was found to be significantly better in lime-alum treatment than in lime treatment (Table II). Thus, alum played an important role

in reducing the alkalinity and ensuring that the effluent pH is in the neutral range.

**Color Removal:** The high concentration of color was possibly due to dissolved recalcitrant organics, such as PAHs. There was a sharp decrease in the concentration of color with increase in lime and alum concentrations initially (Fig. 2b). During lime treatment, the efficiency of color removal was found to rise with increase in lime concentration up to 0.8 g/L, with minimum color of 250 Co-Pt unit. Removal efficiencies were found to be in agreement with results reported by Sapci and Ustun [13] for the removal of color from textile wastewater. Moreover, high color removal efficiencies (92%, with effluent color of 760 ppm) were demonstrated when highly colored effluents generated from paper industries were treated using very high concentrations of lime (20.5 g/L) [14]. The optimum lime dose for reducing the color to 1000 Pt-Co unit was found to be 10.0 g/L in effluents from fermentation industries [15]. In contrast to all the above studies, Asilian et al. [16] demonstrated that lime alone did not cause significant change in the efficiency of color removal from wastewater containing water base color.

Alum treatment was found to be more efficient in color removal compared to lime treatment; alum treatment resulted in minimum color of 96.15 Co-Pt units at 1.0 g/L (Fig. 2). The color-removal efficiency obtained in this study (91.4%) was found to be much higher than reported (54.9%) at the same pH and optimum alum concentration [17]. Furthermore, at a similar concentration of alum (0.6 g/L), this study reports higher color removal efficiencies (70.7%) than reported by Aziz et al. (60.4%) [17]. However, the initial concentration of color reported by Aziz et al. (6450 Co-Pt units) was found to be higher than that reported by this study (1115.4 Co-Pt unit). The efficiency of color removal attained in the present study was found to be in the range observed by Dwyer et al. [18] for the removal of melanoidin from wastewater at pH 6-7. Ghaly et al. [19] reported optical density (OD) as an indication of color present in grease filter wash-water. The optimum dose of alum (2 g/L) observed for reduction in OD was found to be double than that used in the present study (1 g/L) at pH of 4.2. The current study reports greater color-removal efficiency (91.37%) at low alum concentration (0.8 g/L) than that (60%) reported by Mutlu et al. [20] for the treatment of wastewater from baker's yeast plant at alum concentration of 4 g/L.

The combination of lime-alum demonstrated no significant difference in color-removal efficiency at various lime-alum dose ratios ( $t > t_{\alpha,95\%}$ , based on paired t-test) (Fig. 4). Removal efficiency was not very different from lime treatment alone at lime concentration of 0.8 g/L, but was found to be significantly different at high lime concentration of 1.0 g/L. Maximum color removal efficiency of 86.21% was achieved at lime: alum dose of 0.9:1.0 g/L.

**TSS, TDS and TS Removal:** TSS can play an important role in clogging the gas cleaning systems if not efficiently removed in the wastewater treatment plant. Moreover, inefficient removal of TDS can cause scaling in the whole system.

The concentration of TSS in the wastewater was not found to be high. However, it was observed that suspended solids were fine particles with poor settleability. Lime treatment was

found to remove TSS more efficiently than alum treatment. Lime treatment at the optimum concentration resulted in minimum TSS of 10 mg/L; however, alum treatment at the optimum concentration resulted in minimum TSS of 30 mg/L (Fig. 2c). Thus, maximum TSS removal efficiency observed in this system was 87.5%. Researchers reported higher TSS removal efficiencies with other coagulants, such as  $\text{FeCl}_3$  (>90%) compared to alum (~75%). For the treatment of other parameters, alum was found to be a better coagulant than  $\text{FeSO}_4$  [17,21]. Liu and Lien [22] observed 85.9% removal of TSS from bakery wastewater using alum (0.07 g/L) at pH 6 and removal efficiency was found to increase with rise in alum concentration. In this study, during lime treatment, it was however revealed that a thin layer of solids formed in the supernatant when the concentration of lime was increased beyond the optimum of 0.8 g/L. It was suspected that this may have occurred due to the re-stabilization of colloids; this re-stabilization can be caused by charge reversal of particulates [23]. Such an observation was not reported in the literature.

TDS concentration was found to decrease with increase in lime concentration up to 0.8 g/L. However, further increase in lime concentration resulted in a marked increase in TDS levels (Fig. 2c). A similar trend was observed during alum treatment with stabilization of TDS levels (1400-1450 mg/L) at 0.6-0.8 g/L of alum (Fig. 2c). As TSS in this effluent was found to be less, total solids were observed to follow a pattern similar to that of TDS. This outcome supported the one reported by Ghaly et al. [19], where the addition of alum resulted in an initial reduction (3385 to 2358 mg/L) and later increase (2358 to 3088 mg/L) in TS concentration. In addition, during lime and alum treatment, it was found that there was a sharp increase in TDS concentration beyond optimum concentrations (0.8 mg/L for lime and 0.8 mg/L for alum). This was found to be in co-ordination with the sudden increase and decrease (in pH and alkalinity) in the case of lime and alum treatment, respectively. This may be due to the attainment of the saturation point (for removal) at optimum concentrations. Addition of the coagulant beyond optimal concentrations led to the accumulation of excess un-reacted coagulant, leading to high TDS levels in the effluent. However, such an observation was not reported in the literature.

In lime-alum treatment, at various dose ratios, there was no improvement in terms of removal of TSS compared to treatment with either lime alone or alum alone. However, improved removal efficiencies were observed in TDS levels. TDS removal efficiency was found to be 50.3% at optimum lime:alum dose of 0.8:0.8 g/L compared to 38.8% at optimum lime concentration of 0.8 g/L (Table II). Moreover, at constant concentration of lime, increase in alum concentration resulted in decrease in the efficiency of TDS removal. Thus, lime was found to play an important role in TDS removal.

**COD and Phenol Removal:** When either lime alone or alum alone was used for treating the wastewater, COD removal was found to be negligible during the coagulation-flocculation

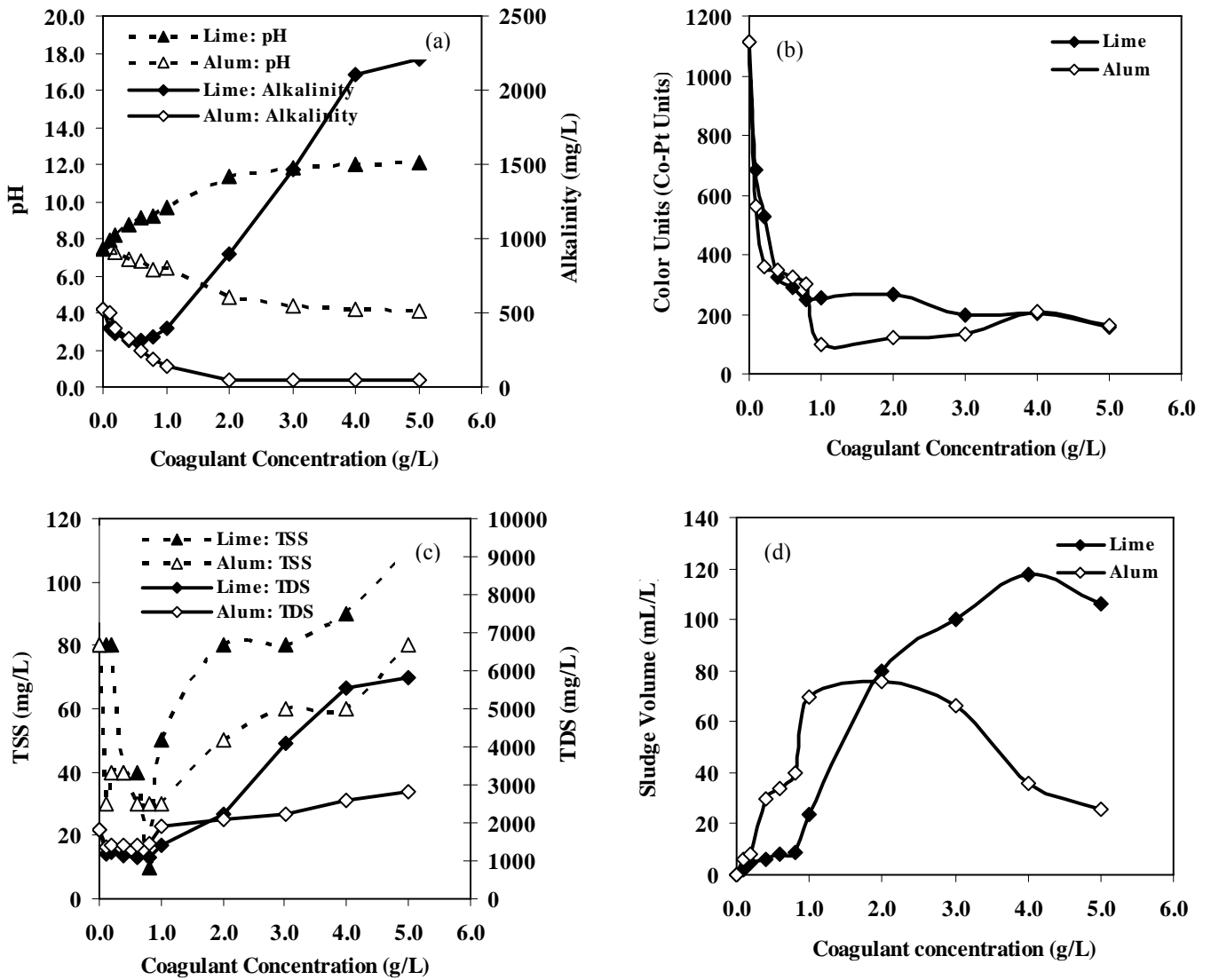


Fig. 2 Treatment of tar-containing wastewater using lime and alum at various concentration: effect on (a) pH and alkalinity, (b) color, (c) TSS and TDS and (d) sludge volume

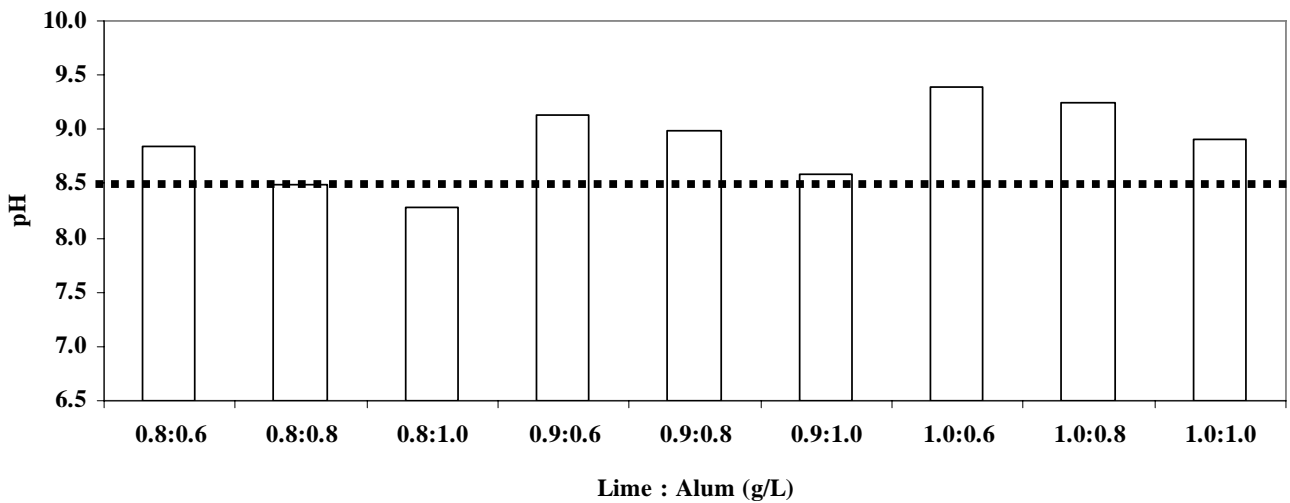


Fig. 3 pH profile of the effluent at various lime: alum doses

process. However, lime was found to perform better than alum in COD removal, with minimum effluent COD of 2743 mg/L and 2857 mg/L respectively. This contradicts the observation described in the literature for the treatment of municipal wastewater [24]. At lime:alum dose of 0.8:0.8 g/L, the maximum COD removal efficiency achieved was 24.03%, with effluent COD of 2691 mg/L (Fig. 4). The literature reports that during the treatment of landfill leachate, 26.9% removal of COD was achieved using high alum concentration of 2.5 g/L and improved COD removal was achieved using  $\text{FeCl}_3$  at the same concentration [17]. Moreover, Zazouli and Yousefi [25] also demonstrated very low COD removal efficiencies from 7 to 15% using 1.4 g/L alum for the solid waste leachate. In the present study, it was revealed that percent decrease in COD was not proportional to percent decrease in color. This contradicts the observation reported by Aziz et al. [17] during leachate treatment. This indicates that COD is mainly because of the presence of organics which are not contributing to the color in the wastewater.

Phenol removal was also found to be insignificant during lime, alum and lime-alum treatment at various concentrations. Lime-alum combination demonstrated better removal efficiencies than either lime or alum alone. At optimum lime:alum dose (0.8:0.8 g/L), phenol removal efficiency of 15.8% was achieved (Fig. 4). During the treatment of olive-mill effluent, coupling lime with cationic poly-electrolytes (200–300 mg/L) led to phenol removal of 30–80% [26]. High treatment efficiency (in removing the phenolic compounds from rubber-textile wastewater) was obtained by using  $\text{FeCl}_3$  and lime at various dosages [27].

**Ammonia Removal:** Increased lime concentration resulted in increased efficiency of ammonia removal. This was associated with the rise in pH. Maximum ammonia removal efficiency was achieved at 2 g/L lime with 63.72% removal at pH of 11.39 (Figure not shown). In contrast, increase in alum concentration led to poor ammonia removal efficiencies due to acidic character of  $\text{Al}^{3+}$  cations leading to low pH. The combination of lime-alum treatment resulted in poor ammonia removal efficiency compared to lime treatment at optimum concentration. Thus, lime-alum treatment showed negligible benefit for ammonia removal, although it was found to benefit to a greater extent in the case of TDS and alkalinity removal.

**Sludge volume and settleability:** Amount of sludge generated and sludge-settleability are important parameters, as they are associated with treatment and disposal cost. The sludge volume was found to increase with increase in lime concentration. However, during alum treatment, the sludge volume was found to increase up to 2 g/L and then reduce gradually (Fig. 2d). This may be due to good compactness of the sludge at high concentrations of alum. The amount of sludge generated at optimum lime concentration (9 mL/L) was found to be significantly less than that produced at optimum alum concentration (40 mL/L) (Fig. 2d). Lime-alum treatment resulted in good compact sludge with better settleability compared to alum treatment. Similar results were reported by Ozbelge et al. [27], where adding lime before the coagulant yielded better results in terms of settling behavior of the flocs.

In the present study, during lime-alum treatment, increase in the lime concentration led to a decrease in the sludge volume generated. At the optimum lime:alum dose of 0.8:0.8 g/L, the amount of sludge generated was found to be 85 mL/L.

### C. Adsorption on Activated Carbon

Adsorption on PAC was found to play an important role in removal of COD and phenol. The time scale required for achieving equilibrium through kinetic studies conducted in multiple completely mixed batch reactors (CMBR) was found to be 1 hr, i.e., no further adsorption occurred beyond this time (steady state). Subsequent equilibrium studies were conducted using varying initial concentration of PAC to obtain the sorption isotherm of organics on PAC for a period of 1 hr. The final COD and phenol concentration in this system was measured after equilibration. The  $q_e$  (adsorption capacity) vs  $C_e$  (equilibrium concentration) data was fitted using the Langmuir and Freundlich isotherm models. The Langmuir model did not provide a satisfactory fit to the data. The Freundlich model provided a good fit to the experimental data in terms of phenol ( $r^2 = 0.94$ ) compared to the one obtained in terms of COD ( $r^2 = 0.78$ ). Fig. 5 illustrates the sorption isotherm data and Freundlich isotherm fit for the sorption of organics in terms of COD and phenol on the PAC. The good fit to the Freundlich isotherm demonstrated multi-layer mode of adsorption. Sorption capacity of phenol was found to be high compared to COD. It is indicated by the high value of the Freundlich constant,  $K_F = 0.55$  and 18.47 mg/g for COD and phenol respectively. The  $n$  value of 1.01 and 1.45 indicates energetically favorable sorption for COD and phenol respectively. In the equilibrium assays, the adsorption capacities ( $q_e$ ) for PAC were 618 and 1001 mg/g for COD and phenol respectively. Adsorption isotherms on synthetic solutions containing phenol concentration (125 mg/L) demonstrated adsorption capacities of 117 mg/g for the granular activated carbon and 143 mg/g for the fibrous activated carbon [28]. However, few researchers demonstrated very low adsorption capacity for phenol, i.e., in the range of 1.48 mg/g [29].

The main advantages of the proposed coagulation-flocculation method for the treatment of tar-containing wastewater are: no requirement for pH adjustment before and after treatment, simplicity, low cost, good removal efficiencies, easy operation and low maintenance. This treatment, when followed by adsorption on PAC, was able to achieve the wastewater effluent quality required for disposal into rivers, oceans, sewers and fields (recommended by Central Pollution Control Board, India). However, whether or not the treated wastewater can be re-circulated into the BGP (for gas cleaning) needs to be studied.

## IV. CONCLUSION

The above study demonstrates that physico-chemical treatment is one of the best options to treat the tar-containing wastewater generated by BGPs. The major conclusions from the study include:

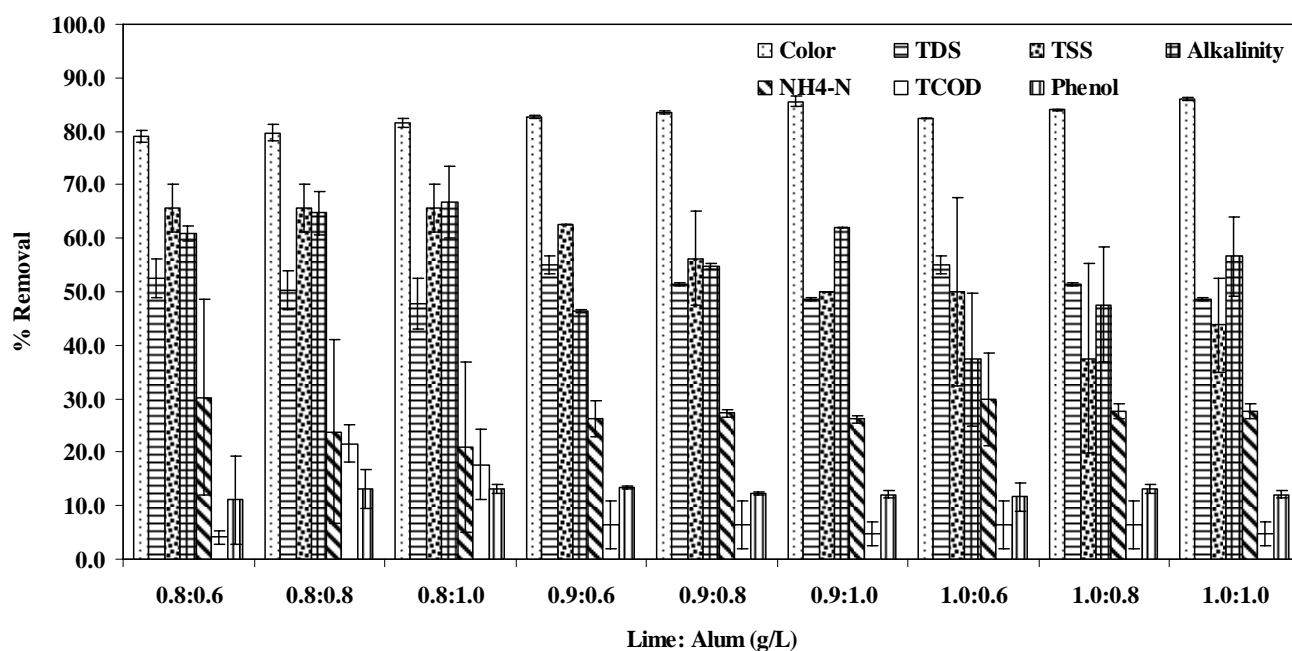


Fig. 4 Removal efficiency for various parameters at various lime: alum ratios

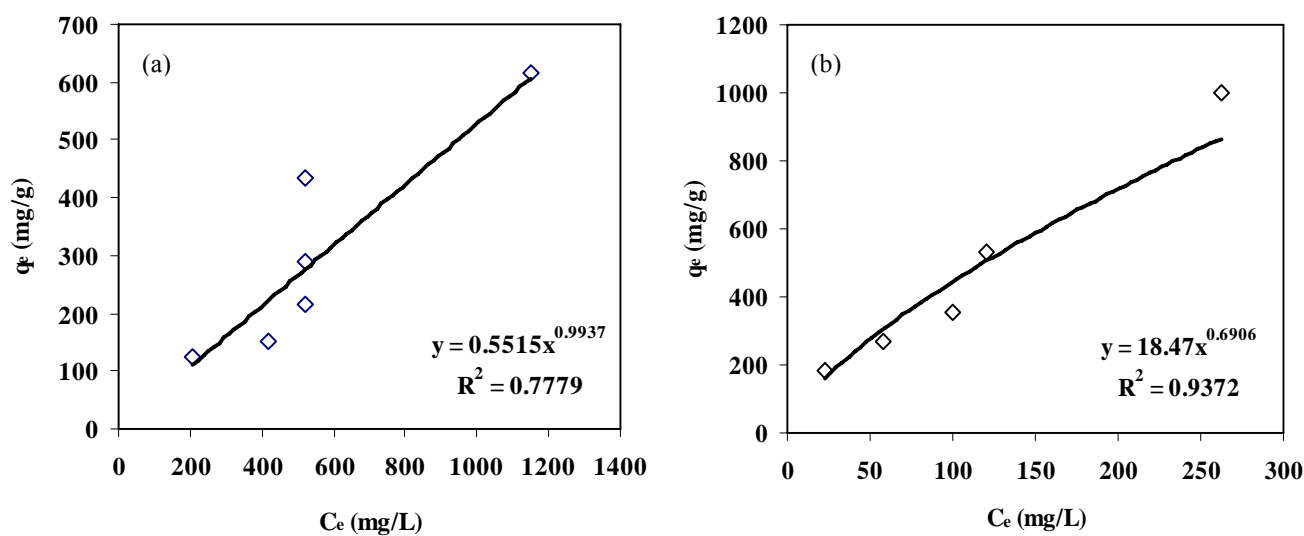


Fig. 5 Equilibrium adsorption isotherms for PAC by the Freundlich model in terms of (a) COD and (b) phenol

TABLE II  
 PERFORMANCE OF THE TREATMENT METHODS AT OPTIMUM CONDITIONS

Treatment Method	Lime (g/L)	Alum (g/L)	Activated carbon (ppm)	pH	Color Removal (%)	TSS Removal (%)	TDS Removal (%)	Alkalinity Removal (%)	NH <sub>4</sub> -N Removal (%)	Phenol Removal (%)	COD Removal (%)
Lime	0.8	--	--	9.18	77.59	87.50	38.88	36.66	28.57	15.47	12.90
Alum	--	0.8	--	6.55	73.10	62.50	19.44	64.76	15.69	6.52	16.13
Lime + Alum	0.8	0.8	--	8.49	79.67	65.62	50.28	64.76	23.87	13.16	21.62
Lime + Alum + Activated Carbon	0.8	0.8	20,000	7.40	98.60	16.66	0.00	20.00	36.17	100.00	92.25

1. The optimum dose of lime-alum combination for the removal of color, TSS, TDS and alkalinity was 0.8:0.8 g/L (lime:alum); however, for obtaining higher ammonia removal efficiencies, 0.9:1.0 (g/L) can be utilized.
2. Good sludge settleability was observed during lime and lime-alum treatments. However, poor sludge settleability was observed in alum treatment at low concentrations.
3. This process requires pH adjustment neither for enhancing the coagulation-flocculation process nor for neutralizing the pH of the wastewater after treatment.
4. Adsorption on PAC follows the Freundlich isotherm, and shows multi-layer adsorption. This adsorption resulted in 92.25% removal of COD and 100% removal of phenol from the wastewater.
5. The efficiency of ammonia removal was found to be 11.7% during the coagulation-flocculation process and 36.2% during adsorption on PAC.
6. The process was found to be simple, low-cost and efficient for the removal of various pollutants present in BGP-generated tar-containing wastewater.
7. The treated wastewater can be easily disposed off into water bodies such as rivers and streams and can also be used for irrigation.
8. Whether or not the treated wastewater can be re-circulated into the BGP for gas cleaning systems needs to be assessed in detail.

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