Eco-Friendly, Economical Viable Chemical Oxygen Demand Reduction Process Using Fly Ash From Industrial and Domestic Waste Water

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Abstract: Reliance on coal as an energy source has led to significant by product management relegated to the storage or disposal of fly ash generated as a result of combustion. Disposal of the ash is a major source of environmental pollution in the areas surrounding the production and disposal site. Therefore an inexpensive by product management technology is needed for the environmentally safe disposal or storage of this material until beneficial uses for this by product are developed. Fly ash has shown quite effective absorbent capacity for COD reduction from the domestic waste water though its capacity lower than that of the activated carbon, The low material cost makes it an attractive option for the treatment of domestic waste water. Hence in the present study was undertaken to identify fly ash as an alternative treatment source. The efficacy of continuous reactor for COD reduction using fly ash with the help of hydraulic free jet was studied .for this purpose a system of standardized continuous reactor under steady state conditions is used to study the effect of this media .for a fixed residence time ,absorbent dose ,pH of the media, and initial COD concentration ,percentage reduction in COD was evaluated. It was found that about 84 percentage reduction in COD Could be achieved under controlled conditions.

KEY WORDS: COD, Fly ash COD Concentration

1.INTRODUCTION

The characterization of the raw waste is essential in planning for effective and economical methods of water pollution control. Due to the varying nature of the industrial wastes, many of the recent installations have designed their treatment units with due consideration to the raw waste characteristics and the effluent characteristics as established by the Bureau of Indian Standards (BIS), State Pollution Control Boards or by local administrative authorities. But the characterization of the municipal waste water prior to a treatment plant design, have not received the attention it deserves, probably because of its lower pollution potential compared to that of industrial waste The organic content of the waste water is also measured by COD. This
parameter as such does not show any chemical identity of the organic matter. During the determination of COD, organic matter is converted to carbon dioxide and water regardless of the biological assimilability of the substances. For example, glucose and lignin are both oxidized completely. As a result, COD values are greater than BOD values and may be much greater when significant amounts of biologically resistant organic matter is present. Generally Ceric sulfate, potassium iodated and potassium dichromate are other oxidizing agents but have been studied extensively for the determination of chemical oxygen demand. Potassium dichromate has been found to be the most practical of all, since it is capable of oxidizing a wide variety of organic substances of almost completely to carbon dioxide and water. Because all oxidizing agents must be used in excess it is necessary to measure the amount of excess remaining at the end of reaction period in order to calculate the amount actually used in the oxidation of organic matter. It is relatively easy to measure any excess of potassium of dichromate, an important point in its favor. In order for potassium dichromate to oxidize organic matter completely the solution must be strongly acidic and at elevated temperature. As a result volatile materials originally present and those formed during the digestion period are lost unless provision is made to prevent their escape. Reflux condensers are ordinarily used for this purpose and allow the sample to be boiled without significant loss of volatile organic compounds. In the present work economically very cheap and toughing martial fly ash is used to Reduce the cod.

Experimental method

2.1 DESCRIPTION OF EXPERIMENTAL SET-UP:

Wastewater of known strength was stored in a tank and pumped to the Mixing Chamber with the help of a Pump. The required flow rate was set by adjusting the surplus flow through a by pass line. The mixing chamber was fabricated out of M.S. sheets and an anti corrosive paint was applied on all internal walls to avoid the corrosive action. The inlet to the mixing chamber was a submerged jet issued through a pipe and the outlet was a suppressed sharp crested weir. The mixing chamber used in the present investigation has a plan area of 1.5m x 1.5m and a liquid depth of 1.0 m. For a proper mixing by a horizontal jet, the optimum depth-wise location of the nozzle could be at three quarters of liquid depth when the liquid depth is equal to the tank diameter. However, the optimum location is at the mid depth of the liquid, when the depth available is smaller than the tank diameter. Moreover, for horizontal position of the nozzle the mixing time was less than that obtained by tilting the nozzle at different angles of inclinations. Failure to establish the desired flow pattern could result in a tangential swirl flow, with very poor top-to-bottom turnover in the vessel. Although tangential swirl may be capable of producing a good mixing, it increases the blend time considerably for a given input power. Further, an incorrectly mounted nozzle may only be satisfactory for providing uniformity of mixing in the lower portion of the vessel. It has been recommended that, the liquid level in the tank should be less than 1.25 times the diameter of the tank or the of the chamber as the case may be. Otherwise it may require either multiple impellers or excessive power (as much as twice the amount necessary for the same degree of mixing). In the present investigation the liquid depth in the mixing chamber
was kept less than axial distance of jet and the jet was injected from its side. Fly ash solution of required strength was stored in a tank and the rate of flow entering the influent pipe to the mixing chamber could be adjusted. It is desirable that fly ash solution be injected rapidly in the plane perpendicular to the receiving stream as a counter-current axial jet. This is because the turbulent velocity intensities in the longitudinal, radial and circumferential directions generally increase from the centre of the pipe towards the wall and would result in more efficient mixing. However, due to practical difficulties in the present case, fly ash solution was injected as a co-current axial jet through a 0.7 mm diameter seamless stainless steel tube with the help of a peristaltic pump, a product of Miclins Pvt Ltd. The flow rate and operation time parameters in the peristaltic pump can be increased or decreased using the Plus or minus key. The desired value of flow rate and time can thus be set on display. The flow rate can be varied from settings of 0.1 to 100 in steps of 0.1 and from 100 to 500 in steps of 1. The time of operation can be varied from 1 minute to 24 hours in steps of 1 minute.
2.2 Experimental Conditions & Results

2.2 (a) PREPARATION OF SYNTHETIC SEWAGE WATER:
Glucose (Dextrose D – Glucose) anhydrous was used to prepare the artificial domestic sewage. It was experimentally proved that glucose imparts chemical oxygen demand to the water (Mall et al., 1994). The COD concentration of these samples were recorded and a calibration chart was prepared which is presented in Fig.(1) This calibration chart was used to predict the required COD concentrations. Fixed quantities of Glucose was added to the water. It was then thoroughly mixed with a magnetic stirrer. Temperature of the synthetic sewage was observed as 23°C. Synthetic wastewater prepared by dissolving glucose in water was characterized for COD, pH and the results are given in the Table.1

![COD vs Glucose Concentration Chart](image)

Table (I) Physico-chemical analysis of synthetic waste water.

<table>
<thead>
<tr>
<th>S.NO.</th>
<th>Parameters</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>pH</td>
<td>7.0</td>
</tr>
<tr>
<td>2</td>
<td>Electrical conductance</td>
<td>2.28</td>
</tr>
<tr>
<td>3</td>
<td>Temperature °C</td>
<td>23.0</td>
</tr>
<tr>
<td>4</td>
<td>Turbidity (NTU)</td>
<td>1.66</td>
</tr>
<tr>
<td>5</td>
<td>Total Suspended Solids (mg/L)</td>
<td>0.0</td>
</tr>
<tr>
<td>6</td>
<td>COD (ppm)</td>
<td>1041</td>
</tr>
</tbody>
</table>
2.3 Determination Of Fly Ash Dosage:

Fly ash was obtained from Vijayawada Thermal Power Plant, Andhra Pradesh. The fly ash was derived out of the bituminous coal. The sample received was washed with distilled water to remove surface dust and dried in sun. Fly ash samples were stored in the laboratory in airtight container. The physicochemical characterization of fly ash was carried out using standard procedures. A Philips PW 1729 X-ray diffraction meter was used for the mineral analysis of the ash samples. The operating conditions were Cu-α radiation, 40 KV voltage and 20 mA current. The samples were scanned from 5 – 60°. The mineral phases were identified based on the Joint Committee Powder Diffraction Standards (1974). A micro structural investigation was carried out to characterize the morphology and texture of the fly ash samples. A JEOL-JSM- 5800 scanning electron microscope (SEM) was used for the study of the fly ash samples (Arpita et al., 2002). The scanning electron microscope was equipped with an X-ray fluorescence detector for energetic dispersion (EDS) for compositional analysis. The operating conditions were 20KV and energy ranges of (0-15) keV and (0-8) keV. Major, minor oxides and trace elements were determined by X-ray fluorescence (XRF) method. The major components of fly ash are alumina, silica, iron oxide, calcium oxide and residual carbon. The results indicate that fly ash is dominantly composed of Silicon dioxide, Aluminium oxide, Iron oxide with minor amounts of Calcium oxide, Magnesium oxide etc. However, the constituents of fly ash vary according to the type of coal used and degree of combustion

<table>
<thead>
<tr>
<th>Chemical Characteristics</th>
<th>(%)</th>
<th>Proximate analysis (%)</th>
<th>General characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon dioxide (SiO₂)</td>
<td>52.5</td>
<td>Ash 72.42</td>
<td>Surface area 13 m²/g</td>
</tr>
<tr>
<td>Aluminium Oxide (Al₂O₃)</td>
<td>22.3</td>
<td>Loss on Ignition 3.2</td>
<td>Bulk density 1000.80kg/m³</td>
</tr>
<tr>
<td>Iron oxide(Fe₂O₃)</td>
<td>9.2</td>
<td>Volatile matter 3.26</td>
<td>Particle size 0.053 mm</td>
</tr>
<tr>
<td>Calcium oxide (CaO)</td>
<td>3.8</td>
<td>Fixed carbon 10.09</td>
<td></td>
</tr>
<tr>
<td>Magnesium oxide (MgO)</td>
<td>0.2</td>
<td>Moisture 1.21</td>
<td></td>
</tr>
<tr>
<td>Phosphorus pentoxide (P₂O₅)</td>
<td>1.35</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table.2: Characterization of fly ash
<table>
<thead>
<tr>
<th>Titaniumoxide (TiO₂)</th>
<th>1.10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkali oxide (Na₂O/K₂O)</td>
<td>2.10</td>
</tr>
<tr>
<td>Sulphurtrioxide (SO₃)</td>
<td>0.62</td>
</tr>
</tbody>
</table>

After considering the earlier facts, the amount of fly ash to be added was decided to be 7.0, 10.0, 15.0g/L for different concentrations of COD (Das et al., 2001).

2.4 Study of initial COD Concentration:

These studies were performed by keeping all the conditions constant except changing the initial COD concentration by using simulated COD bearing solutions prepared by dissolving known amount of glucose in raw water. An initial COD concentration of 1000 mg/L was adopted (Das et al., 2001).

2.5 Study of pH: PH effect was performed by taking a specific concentration, adsorbent dose, and contact time and varying the pH values from 3-4 using dilute NaOH/H₂SO₄ solutions (Mall et al., 1994). The samples were agitated for specific time i.e., 12 hours, filtered and then analyzed for the residual COD concentration.

2.6 Study for Adsorbent dose: A known volume of sample was treated with fly ash dosage of 7.0g/L (Das et al., 2001). The samples were agitated for duration of 12 hours, filtered and then analyzed for the residual COD.

2.7 STUDY OF CONTACT TIME

These studies were conducted by agitating known volume of sample with initial cod of 1000 ppm and known amount of fly ash as an adsorbent agitated it for different time period, 3 hours to 12 hours (Mall et al., 1994). After predetermined time intervals, the samples were withdrawn, filtered and determined the residual cod concentration. The outcome of investigations reveals quite a few interesting features. The results observed after the physico-chemical analysis of the synthetic wastewater as depicted in table 3 showed that the wastewater is high in cod values. The organic load is depicted in terms of COD and BOD values. The COD concentration is much higher than the permissible limit. The composition of typical Indian fly ash in Table-2 depicted that the fly ash is predominantly siliceous followed by the insoluble oxides of aluminum, iron, calcium, magnesium, titanium, alkali oxides and a negligible amount of phosphorous pent oxide and sulphur oxides. In the case of fly ash as an adsorbent the metal salts hydrolyses in the presence of natural alkalinity to form metal hydroxides. The multivalent cations present in fly ash can reduce the
zeta potential while the metal hydroxides are good adsorbents. They form monomolecular layer on the surface of suspended organic matter and removed it by enmeshing them and settling.

3. Results and Discussions:

The following are the various test results obtained:

1) For initial COD of 1000 mg/L, pH 3 and Fly ash dosage 7 g/L (Mott et al., 1992; Liskowitz et al., 1980; Mall et al., 1994)

Table 3: % of COD reductions

<table>
<thead>
<tr>
<th>Contact period (Hours)</th>
<th>% of COD reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>71.0</td>
</tr>
<tr>
<td>6</td>
<td>75.0</td>
</tr>
<tr>
<td>9</td>
<td>77.5</td>
</tr>
<tr>
<td>12</td>
<td>81.0</td>
</tr>
</tbody>
</table>

2) For initial COD of 1200 mg/L, pH 3 and Fly ash dosage 10 g/L (Mott et al., 1992; Liskowitz et al., 1980; Mall et al., 1994)

Table 4: % of COD reductions

<table>
<thead>
<tr>
<th>Contact period (Hours)</th>
<th>% of COD reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>78.0</td>
</tr>
<tr>
<td>6</td>
<td>80.16</td>
</tr>
<tr>
<td>9</td>
<td>83.50</td>
</tr>
<tr>
<td>12</td>
<td>84.90</td>
</tr>
</tbody>
</table>

3) For initial COD of 1500 mg/L, pH 3 and Fly ash dosage 15 g/L (Mott et al., 1992; Liskowitz et al., 1980; Mall et al., 1994)
Table 5: % of COD reductions

<table>
<thead>
<tr>
<th>Contact period (Hours)</th>
<th>% of COD reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>81.13</td>
</tr>
<tr>
<td>6</td>
<td>83.26</td>
</tr>
<tr>
<td>9</td>
<td>85.80</td>
</tr>
<tr>
<td>12</td>
<td>86.40</td>
</tr>
</tbody>
</table>

Effect of adsorbent dose on % COD Reduction by fly Ash:

It was observed that maximum removal occur at the dose of 15 g/L of fly ash with 84.39% of COD reduction. The results showed the tremendous increase in % COD removal with the increment of adsorbent dose, owing to the increase in the number of sites (Mancy et al., 1964). At lower doses, the significant small adsorption is possibly due to the saturation of surface active sites with the adsorbate molecules.

3.1 effect of initial cod concentration on % cod reduction by fly ash

The fly ash seems to be fairly active adsorbent even at higher initial concentrations. At lower initial concentrations, the ratio of the initial number of moles available to the adsorbent surface area is low and subsequently the fractional adsorption becomes independent of initial concentration. At higher concentrations, the available sites of adsorption become fewer and hence the % removal of COD depends upon initial concentration. The COD removal of over 76% -84% obtained with fly ash within the concentration range was investigated. Removal of COD per unit weight of ash was found to increase with increase in initial COD concentration (Mall et al., 1994).
3.2 EFFECT OF pH ON % COD REDUCTION BY FLY ASH:

The runs were taken at the constant initial COD concentration, adsorbent dose and contact time. The results indicate that at all the pH levels below 5.0, the fly ash has consistently higher adsorption capacity for COD. There is more than 80% drop in percent COD by fly ash. At high pH the capacity of the adsorbent get recessed. The reason for the better adsorption capacity observed at low pH levels may be attributed to the larger number of H+ ions present, which in turn neutralize the negatively charged adsorbent surface, thereby reducing hindrance to the diffusion of organics at higher pH (Rao et al., 2002). The reduction in adsorption may be possible due to the abundance of OH- ions, causing increased hindrance to diffusion of organics (contributing to COD) ions. Oxides of aluminium, calcium, silicon, iron etc., are abundant in fly ash. The removal of pollutants from wastewater by adsorption is highly dependent on pH of the solution which affects the surface charge of the adsorbent, and the degree of ionization and speciation of adsorbate as suggested by Elliott and Huang, 1981 (Pandey et al., 1984). Similar observations have also been reported by the workers (Mott et al., 1992; Liskowitz et al., 1980; Mall et al., 1994).

3.3 EFFECT OF TIME ON % COD REDUCTION BY FLY ASH: It seems that COD removal has been achieved to the extent of more than 80% by fly ash at a maximum time period of 12 hours (Mall et al. 2002).

4. Conclusions:
   It is revealed from the studies that the treatment of domestic wastewater can be done by fly ash generated from the thermal power plants to reduce the organic load.
   The adsorptive capacity of the material for COD reduction at different pH range is encouraging. Though the process of adsorption in present investigation needs pH adjustment, but still it is convenient, economical and effective.
   It is observed that the COD can be reduced up to an extent of 84% by the usage of fly ash.
   Trend of COD removal by fly ash are fairly comparable to that of commercial activated carbon.
   It is physically and economically viable approach. The data obtained in this investigation are quite helpful in designing and studying performance of fixed or fluidized bed absorbers for the treatments of industrial wastewaters on a large scale.
   Fly ash does not add BOD to the solution.
   The material being cheap needs no additional investment and the whole process of removal may be carried out at ordinary conditions.
   Suspended solids removal with the incorporation of fly ash proved negligible.
REFERENCES:


