Utilization from Cement Kiln Dust in Removal of Acid Dyes
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Abstract: Problem statement: The growth of industries and day to day changes in human activities has resulted in an increase in the volume and complexity of wastewater to the environment. Textile industry is one of the most water consumers industries of Egypt, thus discharges large amounts of wastewater effluents during processing, especially, in the coloring and washing steps. Cement kiln dust is a solid waste in cement manufacturing. Approximately 2.5-3.0 (6-9%) million tons of cement kiln dust is produced annually in Egypt and that cause significant environmental problems.

Approach: This study aims to investigate removal of some acid dyes from aqueous solution using cement kiln dust and monitoring the dye in colored cement kiln dust. Solution with 0.4 g L\(^{-1}\) concentration was treated with cement kiln dust until the color of dye disappears. The colored cement kiln residue was separate by filtration and dried. The concentration of dye was measured before and after treatment by UV-Vis spectroscopy as well as after washing of colored residue. Also, the colored residue was investigated with, XRD, IR and DSC techniques as well as the loss on ignition at 450°C.

Results: The results found that the cement kiln dust has the power to remove all existing acid dyes and the residue has the same color of dye. When colored residue was washed with water, there was no back diffusion of dye in to water. This may be mainly due to chemical reaction that took place between cement kiln dust and dye. Thus analysis such as IR, XRD and DSC are in agreement with these results.

Conclusion: CKD is efficient in the processes of dye removal from aqueous solutions. The interaction between acid dye and CKD is fast (just minutes). So, we suggest using spent CKD for dye removal of waste water.

Key words: Waste water, cement dust, acid dye, visual inspection, UV-Vis spectroscopy, Acid Red 73 (AR), Acid Blue 74 (AB), washing steps, Chemical Oxygen Demand (COD)

INTRODUCTION

Colored dyes are important water pollutants which are generally present in the effluents of the textile and other industries such as study mills, leather and food. The high level of production and extensive use of dyes generates colored wastewater which produces toxicological and technical problems and environmental pollution. Some dyes, for instance, are reported to cause allergy, dermatitis, skin irritation, cancer and mutation in human. The presence of the dye component in the discharge not only increases the overall loading of Chemical Oxygen Demand (COD) to the receiving water but also creates an aesthetic nuisance to the environment even when the concentration is as low as 1ppm. Thus, the removal of color dyes from wastewater before they are contacted with unpolluted natural water bodies is important (Iqbal and Ashiq, 2007; Li et al., 2010; Mui et al., 2010; Valix et al., 2006; Hameed and El-Khaiary, 2008; Namasivayam and Snggeetha, 2006).

Various techniques have been employed for the removal of dyes from wastewaters (Kavitha and Namasivayam, 2007; Olgun and Atar, 2009; Cestari et al., 2009; Nandi et al., 2009; Nemr et al., 2009; Hameed, 2009; Crini, 2006; Lian et al., 2009; Zhu et al., 2005; Ozcan et al., 2005; Kanawade and Gaikwad, 2011). The most widely used methods for removing color effluents from water include chemical precipitation, ion-exchange, osmosis, ozonation, solvent extraction, adsorption, membrane filtration, but only that of adsorption is considered to be superior to other techniques (Zhu et al., 2005; Ozcan et al., 2005).

Consequently, many researchers have studied the feasibility of using low-cost substances such as agricultural by-products (Kanawade and Gaikwad, 2011; Khan et al., 2010; Yan et al., 2009; Kumar and Porkodi, 2009; Xua et al., 2010; Demirbas, 2009;
Thinakaran et al., 2008a), industrial solid wastes such as fly-ash (Dizge et al., 2008) and coal (Tunali et al., 2006), natural clays such as, bentonite, sepiolite, smectite and montmorillonite (Ozcan et al., 2005; Teng and Lin, 2006 Jano et al., 2007), silica, silica fumes (Tsai et al., 2004) and slag (Ramakrishna and Viraraghavan, 1997) as adsorbents for the removal of dyes from wastewaters.

Acid dyes are organic sulphonic acids; the commercially available forms are usually sodium salts, which exhibit good water solubility. In sequence of their importance, acid dyes are mostly used with certain fibre types such as polyamide, wool, silk, modified acrylic and polypropylene fibers, as well as blends of the aforementioned fibers with other fibers such as cotton, rayon, polyester, regular acrylic. According to their structure, acid dyes belong to the following chemical groups: azo, anthraquinone, triphenylmethane, pyrazolone, nitro and quinoline. Azo dyes represent the largest and most important group followed by anthraquinone and triarylmethane dyes.

Many researchers have studied the removal of some acid dyes. Commercial activated carbon (Prolabo) was used for adsorption of iodine, Acid Blue 74 (AB). Acid Red 73 (AR) and Acid Yellow 23 (AY) from aqueous solution (Attia et al., 2006). Textile dyes (Acid Yellow 17 and Acid Orange 7) were removed from its aqueous solution in batch and continuous packed bed adsorption systems by using thermally activated Euphorbia macroclada carbon (Gercela and Gercela, 2009). Activated carbons prepared from sunflower seed hull have been used as adsorbents for the removal of Acid Blue 15 (AB-15) from aqueous solution (Thinakaran et al., 2008b). Activated carbons, prepared from low-cost mahogany sawdust and rice husk have been utilized as the adsorbents for the removal of acid dyes from aqueous solution (Malik, 2003). Removal of acid dyes Acid Blue 45, Acid Blue 92, Acid Blue 120 and Acid Blue 129 from aqueous solutions by adsorption onto high area Activated Carbon Cloth (ACC) was investigated (Hoda et al., 2006).

The capability of surfactant modified-bentonite for adsorption of dyestuff from aqueous solution was investigated (Koswojo et al., 2010). The adsorption of an acid dye from water onto pristine and HCl-activated montmorillonites in fixed beds was investigated (Teng and Lin, 2006 and Lin et al., 2004). The adsorption of an industrial dye Supranol Yellow 4GL onto Cetyltrimethylammonium-bentonite (CTAB-bentonite) is investigated (Khelifi et al., 2007). Batch adsorption of Methylene Blue and Acid Blue 25 onto ground hazelnut shells was studied (Ferrero, 2007). The adsorption of Acid Red 14 and Acid Blue 92 onto the microporous and mesoporous egg shell membrane was investigated (Arami et al., 2008). Use of slag for removal of Basic Blue 9 dye, Acid Blue 29 dye, Acid Red 91 dye and Disperse Red dye was studied (Ramakrishna and Viraraghavan, 1997). (DP), agricultural wastes were evaluated for its ability to remove acid dye from aqueous solutions such as Durian peel (Hameed and Hakimi, 2008).

Cement kiln dust is a solid waste in cement manufacturing. It is composed of micronized particulates collected from electrostatic precipitators during the production of cement clinker. The chemical composition of cement kiln dust depends both on the raw materials used to produce the clinker. The major constituents are compounds of lime, iron, silica, alumina and some of alkalis. The pH of cement kiln dust water mixtures is generally around 12. Approximately 2.5-3.0 (6-9%) million tons of cement kiln dust is produced annually in Egypt cement kiln dust has the potential for reuse in many different channels, but the proper to reuse this by product material is to reciprocate it in cement making process.

Textile industry is one of the most water consumers industries of Egypt, thus discharges large amounts of wastewater effluents during processing, especially, in the coloring and washing steps. The wastewater contains high amounts of both organic matter and colorants (dyes).

The present study aims to utilization from cement kiln dust in removal of acid dyes from aqueous solution and monitored the dye in colored cement kiln dust.

MATERIALS AND METHODS

Materials: Types of acid dyes were used in this investigation, namely acid orange 10 dye, Acid yellow 17 dye, Acid violet 7 dye, Acid red 88 dye, Acid green 25 dye. These dyes were obtained from ISMA Dye Company, Kafer Eldawar, Egypt and were used without further purification. Chemical structures of acid dyes are shown in Table 1. A stock solution of each dye was prepared by dissolving 0.4 g of dye in 1000 mL water to make a stock solution.

The cement kiln dust was received and collected from Tourah Portland Cement Factory. A complete chemical analysis of the cement kiln dust was done by XRF. The properties of cement kiln dust are shown in Table 2.

Equipments: All spectrophotometric measurements of the acid dyes were done with a PerkinElmer Lambda35 UV-Vis spectrophotometer using 1.0 cm matched quartz cuvettes. The XRD patterns was recorded on (M/S. Shimadzu Instruments, Japan)diffractometer XRD 7000 with Ni filtered CuKa as a radiation source at 20 scan speed of 4° min⁻¹. The
IR absorption measurements were carried out using a Fourier Transform IR (FTIR) spectrophotometer (Perkin Elmer 880). The FT-IR spectra in the wave number range from 400-3500 cm$^{-1}$ were obtained with the use of the KBr pellet technique (1:99) (Perraki and Orfanoudaki, 2004). Some selected colored cement kiln dust was investigated using a differential thermal analysis of the Type a PerkinElmer DTA7 with rate 20°C min$^{-1}$ alumina crucible. The free lime content was determined with ethylene glycol (Strydom et al., 1999).

**Procedure:** Experiments for adsorption equilibrium were conducted at 25°C temperature by shaking 1 g of cement kiln dust with 250 mL of dye solution for the equilibrium contact time, agitation rate 500 rpm. To determine the minimum amount of by-pass kiln dust which realizes good decolonization, amounts of cement kiln dust which were added until the dye color disappears were calculated as show in Table 3.

**Table 1: Structures of the dyes, M wt and C.I.**

<table>
<thead>
<tr>
<th>Dye</th>
<th>Chemical Formula</th>
<th>MW g/mol</th>
<th>C.I.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid orange10</td>
<td></td>
<td>452.36</td>
<td>16230</td>
</tr>
<tr>
<td>Acid yellow17</td>
<td></td>
<td>551.24</td>
<td>18965</td>
</tr>
<tr>
<td>Acid violet 7</td>
<td></td>
<td>566.4</td>
<td>15670</td>
</tr>
<tr>
<td>Acid red 88</td>
<td></td>
<td>312.00</td>
<td>15620</td>
</tr>
<tr>
<td>Acid green 25</td>
<td></td>
<td>583.6</td>
<td>61570</td>
</tr>
</tbody>
</table>

**Table 2 Chemical Composition of Cement Kiln Dust**

<table>
<thead>
<tr>
<th>Oxide</th>
<th>(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>43.87</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>10.17</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>1.880</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>1.030</td>
</tr>
<tr>
<td>MgO</td>
<td>0.520</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>2.660</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>6.270</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>1.150</td>
</tr>
<tr>
<td>Cl</td>
<td>5.600</td>
</tr>
<tr>
<td>Free lime</td>
<td>23.40</td>
</tr>
<tr>
<td>LOI (105°C)</td>
<td>26.85</td>
</tr>
</tbody>
</table>

**Table 3: Amount of cement kiln dust which was consumed for g/250 mL of each dye**

<table>
<thead>
<tr>
<th>Dye</th>
<th>CKD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid orange10</td>
<td>12.5</td>
</tr>
<tr>
<td>Acid yellow17</td>
<td>20.0</td>
</tr>
<tr>
<td>Acid violet 7</td>
<td>20.0</td>
</tr>
<tr>
<td>Acid red 88</td>
<td>10.0</td>
</tr>
<tr>
<td>Acid green 25</td>
<td>15.0</td>
</tr>
</tbody>
</table>

After the sorption experiment, the mixture was filtrated and the residual dye concentration in the supernatant was determined spectrophotometrically. The colored residue dried in microwave oven. Three samples from each dye are weighted and ignited at 450°C for 2 h. The loss on ignition is calculated from the difference in weight before and after ignition and subtracted from blank sample. To study the effect of water on the coloured cement kiln dust and ability of dye to dissolve in water again, 1g of each coloured cement kiln dust washed with 100 g of water, stirred for 15 min. and then filtrated. The concentration of dye in filtrate is determined by a UV-visible spectrometer.

**RESULTS**

**Visual inspection:** The presence of very small amounts of dyes in water (less than 1 ppm for some dyes) is highly visible and undesirable (Robinson et al., 2001). The typical visual inspection of the investigated samples of dyes solution, filtrate after treatment with cement kiln dust and washing of coloured cement kiln dust with water as well as precipitate from dye treatment with cement kiln dust are shown in Fig. 1-5. It was observed that the color of original dye was disappearing after treatment with required amount of cement kiln dust for all dyes, expect Acid yellow17 that still has some color, as show in Table 3. Also, the filtrate was produced from treatment of coloured residue with water don’t have any color visually, that means the water cannot dissolve any dye from coloured residue i.e., there are chemical bonding between dye and Ca$^{++}$. On the other side, the cement kiln dust was dyed with color of investigated dye (Epolito et al., 2005; Lin et al., 2008).

**Fig. 1:** Color of Acid orange 10, 0.4 g L$^{-1}$ (1), filtrate from precipitation by CCK (2), after washing of residue by water (3), residue after filtration (4)

**Fig. 2:** Color of Acid yellow 17, 0.4 g L$^{-1}$ (1), filtrate from precipitation by CCK (2), after washing of residue by water (3), residue after filtration (4)
UV/visible spectrophotometric analysis: The UV-Visible spectra obtained before and after treatment of dye by CKD as well as filtrate of washing colored residue with UV/visible spectrophotometric analysis: The UV-Vis spectra obtained before and after treatment of dye by CKD as well as filtrate of washing colored residue with water are exhibited in Fig. 6-10.

All of the absorbance band in the visible region of the spectra disappears. The adsorption process induces a very significant removing of dyes, diagnosed by the total suppression of the characteristics absorbance signals for each dye. The corresponding spectrum obtained in washing of colored cement kiln dust displayed the complete vanishing of absorptions attributed to the azo group, but the Uv-Vis spectra present a small absorbance.
Fig. 9: UV-Vis spectra of Acid red 88 dye

Fig. 10: UV-Vis spectra of Acid green 25 dye

Fig. 11: Color of colored CKD with Acid orange 7 before (A) and after (B) ignition at 450°C, for 2 h

Fig. 12: Color of colored CKD with Acid yellow 17 before (A) and after (B) ignition at 450°C, for 2 h

Fig. 13: Color of colored CKD with Acid violet 7 before (A) and after (B) ignition at 450°C, for 2 h

Fig. 14: Color of colored CKD with Acid red 88 before (A) and after (B) ignition at 450°C, for 2 h

Fig. 15: Color of colored CKD with Acid green 25 before (A) and after (B) ignition at 450°C, for 2 h

Fig. 16: Loss on ignition at 450°C, for 2 h, of different acid dyes

**Effect of ignition on the colored cement kiln dust:**
Effect of ignition on the colored cement kiln dust is shown in Fig. 11-15. It is show the color of residue disappears after thermal treatment and the color of cement kiln dust returned to its original color. Also, the loss of weight due ignition at 450°C for 2 hrs is graphically plotted in Fig. 16. It is direct proportional with molecular weight of dye.

**FT-IR spectra:** Another parameter which can provide information on the mechanism of dye binding onto CKD sorbent is infrared analysis.
The FTIR spectra of the CKD before and after the sorption of acid dye from aqueous solutions are presented in Fig. 17. The FTIR spectrum of CKD shows that the peak positions at 3640, 3452, 1470, 1136, 970 and 876 cm$^{-1}$. The band at 3640 is due to OH$^-$ and 3452 is due to H$_2$O while the bands at 1470 and 876 reflect the carbonate. Bands at 1136 and 970 cm$^{-1}$ correspond to carbonate and silicate, respectively (Al-Ghouti et al., 2003).

A comparison between the these spectra shows that the intensity of peak assigned to OH$^-$ from calcium hydroxide of cement kiln dust was either minimized or slightly shifted after sorption of acid dye. In addition, two new peaks are found at 1050 and 1420 cm$^{-1}$ due to the sulphonlic substituents and triazine ring of the azo dyes (Thinakaran et al., 2008a). This confirms the attachment of the dyes on cement kiln dust. Other much weaker absorption bands at 2819 and 2920 cm$^{-1}$ due to asymmetric and sym-metric vibration modes of methyl and methylene groups are also detected. All absorption peaks display less absorption intensity after interaction with the cement kiln dust. Also, the intensity of band at 1136 cm$^{-1}$ reduced after treatment with dye due to dissolution of sulfate in water.

**Thermal analysis, DSC:** The thermal behavior of washed cement kiln dust (blank) and coloured cement kiln dust with acid red 88 dyes are illustrated in Fig. 18. DSC curve of CKD show the existence of some endothermic peaks at 60-105, 430-550 and 810-840°C. Also, DSC curve of CCKD show the existence of some endothermic peaks at 58-105, 125-200, 285-350, 430-550 and 717-770°C.

The peaks around 60-105°C is due to the evaporation of free water and 430-550°C is due to dehydration of calcium hydroxide as well as 717-770, 810-840°C is due calcination of calcium carbonate (Ramachandran and Beaudoin, 2003). There are new peaks at 125-200 and 285-350 in CCKD related to the decomposition of organic compound (dye) which is confirmed the binding of dye with cement kiln dust. On the other side the area under peak related to calcium hydroxide in CCKD is lower than that of CKD as a result of consumption of calcium hydroxide in chemical reaction with dye.

**X-ray diffraction, XRD:** Figure 19 shows the XRD pattern of washed cement kiln dust and coloured cement kiln dust with acid yellow 17 and acid red 88. It is show the characteristic peaks of calcium hydroxide, at 2.628 and 4.90, and also the peaks of silicate overlapped with calcium carbonate at 3.03 (Ramachandran and Beaudoin, 2006). The identification of all samples were
confirmed by computer-aided search of the PDF Database obtained from the Joint Committee on Powder Diffraction Standards-International Center for Diffraction Data (JCPDS-ICDD), 2001).

**DISCUSSION**

In this study we have exposed cement kiln dust to removal of some acid dyes from aqueous solution by cement kiln dust and followed the dye in colored cement kiln dust. Solution with 0.4 g L\(^{-1}\) concentration was treated with cement kiln dust until the color of dye disappears, as shown from visual tests. This is mainly due to a chemical reaction which occurred between the dye molecules and the dissolved portion of the dust. The soluble substances may help in the removal process by very rapid homogeneous chemical reaction that may occur in addition to the adsorption process. Also, the filtrate was produced from treatment of coloured residue with water don’t have any color visually, that means the water cannot dissolve any dye from coloured residue i.e., there are chemical bonding between dye and Ca\(^{++}\). On the other side, the cement kiln dust was dyed with color of investigated dye. This is indicating that the process involves color removal of the dye solution without -N=N-bond cleavage or degradation (Lin et al., 2008; Al-Ghouti et al., 2003). These changes can be attributed to electrostatic interactions between positively cations of cement kiln dust and the anionic dye and confirms the chemical nature of the sorption process (Monem et al., 1999). The UV-Vis spectra obtained before and after treatment of dye by CKD as well as filtrate of washing colored residue with water conformed to these results. The loss on ignition of colored cement kiln dust is showed the loss of weight proportion with M wt of dye as indication on the presence of dye and changes its color to original. Also, the thermal analysis confirmed appear new peaks don’t present in original cement kiln dust. This is mainly due to decomposition of dye which is presented in cement kiln dust.

The FTIR spectra of the CKD before and after the sorption of acid dye from aqueous solutions are showed that two new peaks are found at 1050 and 1420 cm\(^{-1}\) due to the sulphonic substituents and triazine ring of the azo dyes (Epolito et al., 2005). This confirms the attachment of the dyes on cement kiln dust. Other much weaker absorption bands at 2819 cm\(^{-1}\) and 2920 cm\(^{-1}\) due to asymmetric and sym-metric vibration modes of methyl and methylene groups are also detected (Koswojo et al., 2010).

**X-ray diffraction, XRD:** shows the decrease of the peak intensity of CH phase in case of coloured cement kiln dust indicates that the removal process is mainly accompanied by a chemical reaction which occurred between the dye molecules and the dissolved portion of the dust.

**CONCLUSION**

The main conclusions derived from this study may be summarized as follows:

- Cement kiln dust is able to decolorize synthetic solution different types of acid dye
- The color removal process was very fast and can be occur at room temperature
- Cement kiln dust can be used dust for decolorization of an industrial effluent as a low price sorbent
- Colored CKD may be used for brick, asphalt or concrete (future work)

**REFERENCES**


