

Copper-Cobalt Mixed Oxide Matrix: A Better Adsorbent for the Treatment of Textile Dye

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Abstract: Recently, mixed metal oxide (MMO) appears to be a promising material for the removal of textile dyes. In our previous investigation with nickel-cobalt mixed oxide, anionic dye was removed (~70%) by the matrix. In the extension of our study, copper-cobalt mixed oxide is studied to search for a superior adsorbent. Results demonstrated copper-cobalt mixed oxide as a better option to other oxide adsorbents.

A simple chemical route was followed to prepare MMO matrix by precipitating the corresponding metal carbonates and heating the mixture of carbonates at 650°C under ambient atmosphere. IR, SEM and XRD methods were used to inspect the prepared MMO, while composition was studied by EDX analysis. UV-Vis was carried out for the adsorption studies. An anionic dye and a cationic dye were used to study the oxide matrix as adsorbent. It has been shown that anionic dyes can be removed completely at low pH with the MMO matrix.

Key words: Dye removal, adsorption, pH, Cu-Co mixed oxide, procion red, methylene blue.

Introduction

Water is a growing concern today and its efficient use will be one of the larger challenges of this century. The anticipated water shortage is both a national and international issue. Currently, it is estimated that 2.2 million people die each year from consumption of contaminated water (Sciperio Inc.: The Water Problem, 2009). The ninety percent of the reactive textile dyes using conventional dye removing method was known to pass through water streams as unchanged material and discharge to rivers (Pierce, 1994). This growing issue provokes intense research to establish a suitable method for removing the toxic organic and inorganic pollutants from water. Dyes, a major water contaminant, used by textile industries not only are aesthetically displeasing, but also reduce light penetration and hinder photosynthesis in aquatic plants (Judkins and Hornsby, 1978; Grau, 1991; Sloker and Marechal, 1998), thus

upsetting biological processes and productivity within a stream. Some dyes are recognised as hazardous to health, even carcinogenic (Brown and De Vito, 1993) and also toxic to some organisms. Therefore, it is important to find a viable environment friendly method to treat the waste water released from the textile industries. Coagulation, flocculation, biological oxidation, chemical precipitation and activated carbon adsorption are usually used for the removal of dyes from textile wastewaters, but the cost of these processes is the major drawback of these techniques (Mishra and Tripathy, 1993; Kannan and Sundaram, 2001). Some industries also use the combined method like activated sludge and coagulation—activated sludge include adsorption or coagulation with chemical oxidation (Lin and Chen, 1997). However, conventional activated sludge and some combination of biological, chemical or physical methods are unable to efficiently treat textile wastewater containing significant concentration of dyes (Correia et al., 1994). Using of ozone is another method

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in textile water treatment to destroy the conjugated chains of the dye molecules to impart colour (Saunders et al., 1983; Carriere et al., 1993; Gähr et al., 1994; Perkowski et al., 1996; Sevimli and Sarikaya, 2002; Poznyak et al., 2007). However, the adsorption techniques draw more attention in recent years for their competency in removing dye stuffs and also because of their economic feasibility (Choy et al., 1999; Erdem et al., 2005).

The development of economical and efficient methods for the removal of dyes from textile waste water is an important issue. The objective of this study is to search and prepare a better adsorbent for the removal of textile dyes, in an economically acceptable manner. The efficiency of the newly prepared mixed metal matrix as adsorbent was checked by studying removal of a cationic dye (methylene blue) and an anionic dye (procion red) from aqueous solution.

Materials and Methods

Reagents

In this study, an MMO matrix was prepared from copper and cobalt nitrates obtained from Uni-chem, China. The dyes, procion red (PR) and methylene blue (MB), were obtained from E. Merck, Germany. The chemical structures of the dyes are presented in Table 1. All other reagents used in this study were also of analytical grade and utilized as received. Double distilled water was used all through the experiments.

Sample Preparation

Preparation of MMO Adsorbent

'Carbonate decomposition' method (Tarasevich and Efremov, 1980; Marco et al., 2000) was followed to prepare Cu-Co mixed oxide. In brief, copper and cobalt

nitrate solution having concentration of 0.25M were mixed with 1.0M ammonium carbonate. Carbonate of copper-cobalt was produced at the pH range of 6.60 to 7.50. The precipitate was filtered and washed with excess distilled water to remove unreacted NH_4^+ and CO_3^{2-} ions. The sample was dried in an oven at 110°C for three hours followed by six hours heating in a furnace at 650°C. The dried mixed oxide product was then grounded and sieved using 100 mesh sieves, and stored in a desiccator.

Preparation of Adsorbate

The dye solutions were prepared by dissolving precisely weighed PR and MB in double distilled water to the concentrations of 615.4 mg/L and 72 mg/L, respectively. The dye stock solutions were then diluted in accurate proportions to varied initial concentrations for studying as adsorbate. pH was maintained by adding dilute HCl or NH_4OH .

Analytical Measurements

Cu-oxides, Co-oxides and Cu-Co mixed oxides materials were analysed for their X-ray diffraction [Philips, Expert Pro, Holland] pattern in the powder state. For this purpose, the samples were prepared as the procedure described in sample preparation.

IR spectra of all the dried samples of Cu-oxides, Co-oxides and Cu-Co mixed oxides were recorded on an IR spectrometer [IR-470, Shimadzu, Japan] in the region of 4000-400 cm^{-1} . IR spectra of the solid samples were frequently obtained by mixing and grinding a small amount of materials with dry and pure KBr crystals; and making a pellet under pressure of 8-10 tons. The pellet was then placed in the path of IR beam for measurements.

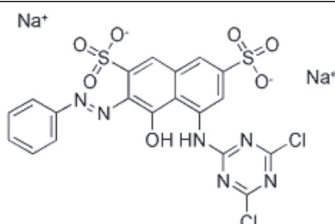
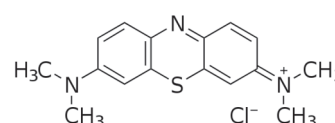
The UV-Vis spectral analysis of the sample solutions employed a double beam spectrophotometer [UV-1601 PC, Shimadzu, Japan]. UV-Vis spectroscopic analysis for the adsorption and degradation studies of the dyes involved the aqueous solution at different pH. The references in these cases were the corresponding aqueous solutions used for preparing the adsorbate solutions.

Elemental analysis of the mixed oxide sample was performed by EDX spectra. The sample was placed in the main SEM chamber integrated with the EDX machine [Philips XL30, Netherlands].

Surface Analysis

The surface morphology was examined by scanning electron microscopy [Philips XL30, Netherlands]. The dried powder samples of Cu-oxides, Co-oxides and Cu-Co mixed oxides were dispersed on a conducting carbon glued strip. The strip was mounted to a chamber

Table 1: Chemical structures of PR and MB

Dye	Chemical structure
Procion red (PR)	
Methylene blue (MB)	

and a very thin gold layer was sputtered on the sample to ensure the conductivity of the sample surface. The sample was then placed in the main SEM chamber to view its surface.

Adsorption Studies

For adsorption process, exactly 0.2 g of mixed oxide was taken to each of the six reaction vessels. Each vessel was charged with 100.0 mL dye solution of desired concentration. Immediately after the addition of dye solution, the shaking device was allowed to function. The bottles were put down from the shaker by turn after definite time intervals (i.e. 15 min, 30 min, 45 min, 60 min, 90 min and 120 min respectively). After shaking, the solutions were centrifuged and the clear solutions were taken for spectroscopic analysis to determine the change in the concentration of selected textile dyes. Adsorption experiments were performed at 30°C both in different acidic pH and alkaline pH. PR and MB were measured at λ_{max} of 664 and 537 nm, respectively.

Photolysis

A typical experiment of photolysis was also carried out to find any effect of photolysis on dye removal by the mixed oxide matrix.

Results and discussion

Characterisation of the Adsorbent, Cu-Co Mixed Matrix

EDX Analysis

Thermal carbonate decomposition was adopted in this study to synthesise the Cu-Co mixed oxide. EDX analysis was carried out to determine the composition of the oxide matrix. The EDX data provided the percentage of each element present in the matrix. Consequently, it allowed us to estimate the approximate composition of the samples studied. The composition of the present mixed metal matrix sample was found to be $\text{Cu}_{0.4}\text{Co}_{0.4}\text{O}_{0.2}$. The EDX spectra are shown in Figure 1.

FT-IR Spectral Analysis

In order to acquire some insight about the structure of the synthesized matrices, IR spectra of Co-oxide, Cu-oxide and Cu-Co mixed oxide were recorded. FT-IR data also confirmed the formation of pure Cu and Co oxides after heat treatment at 650°C. The result showed two bands at 578.6 and 667.3 cm^{-1} for Co-oxide and at 478.3 and 532.3 cm^{-1} for Cu-oxide. These peaks are characteristic of Co-O and Cu-O vibrational modes (Kliche and Popovic, 1990; Belous et al., 2006; Tang et al., 2008), suggesting that

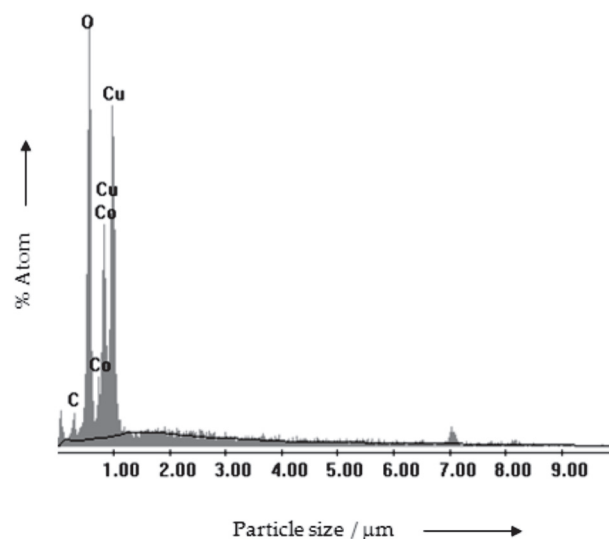


Figure 1: Elemental analysis of Cu-Co mixed oxide.

the oxide products are pure inorganic Co and Cu oxide species after calcinations at 650°C.

In case of mixed matrix, the formation of Cu-Co oxide species in the sample was also identified by FT-IR. Two sharp and two weak peaks are observed at 565.1, 667.3 and 457.0, 518.8 cm^{-1} respectively. The spectrum is shown in Figure 2(c). The formation of Cu-Co mixed oxide is evident evaluating its single oxide spectra. The individual peak position of Cu-oxide and Co-oxide shifted to 457.0 cm^{-1} , 518.8 cm^{-1} , 565.1 and 667.3 cm^{-1} from their original values of 478.3 cm^{-1} , 532.3 cm^{-1} , 578.6 cm^{-1} and 667.3 cm^{-1} , respectively (Figures 2(a) and 2(b))

XRD Analysis

The solid matrices, viz. Cu-oxide, Co-oxide and Cu-Co mixed oxide prepared by precipitation and thermal decomposition methods were examined for their structural analysis in the powdered state by using wide angle X-ray diffraction. Figure 3(a) shows the XRD pattern of the species, Co-oxide. In this figure one sharp and several weak peaks are observed. It indicates that the species is polycrystalline and the structure is Co_3O_4 . This result is in agreement with previous workers (Belous et al., 2006; Tang et al., 2008). On the other hand, the existence of strong and sharp diffraction peak at 2θ values of 35.61 and 38.79 corresponding to (111) and (200) crystal planes indicated the formation of crystalline monoclinic structure of tenorite as CuO at 650°C (Figure 3(b), JCPDS No. 05-0661) (Guo et al., 2005; Sun et al., 2005; Molteni et al., 2006; Chen et al., 2008).

From XRD pattern of Cu-Co mixed oxide (Figure 3(c)), we can see the characteristics diffraction peaks of Cu- and Co-oxide and changes in their peak positions. It indicates that the crystallinity is changed and Cu-Co

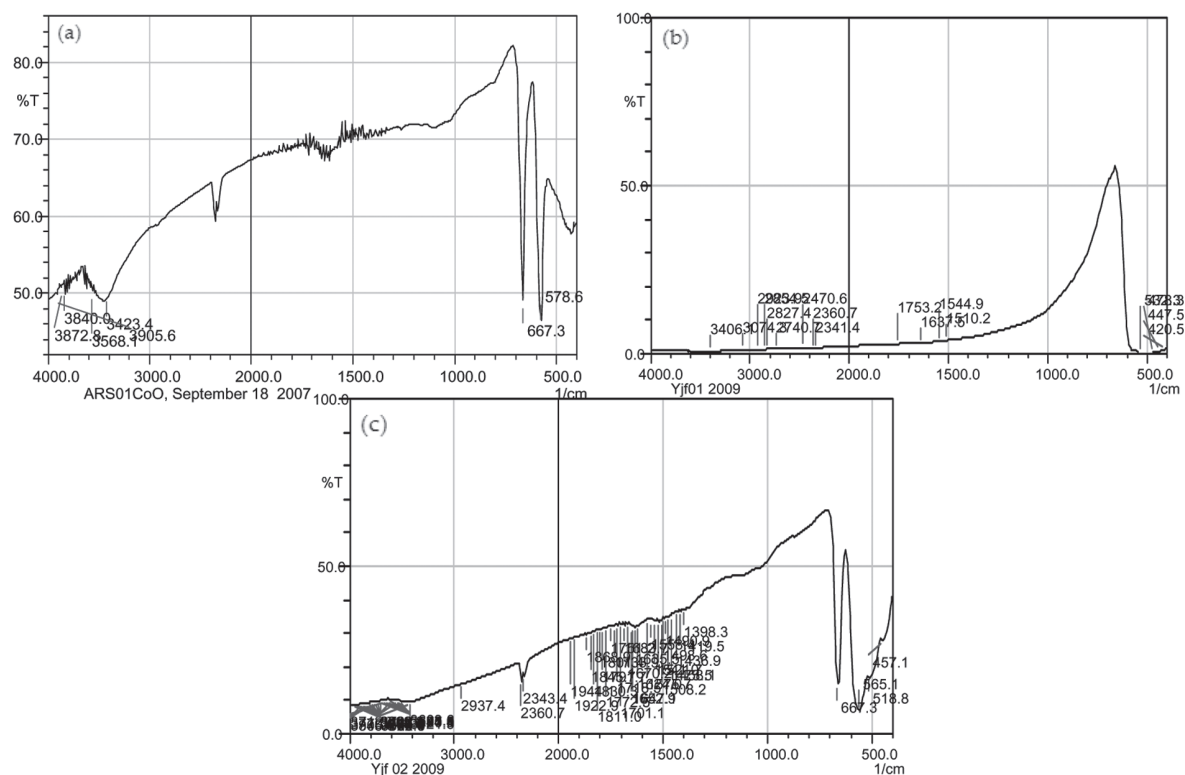


Figure 2: IR spectra of (a) Co-oxide, (b) Cu-oxide and (c) Cu-Co mixed oxide.

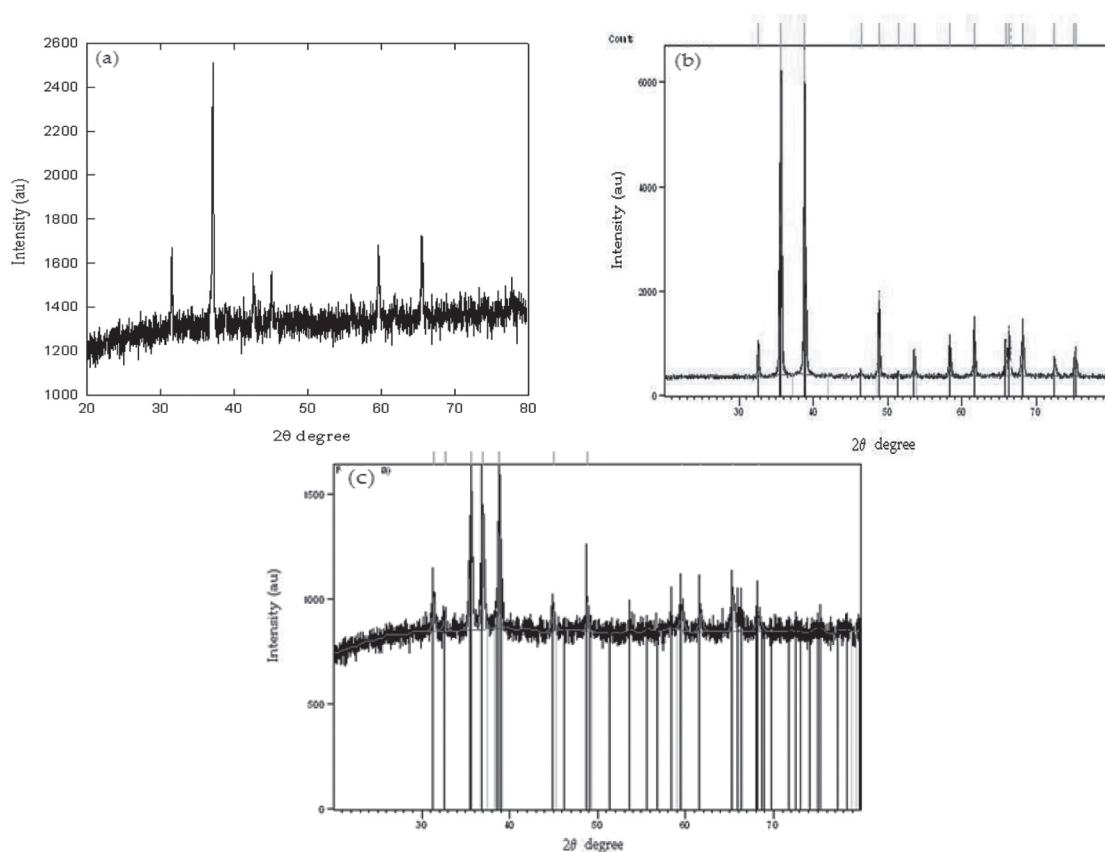


Figure 3: XRD patterns of (a) Co-oxide, (b) Cu-oxide and as prepared (c) Cu-Co mixed oxide.

mixed oxide is formed. The pattern of the mixed oxide is also consistent with the data obtained by Li (1990).

SEM Analysis

SEM image of Cu-Co mixed oxide is shown in Figure 4(c). With respect to Co-oxide and Cu-oxide (Figures 4(a) and 4(b)), particles are distributed with granular shape and packed with each other. The average particle size seems to be in the range of 10-20 μm . The SEM result showed that the surface contains also rather smaller particles as down to 1 μm or less. It is, certainly, to be of high interest to obtain smaller size, especially nano-sized mixed oxide particles by preventing aggregation. This might be possible by means of some capping agent like poly vinyl acetate (Dharmaraj et al., 2006) during the synthesis of mixed oxide.

Adsorption of Dyes on Cu-Co Mixed Oxide Surface

We studied the adsorption of MB on Cu and Co oxide individually to compare the results with their mixed matrix. It is found that adsorption of textile dyes like MB on Cu-oxide and Co-oxide is not so significant. About 26-32% MB was found to be adsorbed on these oxides for two hours. As a result, further experiments were not carried out using copper and cobalt oxide.

The preparation of mixed oxide from individual oxide possibly changes the surface property of the former. Thus, the extent of dye adsorption on the oxide is different. Our aim was to use the mixed matrix as a superior adsorbent to the individual oxides and also to other mixed oxides.

The study (Figure 5(b)) showed the adsorption of MB on Cu-Co mixed oxide, at pH 6.73, is ca. 33% at time 120 minutes. The amount of MB adsorbed here at this pH is better than that of the individual oxides. However, the result was not so satisfactory. Another experiment was run at pH 9.95, which is shown in Figure 5(a). At this pH, amount of adsorption is high ca. 46% than at pH 6.73. It is known that MB is a cationic dye. It would be adsorbed more at high pH because of having the negative surface. Therefore, the adsorption of MB carried out at high pH on Cu-Co oxide is high, due to the electrostatic attraction between MB and negative surface as well as Vander Waals forces (Demirbas et al., 2002; Chowdhury et al., 2004).

Another textile dye PR was studied for the adsorption on mixed oxide. At pH 7.12, PR adsorption was significant (Figure 6(b)). At pH 9.98, a low adsorption was evident (Figure 6(c)). As the PR is an anionic dye, it is likely to be adsorbed more at low pH.

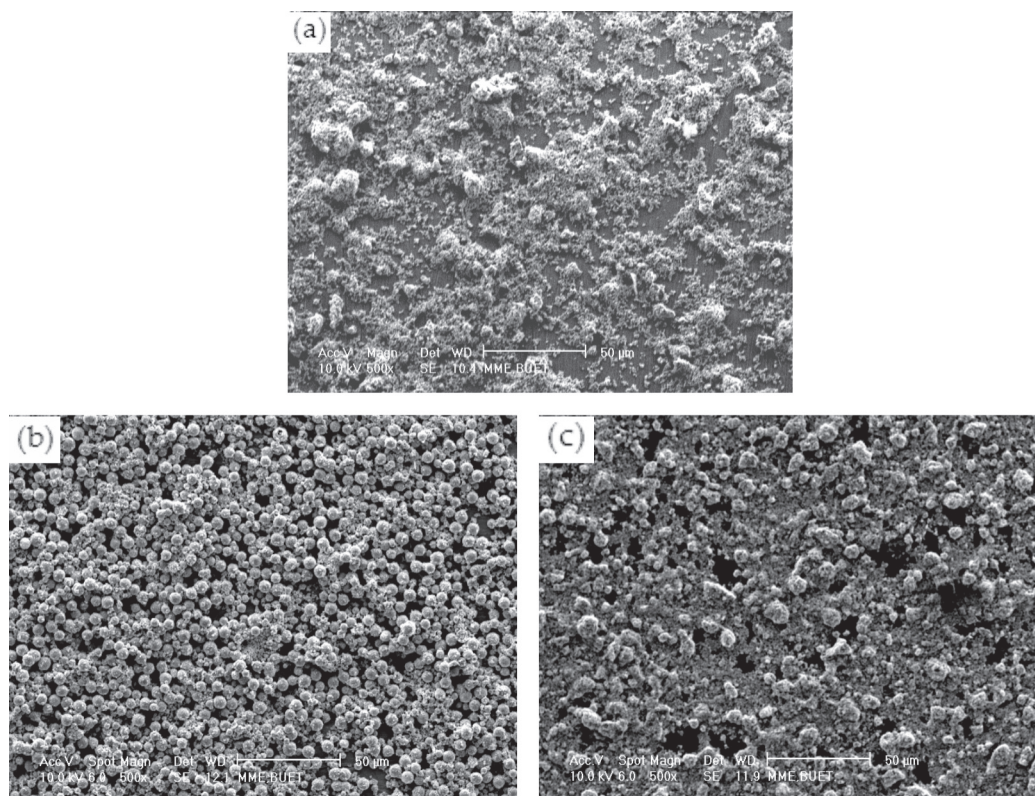


Figure 4: SEM micrographs of (a) Co-oxide, (b) Cu-oxide and (c) Cu-Co mixed oxide.

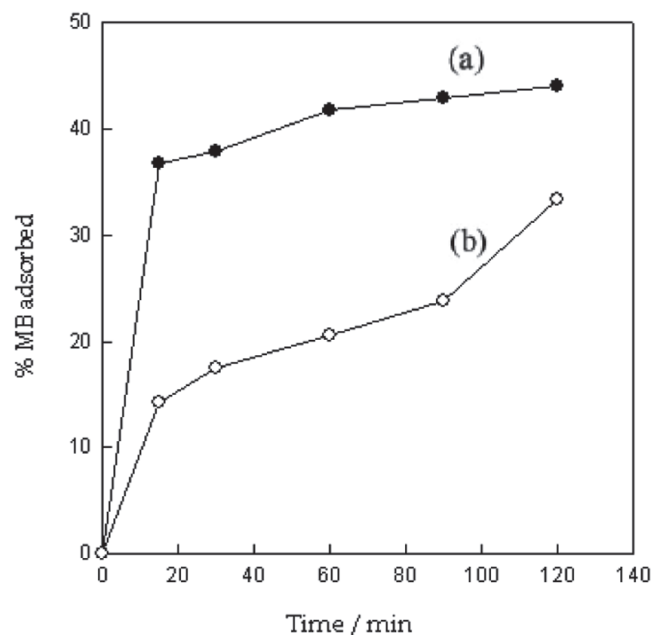


Figure 5: Adsorption of MB on Cu-Co mixed oxide surface: (a) pH 9.95 and (b) pH 6.73.

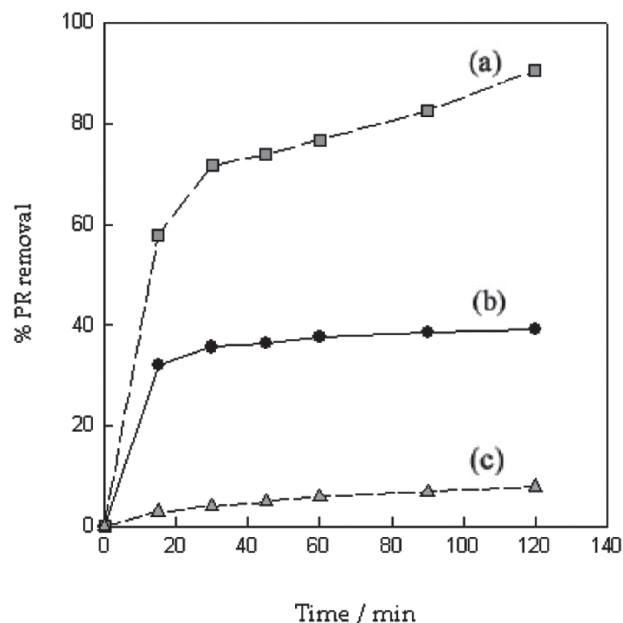


Figure 6: Adsorption of PR on Cu-Co mixed oxide: (a) pH 4.74, (b) pH 7.12 and (c) pH 9.98

At pH 4.74, surface of PR is positive. Hence, it was observed that PR adsorbed very strongly on mixed oxide at this pH (Figure 6(a)). It is due to the electrostatic attraction between PR and surface of mixed oxide. Vander Waals forces are another cause for this high adsorption. As the adsorption of PR at low pH was found

very effective, the study was extended further considering other low pH levels. At this stage the observation was quite remarkable. The 100% PR was found to be adsorbed on mixed oxide matrix at pH 4.17. At pH of 3.74, 100% PR was also removed even after taking the concentration as high as 2.0×10^{-3} M.

At high pH, surface is negative, and electrostatic repulsion between PR and surface of mixed oxide occurs. As a result adsorption is quite low ca. 8%, whilst it is very high at low pH like 4.74, which is ca. 91% (100% at pH 4.17). The adsorption is due to Vander Waals forces between PR and mixed oxide.

The present study established a complete adsorption of the anionic PR dye on the Cu-Co mixed oxide in acidic medium, where the adsorbent surface acquires a net positive charge. Conversely, the cationic MB shows higher affinity to be adsorbed on the oxide matrix in the alkaline medium, where the surface has a net negative charge (Chowdhury et al., 2004).

Isotherm study also showed very consistent output at different pH (Figures 7(a-d)). All the isotherms found at different pH matched identically with one of the six available isotherms (Nolan et al., 1981; Findenegg, 1984).

Photolysis

Another technique for the removal of toxic or biologically persistent compounds is photolysis (McCullagh et al., 2007). Photolysis of PR in the presence of mixed oxide suspension was carried out. At pH 7.12, photolysis of PR is quite significant. A parallel experiment was studied at the same condition without irradiation of light. About 43% of PR was removed by adsorption from the system; whereas, about 46% PR was removed by photolysis. A comparison of photolysis and adsorption is shown in Figures 8 and 9. It can be concluded that the amount of photolysis is quite low and adsorption is comparatively high. For this reason, further experiment at other pH level has not been conducted.

Photolysis will be increased when photocatalyst generates photoelectrons and holes after irradiation of light. These electrons and holes produce different active radicals which attack dye or other organic or inorganic molecules (CaluTech UV Air 2005). In the present experiment, a fewer photogenerated electrons and holes have been produced due to *p*-type mixed oxide semiconductor. Thus, mixed oxide cannot play a significant role in photolysis but plays a vital role as an adsorbent for the removal of textile dyes.

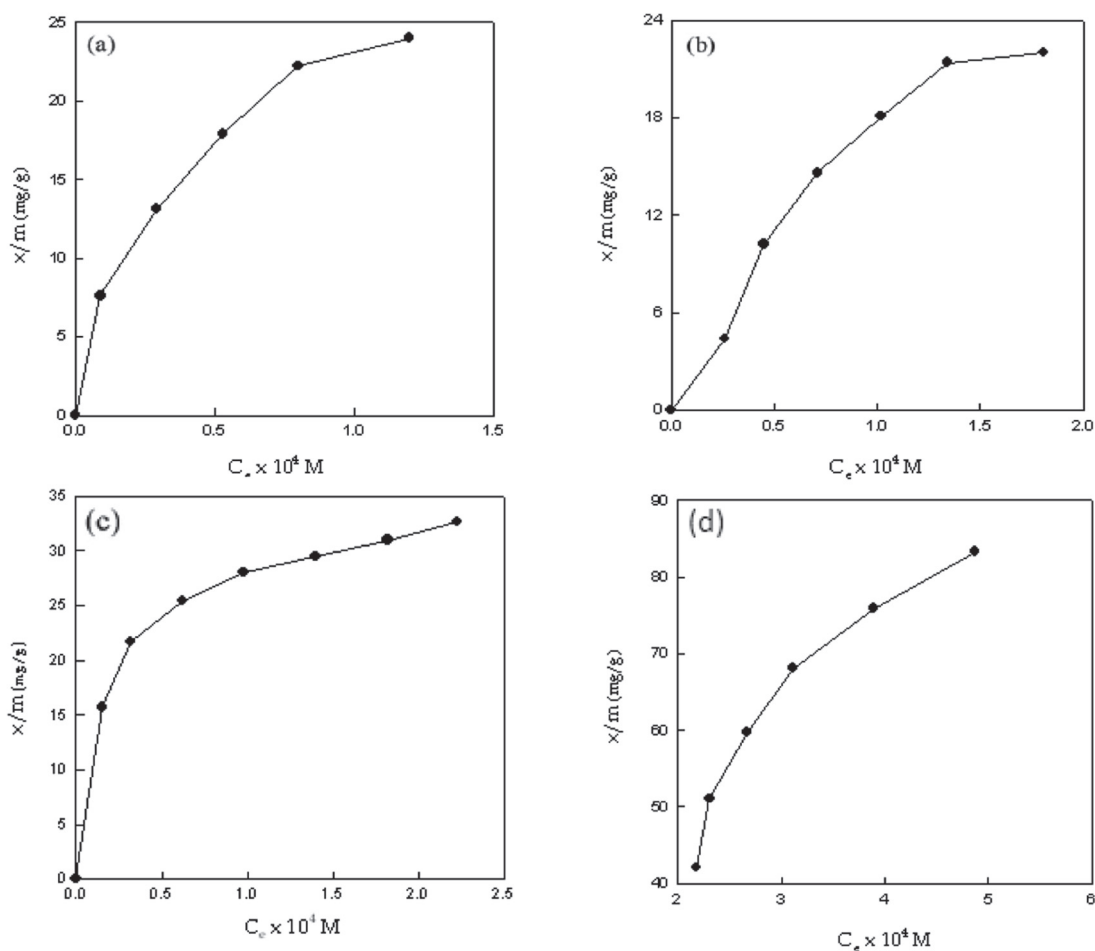


Figure 7: Isotherms for the adsorption of PR on Cu-Co mixed oxide at (a) pH 7.12, (b) pH 9.98, (c) pH 4.74 and (d) pH 4.17.

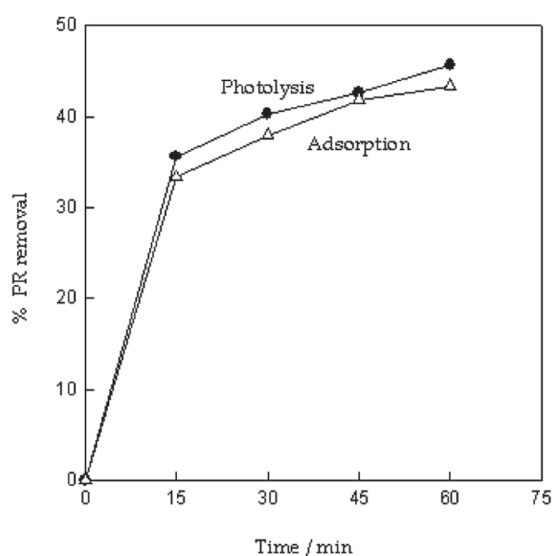


Figure 8: Comparison of adsorption and photolysis of PR in the presence of Cu-Co mixed oxide suspension at pH 7.12.

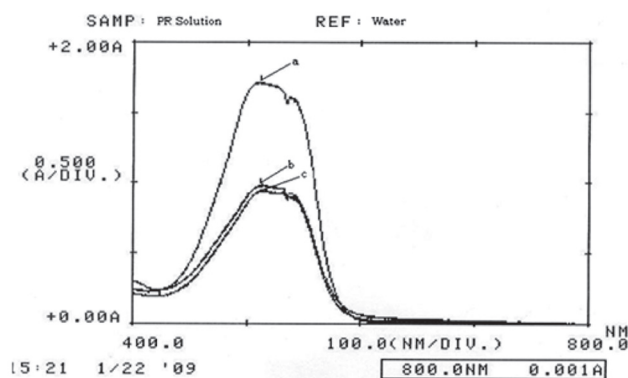


Figure 9: Spectra of adsorption of PR: (a) initial concentration, (b) without irradiation of light and (c) with irradiation of light.

Conclusions

A Cu-Co mixed oxide matrix ($Cu_{0.4}Co_{0.4}O_{0.2}$) is obtained by a simple route of carbonate decomposition at $650^{\circ}C$.

This MO matrix showed a good result to degrade the dye stuff efficiently. Particularly, the present study showed that the anionic dye PR can be adsorbed onto the MMO surface to a much greater extent than that of MB, suggesting the Cu-Co MO is an effective adsorbent for the PR removal by adsorption. PR was removed completely at lower pH value that suggests Cu-Co MO matrix, a better adsorbent than other oxide system (Chowdhury et al., 2010). In case of MB, however, a better result was possible at high pH value up to a certain extent. The adsorption most likely occurs via electrostatic interaction between the ionic dyes and the charged Cu-Co mixed oxide surface. The isotherms thus obtained from the adsorption data are quite consistent with the Langmuir isotherm (Nolan et al., 1981; Findenegg, 1984).

Photolysis of PR under UV light was also examined. However, the extent of dye removal was found to be almost unaffected, indicating that the superior performance of the MMO can be obtained without external UV illumination.

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