

## Adsorption of cobalt onto activated charcoal and its utilization for decolorization of bromocresol green dye

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Activated charcoal was prepared from pine tree cones and was treated with 5M HNO<sub>3</sub> and HCl solutions. The acid-treated charcoals (ATC) were used for the adsorption of cobalt ions from aqueous solution and then utilized for the decolorization of bromocresol green (BG) dye in aqueous medium. The adsorption study revealed that ATC adsorbed 9.063 mg/g of cobalt within 2 h. The ATC and cobalt-adsorbed ATC (Co-ATC) were characterized by scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDX). The SEM images showed that Co nanoparticles are adsorbed and dispersed on the surface of ATC. The presence of Co nanoparticles was also confirmed by EDX. The decolorization study was carried out using UV/Vis spectrophotometry and the results revealed that ATC decolorized 16.85% of the dye while Co-ATC decolorized about 40.5% of the dye within 12 h.

**Key words:** Adsorption, Activated carbon, Decolorization, Cobalt, Bromocresol green

### INTRODUCTION

The presence of heavy metals in surface waters and wastewaters is a major source of aquatic pollution and is becoming a severe environmental and public health problem due to various industrial waste water discharges. Heavy metals have attained relatively more significance due to their persistence, bio-magnification and toxicity. Heavy metal-contaminated effluents come from various industries like mining, radiator manufacturing, alloy industries, metal electroplating, and storage batteries manufacturing industry [1, 2]. Various physical and chemical methods were proposed for the removal of these contaminants, such as membrane filtration, chemical precipitation, ion exchange and adsorption [3]. Among these methods, adsorption is the most suitable method because of profitability, low-cost adsorbents, ease of operation and efficiency [4]. Several adsorbents have been synthesized in the past in order to find out a sustainable and cost-effective way of removal of metals from the environment [5]. Activated carbons are the most potential adsorbents for heavy metal adsorption due to their high surface area, high adsorption capacity, micro porous character, chemical nature of their surface and can be prepared from various feedstocks' [6, 7].

Similarly, dyes are widely applied for various purposes in different industries because of their durability and effectiveness [8]. Dyes and pigments are discharged into waste water effluents from various industries like paper, food, leather, textile

and dye manufacturing industries. Due to their large size and complex structure, these coloring effluents are toxic and resistant to destruction [9]. The dye-containing waste waters are toxic to aquatic organisms, human beings and cause biological magnification, eutrophication, toxicity, non-aesthetic pollution and perturbation in aquatic life [10]. The treatment of wastewater containing dyes is a challenging task as most of the dyes are non-degradable and persist for a very long time [11]. If these pollutants are not removed from the effluents then the color and toxicity of dyestuffs may cause objectionable impact on the ecosystem [12].

Various physical, chemical, and biological methods such as adsorption, ozonation, precipitation, reverse osmosis, flocculation, precipitation and ultra filtration are used for the purification and removal of color from waste water [13]. Presently advanced oxidation processes (AOPs) such as H<sub>2</sub>O<sub>2</sub>/UV, O<sub>3</sub>/UV and heterogeneous photocatalysis are widely used for waste water purification. Among these processes, heterogeneous photocatalysis is an effective method for the degradation of organic pollutants (such as dyes present in wastewater), which is based on UV-light irradiation [14]. For example Tolia *et al.* studied the photocatalytic degradation of malachite green dyes using doped and undoped ZnS nanoparticles [15].

In the present study, first Co was adsorbed onto ATC from aqueous solution and then it was utilized for the decolorization of bromocresol green (BG) dye in aqueous medium. BG is an anionic triphenylmethane dye, highly water-soluble and

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hardly biodegradable [16]. Various approaches have been introduced for the removal of BG dye from waste water, for example Fassi *et al.* removed BG dye by various photochemical processes such as direct UV photolysis, acetone/UV and advanced oxidation processes ( $\text{H}_2\text{O}_2/\text{UV}$  and  $\text{S}_2\text{O}_8^{2-}/\text{UV}$ ) [17]. Similarly, Chaleshtori *et al.* photocatalytically degraded BG dye by using porous titanium–niobium oxide as a photocatalyst under UV light irradiation [18]. In this study the effect of several parameters such as irradiation time, catalyst dosage and recycled catalyst on dye removal was studied. The main aim of the present study is to remove both heavy metal and dye from water using a low-cost adsorbent. Firstly, the AC was used for the adsorption of Co from aqueous medium and then Co-ATC was utilized for the decolorization of BG dye in aqueous medium.

## MATERIALS AND METHODS

### *Materials*

Pine cones were collected around the University of Malakand.  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  was supplied by Merck, Darmstadt, Germany and used as such without any further purification.  $\text{HNO}_3$  was purchased from Sigma Aldrich.  $\text{HCl}$  (37%) was supplied by Riedel-de Haen. BG dye was purchased from Peking Chemical Works, Peking, China.

### *Charcoal synthesis and its activation*

The pine cones were grinded into small pieces and then heated in a pressure cooker for 1 h. The obtained charcoal was grinded and sieved through a screener having 100  $\mu\text{m}$  mesh size. 5 g of charcoal, 100 mL of  $\text{HNO}_3$  (5M) and 100 mL of  $\text{HCl}$  (5M) were put in a reaction vessel and refluxed at 70 °C for 2 h. The sample was filtered and the obtained acid treated charcoal (ATC) was washed several times with deionized water in order to remove acids from charcoal.

### *Adsorption of Co onto acid-treated activated charcoal*

15 mL of cobalt chloride solutions of different concentrations (100, 200, 300 and 400 ppm) were taken separately in vials and then 0.2 g of ATC were added in each vial and shaken on a mechanical shaker for 2 h. The adsorption was performed at neutral pH, room temperature with a shaking speed of 60 Hz. The Co-ATC was separated by centrifugation and maximum adsorption capacity was determined by atomic adsorption spectrometry.

10 mL of BG (250 ppm) and 0.02 g of Co-ATC were put in a 50 mL beaker and kept under UV-light irradiation (254 nm, 15 W) under constant stirring. After a specific irradiation time, the catalyst was separated from the irradiated dye through centrifugation at a speed of 1200 rpm for 10 min. The catalyst was recycled by washing several times with distilled water through sonication and then dried in an oven at 80 °C. The recycled catalyst was reused for the decolorization of BG in order to compare its efficiency with that of the original catalyst. The dye removal study of dye was performed by UV-Vis spectrophotometry. The percent removal of BG dye in aqueous medium was calculated by the following equations [13]:

$$\text{Degradation rate (\%)} = \left( \frac{C_0 - C}{C_0} \right) \times 100$$

$$\text{Degradation rate (\%)} = \left( \frac{A_0 - A}{A_0} \right) \times 100$$

where  $C_0$  and  $C$  stand for initial dye concentration and dye concentration after UV irradiation, respectively.  $A_0$  and  $A$  show initial absorbance and dye absorbance after UV irradiation, respectively.

### *Instrumentation*

The morphological study of ATC and Co-ATC was carried out on JEOL, JSM-5910 SEM. The EDX spectrometric analysis of Co-ATC was performed on Model INCA 200/Oxford Instruments, UK, company Oxford, in order to determine the elemental composition of the sample. The photodegradation study of BG was performed on a UV-Vis spectrophotometer (UV-1800, Shimadzu, Japan).

## RESULTS AND DISCUSSION

### *Adsorption study*

The adsorption technique is commonly used for the removal of pollutants like dyes, heavy metals, etc., but after adsorption the adsorbents are commonly discarded. In our study, we used ATC for the removal of Co from aqueous solution and then utilized the Co-adsorbed ATC for dye decoloration. Table 1 show that the adsorption of Co increases as its concentration increases. The results revealed that ATC adsorption capacity increases as Co concentration increases up to a certain limit (300 ppm) and then levels off. It was also found that the adsorption capacity is almost constant after 300 ppm, which might be due to the saturation of active sites present on the surface of ATC.

**Table 1.** Adsorption of Co by ATC

Solution Concentration (ppm)	Adsorption of Cobalt (mg/g)
100	5.709
200	6.602
300	9.063
400	9.165

*Morphological study*

Figure 1 shows the surface morphology of ATC and Co-ATC. Figure 1a reveals that the surface of charcoal is not damaged by treating with strong nitric acid. Figure 1b clearly shows that Co is adsorbed on the surface of charcoal. The size of Co was below 600 nm. The micrographs also illustrated that Co particles were dispersed on the surface of activated charcoal.

*EDX Study*

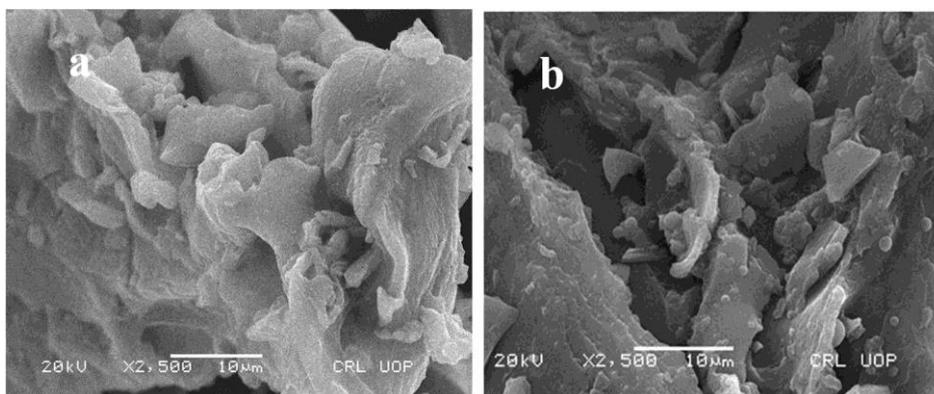
Figure 2 shows the EDX spectrum of Co-ATC. The EDX study reveals that carbon is present in large quantity as compared to other elements. The spectrum also shows the presence of an oxygen peak, which indicates that carboxylic functional groups were introduced during the functionalization of charcoal by treating with concentrated HNO<sub>3</sub> and

HCl. Figure 2 also shows that Co is adsorbed in high quantity on the surface of Co-ATC. The adsorption of Co was also confirmed by atomic absorption spectrometry and the results are shown in table 1.

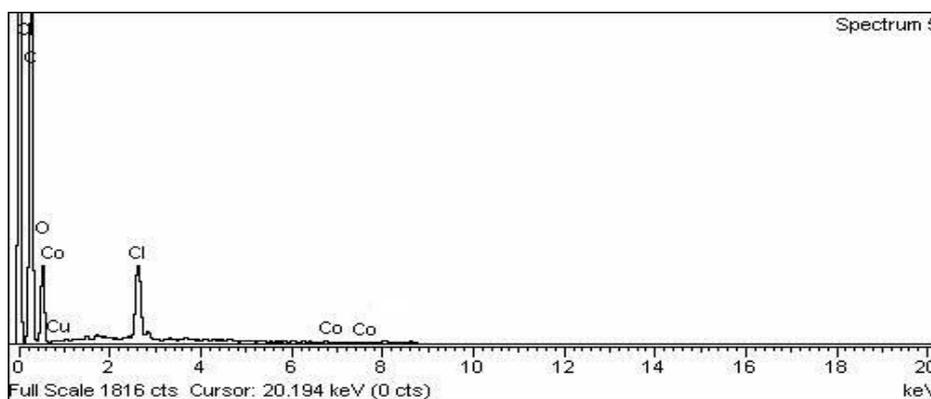
*BG dye decolorization study*

The ATC and Co-ATC were used for the decolorization of BG under UV-light irradiation. Figure 3a shows the UV/Vis spectra of BG before and after UV irradiation in aqueous medium in the presence of ATC. The removal of BG was measured by the relative intensity of the UV/Vis spectra, which gave maximum absorbance peak at 438 nm. Figure 3a also shows that the decolorization of BG increased slowly as irradiation time increased. The decrease in peak intensity illustrated that BG decolorization occurred in the presence of ATC.

The UV/Vis spectra of BG before and after UV irradiation in aqueous solution in the presence of Co-ATC are shown in figure 3b. The spectra revealed that the photodegradation of BG gradually increased as the irradiation time increased. The results also illustrated that the dye was significantly removed in the presence of Co-ATC as compared to ATC.



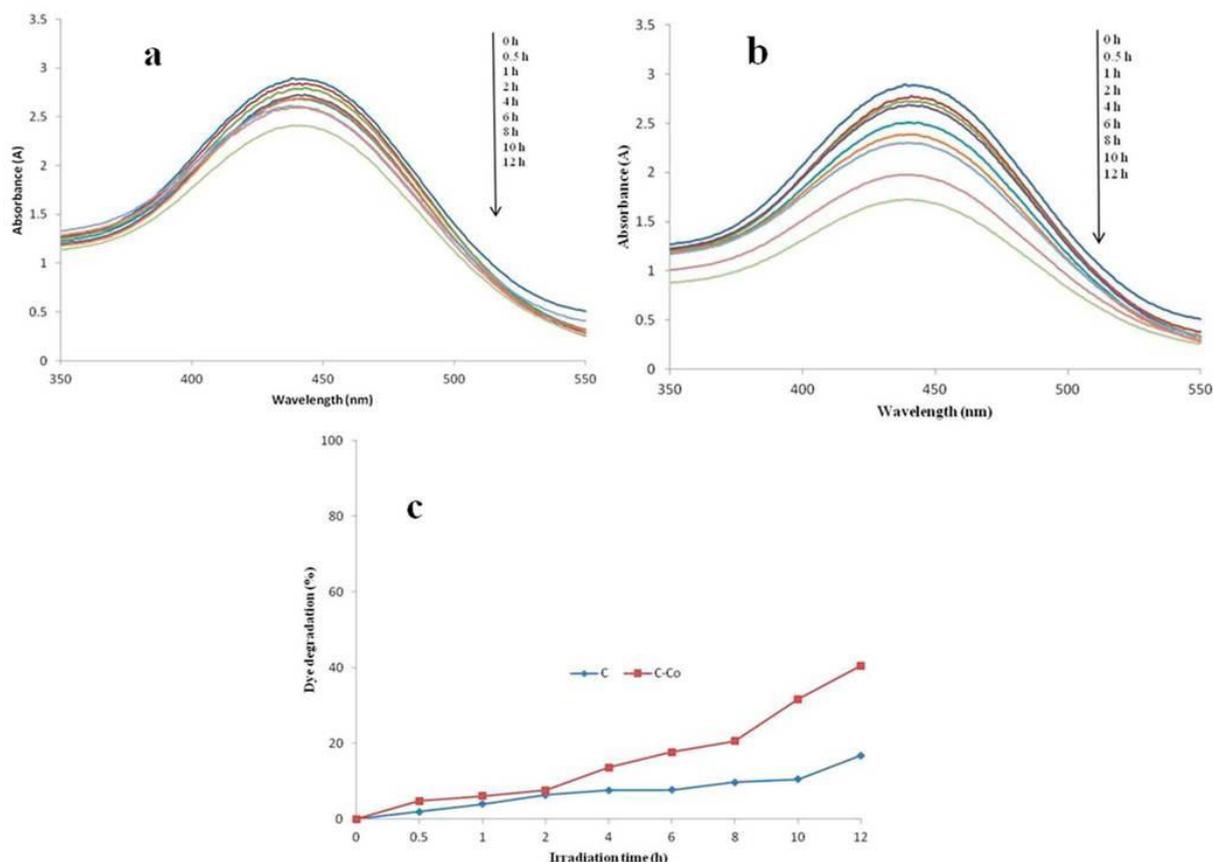
**Fig. 1.** SEM images of (a) ATC and (b) Co-ATC



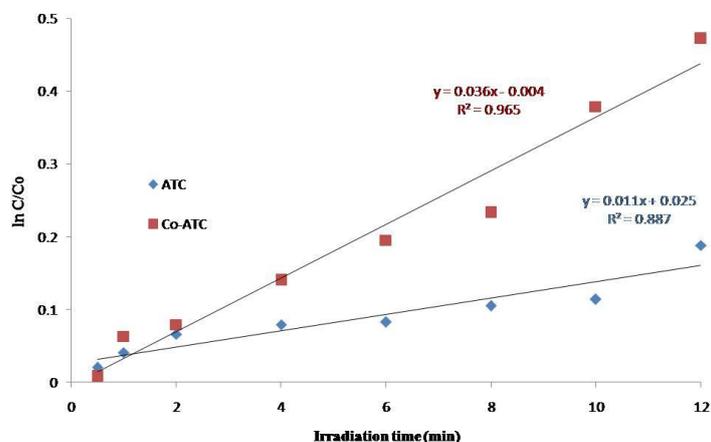
**Fig. 2.** EDX spectrum of Co-ATC

Figure 3c shows the difference in % removal of BG dye in the presence of ATC and Co-ATC. The results showed that only 16.85 % of the dye was removed in the presence of ATC, while Co-ATC removed 40.5 % of the dye within 12 h. The increase in the catalytic efficiency of Co-ATC was due to the presence of Co on the surface of charcoal. Chaleshtori photocatalytically degraded

BG dye under UV light in aqueous medium using non-porous and porous titanium–niobium oxides derived from  $\text{KTiNbO}_5$  but their photocatalysts are not economical [19]. Figure 4 shows the kinetic study of the photodegradation reaction of BG dye in the presence of ATC and Co-ATC. The correlation coefficients ( $R^2$ ) values are also shown in the graph (Figure 4).

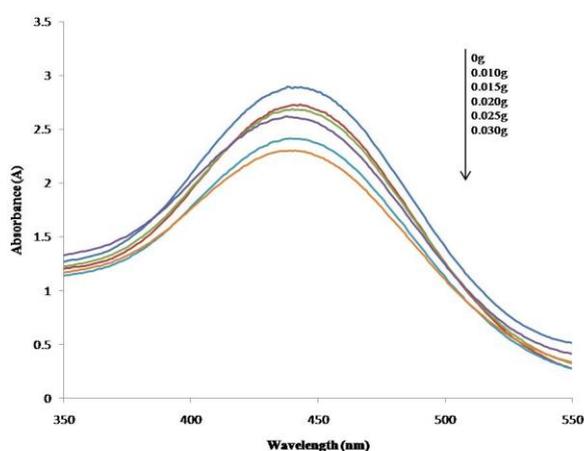


**Fig. 3.** UV–Vis absorbance spectra of BG decolorization by (a) ATC, (b) Co-ATC under UV-light irradiation vs. time, and (c) % removal of BG with ATC and Co-ATC.



**Fig. 4.** Kinetic study of BG dye decolorization reaction in the presence of ATC and Co-ATC

The effect of catalyst amount on the decolorization of BG dye was also studied by applying different amounts of catalyst. Different amounts of ATC and Co-ATC such as 0.010, 0.015, 0.020, 0.025 and 0.030 g were added to each 10 mL of dye and their effects were studied under the same experimental conditions at a constant time of 4 h. Figure 5 shows the UV/Vis spectra of BG in aqueous solution before and after UV-light irradiation using different amounts of ATC. The results clearly demonstrated that the removal of dye increased as the amount of ATC increased. Figure 6 shows the UV/VIS spectra of BG before and after UV-light irradiation using different amounts of Co-ATC photocatalyst. The spectra show that the rate of decolorization increased as the amount of Co-ATC increased.



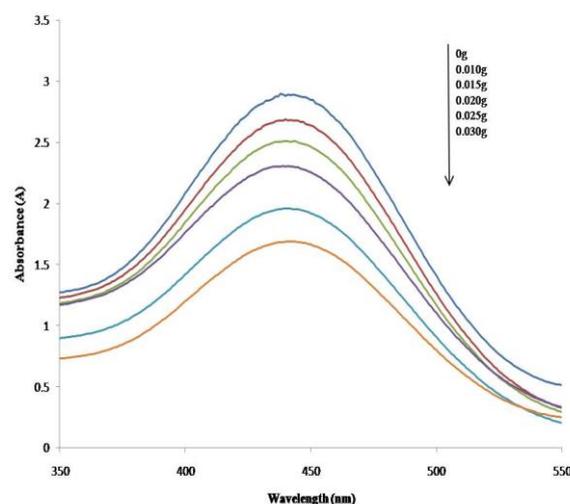
**Fig. 5.** UV-Vis absorbance spectra of BG photodegraded by ATC under UV irradiation vs. catalyst dosage.

Figure 7 shows the difference in % removal of BG dye using different quantities of ATC and Co-ATC under UV-light irradiation. The results illustrated that at every dosage Co-ATC decolorized more dye as compared to ATC. The results show that 0.010 g of ATC decolorized about 6.46 % of dye while 0.030 g of charcoal decolorized 20.62 % of dye. Similarly, 0.01g of Co-ATC decolorized 7.6 % while 0.030 g decolorized 41.86 % of dye within 4 h as is clear from table 2. The same results are also reported by Fassi *et al.*

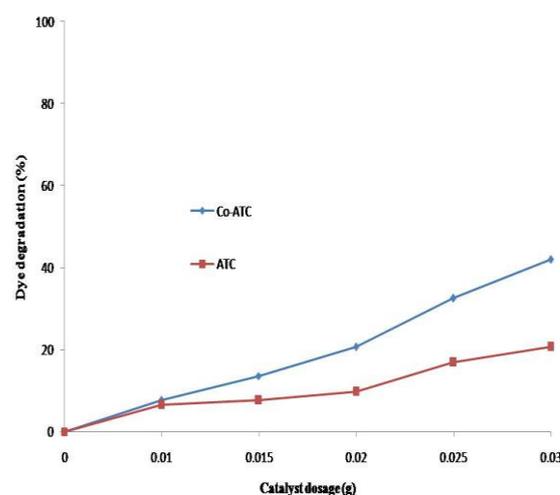
**Table 2.** % Removal of BG vs. catalyst dosage

Catalyst dosage (g)	% Removal by ATC	% Removal by CO-ATC
0.010	6.46	7.6
0.015	7.6	13.57
0.020	9.67	20.62
0.025	16.85	32.5
0.030	20.62	41.86

[20] using TiO<sub>2</sub>/UV for photodegradation of BG dye, who found that dye degradation/removal rate increased with an increase in the amount of catalyst.



**Fig. 6.** UV-Vis absorbance spectra of BG decolorized by Co-ATC under UV irradiation vs. catalyst dosage



**Fig. 7.** Difference in % removal of BG in aqueous medium by different dosages of ATC and Co-ATC

## CONCLUSION

Cobalt ions were adsorbed on AC and utilized for the decolorization of BG dye in aqueous medium. The SEM images showed that the acid treatment did not affect the surface morphology of charcoal. The SEM study illustrated that Co ions gets agglomerated on the surface of ATC. The dye decolorization study revealed that Co-ATC decolorized a larger quantity of BG than the ATC. The high removal efficiency of Co-ATC is attributed to the catalytic effect of Co present on the surface of ATC. Both ATC and Co-ATC can be easily removed after reaction but Co-ATC can be more efficiently separated due to the additional mass of adsorbed cobalt. The Co-ATC decolorized about 40 % of dye while ATC decolorized about 16 % of dye within 12 h. The % removal of dye increases by increasing catalyst dosage and 0.030 g of Co-ATC decolorized 41.86 % of dye within 4 h.

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