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ADSORPTIVE DECOLORATION OF *o*-PHENYLENE DIAMINE USING BENTONITE MINERAL

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ABSTRACT

Organic dyes pose a serious threat to the environment due to their carcinogenicity as well as metabolic disturbances, and need to be removed for the protection of the environment. Orthophenylene diamine, used as a component of a polymer, induces apoptosis through binding with DNA. Bentonite, a smectic group of minerals, having a 2:1 structure, was used as a potential absorbent of the dye due to its high surface area and cation exchange capacity. The absorbance of the dyes was recorded at different initial concentrations and pH values by a UV double-beam spectrophotometer, Systronic model 2203. The percent decolorisation at different time intervals and initial concentrations has been studied with orthophenylenediamine to determine the optimum condition. Bentonite mineral has been characterized by XRD, SEM, FTIR, TGA, and DTA. The experimental data show that decoloration of the dye follows the Lagergren first-order kinetic model. The linearity of the graph shows that the removal of dye follows a first-order kinetic model. The maximum removal efficiency is 98 %. Thus, the present paper deals with the adsorption of the dye using bentonite. Recyclability of bentonite has made it an excellent decolorant of dyes.

Keywords: Bentonite, Orthophenylenediamine, Decoloration, Surface Area, Adsorption

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INTRODUCTION

Environmental pollution is one of the most serious threats facing our planet today. Organic contaminants, amongst other pollutants, are extremely dangerous because of their long-term consequences.[1] Some of them are carcinogenic, and they react with organic compounds in the body that play a role in the synthesis of proteins, enzymes, and hormones.[2-3] Industrial wastewater contains many hazardous organic compounds, leading to adverse health effects. A number of industries like pharmaceuticals, textiles, paper, leather, cosmetics, and food produce a large number of hazardous chemicals. Aromatic amines and their derivatives are a few prominent carcinogens. The *o*-phenylene diamine (OPD) has uses in drugs, biosensors of glucose, and dyeing of textiles.[4-5] However, in case of ingestion, inhalation, or eye contact, it is mutagenic. The Ortho-phenylenediamine (OPD) is one of the most common and most well-known components of a polymer. OPD is very toxic, which includes asthma attacks, chest congestion, and allergic effects.[6] The proposed mechanism of these adverse effects induced by the dye is still not very clear. Apart from that, OPD has potential toxicity, which includes acute toxicity, such as allergic contact dermatitis, and subacute toxicity.[7-8] OPD can cause skin irritation, rhabdomyolysis, renal impairment, and severe edema.[9-11] It can induce anemia, nose irritation, and throat soreness.[12] Aryldiamines, OPD, and their transformation products are toxicological and of environmental concern. The carcinogenicity of phenyldiamines has been established as per a report by the International Agency for Research on Cancer.[13-14] In the year 2012, the permanent senate commission for the investigation of health hazards of chemical compounds assessed OPD as a carcinogenic occupational substance.[15] The population may be affected due to prolonged intake of water contaminated with OPD as well as air exposure. Typically, a variety of techniques, including coagulation/flocculation, adsorption, membrane filtration, photo-degradation, and oxidation, have been widely used to eliminate organic dyes from polluted wastewater.[16-18] Several adsorbents have been utilized for the removal of organic dyes from aqueous media. Prominent among them are carbon nanotubes, activated carbon, quantum dots, cellulose, and magnetic nanocomposites. Agriculture byproducts and wastes have also been utilized for the adsorptive removal of dyes. Most of these techniques, having high operational costs, are not easy to handle.[19-20] They produce chemical sludge due to the purifying process and require higher energy consumption. Adsorption by

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locally available bentonite might be a potential technique due to its low cost, eco-friendliness, and adsorbent regeneration. Bentonite, a smectite group of minerals having a 2:1 structure, has a montmorillonite unit.[21-22] The structure of montmorillonite confirms that one octahedral unit is sandwiched by two tetrahedral units.[23-24] The color varies from grey to brown. The mineral is mined 1-2 m deep below the surface. Upon treatment with benzidine solution, a blue color is obtained. Bentonite mineral has been characterized by XRD, TGA, DTA, FTIR, and SEM images.[25-26] Bentonite is abundant in almost all parts of the world, as well as the Rajmahal hills of Jharkhand, Barmer, Rajasthan, and J&K.[27] The experimental data was fitted into the Freundlich and Langmuir adsorption isotherms, which are the most commonly used isotherms.[28] Freundlich and Langmuir adsorption isotherms refer to multilayer and monolayer adsorption, respectively. The present paper deals with the removal of o-phenylenediamine by the use of bentonite. Owing to high cation exchange capacity, mesopores, and high surface area, bentonite has been utilized as an eco-friendly and low-cost adsorbent of organic dyes.

EXPERIMENTAL

Different ortho-phenylenediamine concentrations, such as 10 ppm,20 ppm,30 ppm,40 ppm,50 ppm, and 60 ppm, were prepared from the stock solution by the dilution method and stored in a dark place to avoid photodegradation. 100 ml of OPD dye is taken in a conical flask, and 1g of bentonite is added and shaken on a mechanical shaker at 220 rpm for different time intervals. This experiment is repeated for different initial concentrations of OPD. The absorbance of the residual solution is recorded by a double-beam spectrophotometer, 2203 Systronics. The maximum absorbance was recorded at a wavelength of 220 nm. Thus, the dye concentration is determined spectrophotometrically at the maximum absorbance wavelength for OPD. The peaks in the graph between glancing angle and intensity clearly indicate the presence of the montmorillonite unit. TGA was done by the model number. Pyris Diamond TG/DTA (Perkin Elmer), STA-600 Thermal analyzer. FTIR by model no. Perkin Elmer Version 10.4.1, US, SEM analysis by ZEISS EVO-MA 10, Germany, XRD by Bruker D8 Advance, having a specimen length of 10 nm-0.1000 mm of a receiving slit size. Percentage removal is calculated from the formula,

$$\% \text{ Removal} = \frac{C_i - C_t}{C_i} \times 100$$

Where C_i stands for the initial concentration and C_t stands for the concentration at time t.

RESULTS AND DISCUSSION

Figure-1 clearly shows the percent decolourisation of different concentrations of OPD at different time intervals, whereas Fig.-2 indicates the absorbance of o-phenylenediamine at different time intervals and concentrations.

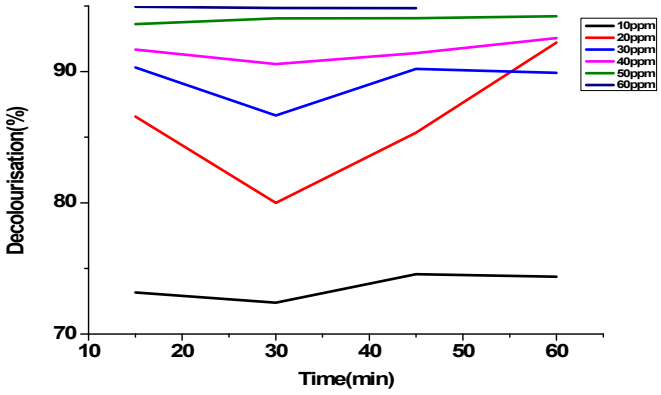

Fig.-1: Percent Colour Removal at the Maximum Absorbance Wavelengths of OPD at different Concentrations

The concentration of OPD ranges from 10 ppm to 60 ppm, whereas the time ranges from 15 to 60 minutes. It was established that the maximum decolourisation percentage was obtained in 10 minutes only for an initial concentration of 60 ppm at a p^H 7.

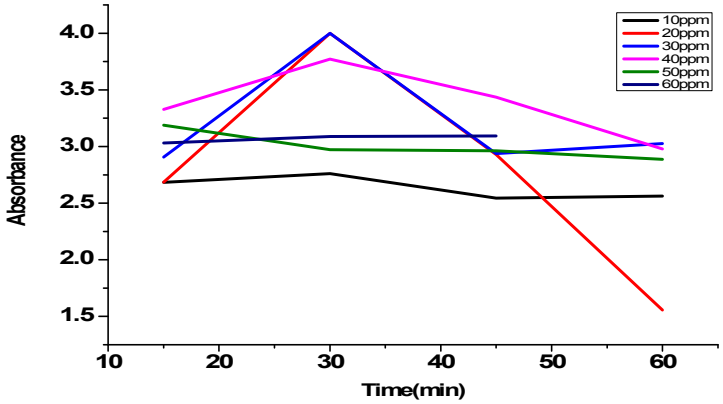

Fig.-2: Absorbance of o-phenylenediamine at different Time Intervals andConcentrations

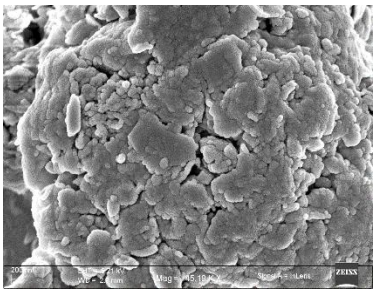

Fig.-3: SEM image of Bentonite Mineral

Figure-3 shows the surface morphology of bentonite, whereas Fig.-4 shows the diffraction pattern of the mineral.

FTIR spectra of bentonite show a stretching vibration band of the hydroxyl groups (-OH) at 3620.85 cm^{-1}. Absorption band at 1633 cm^{-1} reflects Si-O-Si vibration (Fig.-5). The peaks at 917 cm^{-1} show Al-OH-Al bending. A weight loss of 16% in TGA confirms the presence of bentonite mineral (Fig.-6).

Table-1: XRD Data of Bentonite

No	2-theta(deg)	Height(cps)	FWHM (deg)	Phase name	Chemical formula	DB card number	Rel. int. I(a.u.)
1	19.824(18)	3413(169)	0.48(3)	Unknown	Unknown	0	15.64
2	20.921(8)	14016(342)	0.192(8)	Unknown	Unknown	0	24.94
3	22.07(3)	1878(125)	0.14(4)	Unknown	Unknown	0	2.19
4	25.57(15)	643(73)	0.27(12)	Unknown	Unknown	0	1.14
5	26.720(4)	72967(780)	0.185(4)	Unknown	Unknown	0	100.00
6	27.56(2)	2345(140)	0.10(4)	Unknown	Unknown	0	2.10
7	27.98(2)	4772(199)	0.26(3)	Unknown	Unknown	0	11.07
8	29.90(7)	1004(91)	0.52(9)	Unknown	Unknown	0	3.38
9	31.32(7)	501(65)	1.0(4)	Unknown	Unknown	0	3.35
10	34.964(8)	3373(168)	0.36(4)	Unknown	Unknown	0	13.99
11	36.604(5)	9403(280)	0.132(7)	Unknown	Unknown	0	10.81
12	37.39(8)	513(65)	0.65(19)	Unknown	Unknown	0	4.14
13	39.521(10)	5753(219)	0.165(9)	Unknown	Unknown	0	6.16
14	40.376(10)	3248(165)	0.161(10)	Unknown	Unknown	0	3.41
15	42.510(8)	6160(227)	0.162(10)	Unknown	Unknown	0	8.36
16	45.872(5)	2656(149)	0.258(16)	Unknown	Unknown	0	6.72
17	50.196(3)	14136(343)	0.143(3)	Unknown	Unknown	0	15.44
18	50.68(3)	795(81)	0.18(5)	Unknown	Unknown	0	1.08
19	54.932(10)	4013(183)	0.142(15)	Unknown	Unknown	0	5.72

20	55.369(18)	1722(120)	0.19(3)	Unknown	Unknown	0	3.27
21	60.006(4)	9216(277)	0.145(4)	Unknown	Unknown	0	10.75
22	61.71(5)	1206(100)	0.78(4)	Unknown	Unknown	0	6.97
23	64.078(15)	1596(115)	0.149(16)	Unknown	Unknown	0	1.78
24	67.786(4)	5579(216)	0.155(4)	Unknown	Unknown	0	6.36
25	68.171(4)	5098(206)	0.102(6)	Unknown	Unknown	0	3.87
26	68.355(8)	4606(196)	0.274(15)	Unknown	Unknown	0	9.13

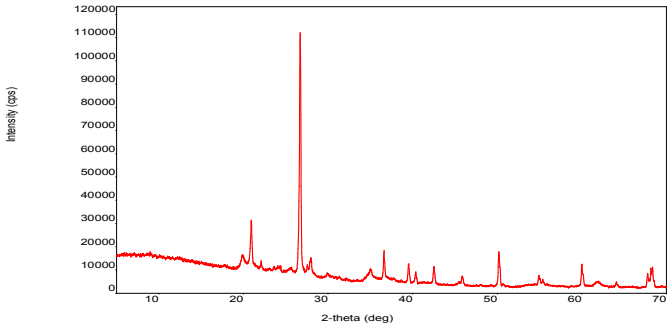

Fig.-4: XRD of Bentonite Mineral

The first loss at 100℃ can be attributed to loss of hygroscopic water, the second loss due to removal of water composition, and the third due to lattice dehydroxylation. The peaks in the graph of glancing angle versus intensity obtained during the XRD analysis confirmed that Si and Al were the principal constituents of bentonite mineral. Endothermic peaks in DTA also confirm the presence of bentonite. SEM image of bentonite mineral shows the microscopic texture of bentonite. Grains show a spongy texture.

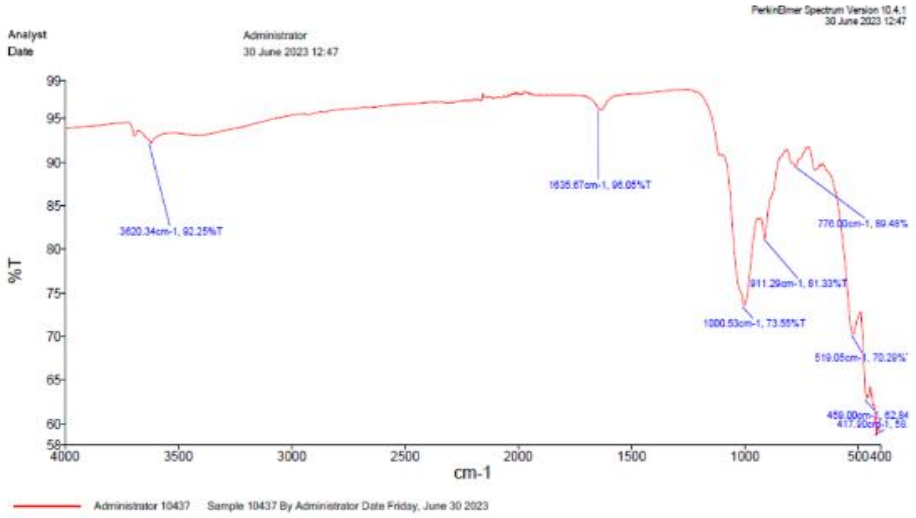

Fig.-5: FTIR of Bentonite Mineral

Effect of Initial Concentration

The effect of initial concentration, such as 10 ppm, 20 ppm, 30 ppm, 40 ppm, and 60 ppm, was studied on adsorption by bentonite at 220 rpm. The results obtained indicated that the adsorption increased with increasing dye concentration (Fig.-1). The maximum percentage removal was recorded for an initial concentration of 60 ppm. The equilibrium was attained within 45 minutes. At an initial concentration of 20 and 40 ppm, the percentage of dye removal decreased and then increased after 30 minutes and attained equilibrium at 60 minutes. For an initial concentration of 10, 20, 30, 40, 50, and 60 ppm, the equilibrium was attained in 45 minutes.

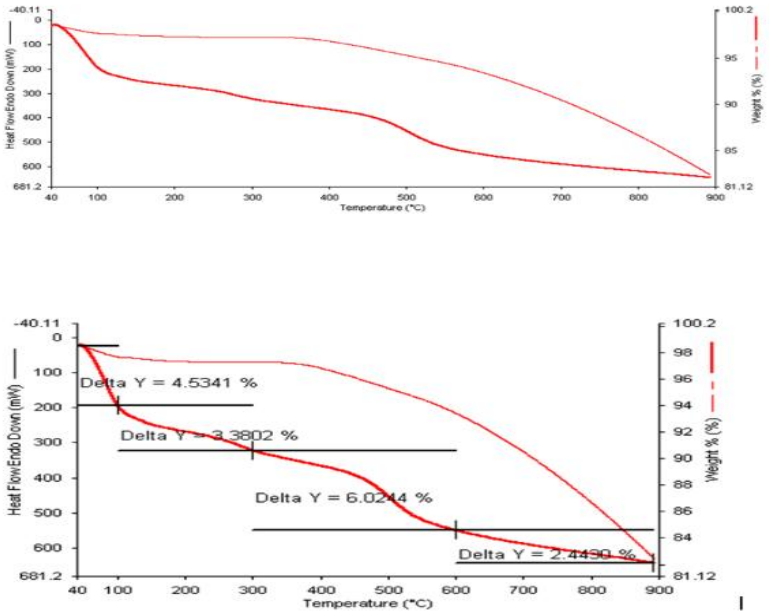

Fig.-6: DTA and TGA of Bentonite Mineral

Effect of Time

Studies were done with a fixed amount of 1g bentonite at P^H 7 at different time intervals (15, 30, 45, and 60 minutes) at 220 rpm. With increasing time, the percentage removal increased as the adsorption sites remained in contact with the adsorbate for a longer time. The removal percentage can be attributed to time, initial concentration, interaction between adsorbate and adsorbent, the no. of molecules covering mesopores and micropores, and the entire surface of the adsorbent. The negative charge of bentonite is balanced by the exchangeable cations such as K^+ and Na^+. Amine groups of the o-phenylene diamine were attached to the surface of the bentonite, and thus, decoloration was achieved.

CONCLUSION

The bentonite minerals can be applied as an eco-friendly and low-cost alternative for the removal of O-phenylenediamine. The effect of time and initial concentration of the dye was confirmed through experimental results.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

The present work is related to *SDG-6: Clean Water and Sanitation*. The authors contributed significantly to this manuscript, participated in experimental and data collection, and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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