Sodium Docusate Surface-Modified Dispersible and Powder Zinc Peroxide Formulation: An Adsorbent for the Effective and Fast Removal of Crystal Violet Dye, an Emerging Wastewater Contaminant

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ABSTRACT: Crystal violet (CV) dye is one of the most toxic dyes majorly generated by textile industries. It may cause health issues if enters human beings. A lot of research has been reported for the removal of CV dye from wastewater; however, most of them are time-consuming and hardly remove more than 95% of the CV dye. In the last few years, we have tested several materials, and most of them have exhibited very low efficacy toward adsorption of CV including zinc peroxide (ZnO₂). To enhance adsorption efficacy, dispersibility, and stability, the surfaces of several reported materials were modified using different wetting agents and nonionic surfactants. Interestingly, ZnO₂, which was earlier very less effective after surface modification by sodium salt of dioctyl sulfosuccinate, efficiently adsorbed >99.5% of CV from contaminated water within 5 min of contact time at pH ∼10. The adsorption capacity obtained for the sodium docusate surface-modified zinc peroxide (ZnSD) adsorbent was found to be 123 mg/g, which is much better than the other reported for CV removal. Different physiochemical experiment parameters like pH, contact time, initial dye concentration, adsorbent dosages, and temperature were optimum to achieve maximum adsorption of the CV dye. The adsorption rate and adsorption mechanism studies show that the adsorption of CV follows pseudo-second-order kinetics and the Freundlich isotherm model. The adsorption results are consistent, and even treated water can be reused for various applications.

INTRODUCTION

Water is an essential component and plays an important role in the regular functioning of our ecosystem. Every living creature needs water for its survival. In spite of this, today almost 40% of the total population is facing water crises.⁵ Being the world’s second most populated country, India is also facing the severe problem of contaminated drinking water. The rapid growth of dye-based industries has resulted in the contamination of water bodies at an alarming rate.⁶ Across the world, the situation is very critical and literature data tells that most people suffer and die due to water-borne diseases.⁷

Contamination of water is a serious issue, as it affects human lives⁸−⁹ and is expected to worsen in coming years. Water may contain organic (dyes, antibiotics, pesticides, etc.) and inorganic (heavy metals) contaminants. These contaminants are dangerous for humans and animals because of their highly toxic and carcinogenic nature.⁷,⁸ Dyes are one of the major organic toxic contaminants found in water. Dyes in water come from industries such as textile, paper, and plastic industries.⁹ CV is one of the toxic dyes and well known for its teratogenic and mitogenic poisoning and mutagenic effect in nature.¹⁰ It can also damage the cornea and be toxic for mammalian cells. However, CV dye is extensively used by the medical community as a bacteriostatic agent¹¹ and as an external skin disinfectant in humans and animals.¹²,¹³ The IUPAC name of CV dye is N-[4-[bis[4-dimethylamino)-phenyl]-methylene]-2,5-cyclohexadien-1-yldine]methylmethanaminium chloride (molecular formula C₂₅H₃ON₃Cl and molecular weight 407.98).¹⁴

Many advanced techniques exist for the removal of dyes such as oxidative degradation,¹⁵ electrocoagulation,¹⁶,¹⁷ photodegradation,¹⁸ biochemical degradation,¹⁹ ozonization process,²⁰ solvent extraction method,²¹ and adsorption.²² Out of them, adsorption is one of the most feasible and potential technique²³ because of its low cost, eco-friendlyness, and...
simplicity. Many adsorbents have been utilized by a number of researchers for the uptake of CV dye from wastewater. Some researchers have utilized natural products or byproducts as adsorbents such as activated carbon,24 rice husk,25 grapefruit peel,26 ginger waste,27 pinus bark powder,28 and Chitosan composites29 and several others have utilized synthetic adsorbents such as iron oxide (Fe₃O₄)-coated biochar,30 Mn-doped ZnO nanocrystals,31 manganese ferrite,32 etc. Most of the cited materials require several hours to remove CV from contaminated water and no one has reported adsorption capacity above 80 mg/g.

ZnO₂ is a highly potent adsorbent for the uptake of several dyes.33 To remove CV from water and make it reusable in the same process, surface modification of ZnO₂ material has been carried for high functionality, dispersibility, and stability after treating with nontoxic SD (C₂₀H₃₇O₇SNa). The structures of SD and CV have been illustrated in Figure 1.

MATERIALS AND METHODS

All of the reagents utilized for the synthesis and experiments like zinc acetate, sodium chloride, magnesium sulfate, ammonium hydroxide, sodium hydroxide, and hydrochloric acid used were of analytical grade. The CV was commercial grade of >96% purity. Deionized (DI) water of 18.2 MΩ cm resistivity used in the experiments was obtained from the Millipore Milli-Q element water purification system. The stock solution of 1000 mg/L of CV dye was prepared by taking a requisite amount of dye in 1000 mL of DI water. The stock solution of the dye was diluted to the desired concentration for further studies. NaOH (0.1 M) and HCl (0.1 M) were used to adjust the pH of the solution with the help of an Orion benchtop pH meter from Hitachi. A UV–vis spectrophotometer (model U-3900H) was used to study the concentration of the dye in the solution. NaCl (0.1 M) and MgSO₄ (0.1 M) are used for the study of the anti-interference ability of ZnSD.

Synthesis Process for ZnSD. Ten grams of zinc acetate dihydrate was dissolved in 100 mL of ammonia solution (10%) and further diluted to 200 mL by water:methanol (4:1) mixture. The above mixture was stirred for 10 min at a constant temperature (50–55 °C). Then, 50 mL of hydrogen peroxide solution (30%) was added drop by drop, and white precipitates of ZnO₂ were formed. The formed ZnO₂ precipitate was washed several times with distilled water and then dried at 105 °C in an oven. The synthesized ZnO₂ was treated with the sodium salt of dioctyl sulfosuccinate (sodium docusate) as a wetting agent and nonionic surfactant. The rheology of the suspension was modified using urethane, and the thickness was improved using pharmaceutical xanthan gum. Isothiazolinone was added as a preservative or antibacterial agent to protect the dispersion from microorganisms that would grow in stagnant water over a long period of time. The dispersion of ZnSD thus made was found to be stable for more than three years below 40 °C temperature.

Figure 1. Structures of (a) sodium docusate and (b) CV dye.

Figure 2. Schematic presentations of adsorption of CV dye over adsorbent.
Adsorption Studies. Adsorption studies were carried out using batch studies. Each study involved 25 mL of dye solution of predetermined concentration containing a known amount of adsorbent. Experiments were performed by changing the experiment conditions such as pH, contact time, adsorbent dosages, and initial dye concentration of the solution. The pH range from 2 to 10 was adjusted using 0.1 M HCl and 0.1 M NaOH. For adsorbent dosage studies, adsorbent from 0.01 to 0.1 g was taken. All of the experiments were performed at room temperature. The percentage removal and removal capacity of the adsorbent was calculated by eqs 1 and 2, respectively.

\[
\text{% removal of CV (\%) = } \frac{C_i - C_f}{C_i} \times 100
\]

\[
\text{adsorption capacity (} q_e \text{ (mg/g) = } \frac{C_i - C_f}{m} \times V
\]

where \(C_i\) and \(C_f\) are the initial and final concentrations of CV dye solution in mg/L, \(q_e\) (mg/g) is the adsorption capacity of the adsorbent, \(V\) is the volume of CV solution taken in liters, and \(m\) is the mass of adsorbent in grams. The schematic presentation of adsorption of CV dye over ZnSD is given in Figure 2.

## RESULTS AND DISCUSSION

Mechanism. Zinc peroxide, which was inactive for the uptake of CV dye from wastewater, is made highly active by surface modification with the help of SD. The long hydroscopic chain contains an aliphatic hydrocarbon chain of SD and a polar part of SD creates the \(\text{SO}_3^−\) group over the surface of \(\text{ZnO}_2\). Further, the surface modification of ZnSD in the presence of xanthan gum forms a reverse micelles system around the CV dye present in water. This micelle formation results in the uptake of CV dye from water by ZnSD. Besides, this electrostatic interaction between the \(\text{SO}_3^−\) group of ZnSD and the cationic nitrogen of CV dye also enhances the adsorption capacity. The probable mechanism has been illustrated in Figure 3. Also, the zeta-potential studies indicate that the potential of ZnSD decreases from \(-15\) to \(-60\) mV as we increase the pH from 3 to 9, which suggests a higher negative charge on adsorbent at higher pH and results in more electrostatic interaction between ZnSD and CV dye at higher pH.

XRD Analysis. The phase analysis of the ZnSD adsorbent was carried out in the 20 range from 0 to 80°. The pattern obtained using powdered XRD of adsorbent is shown in Figure 4. The XRD pattern obtained contains the characteristics peaks of zinc peroxide, sodium dioctyl sulfo succinate, and xanthan gum.

ASR Analysis. FTIR analysis of the adsorbent before and after the adsorption of CV was performed in the transmittance mode to identify the functional groups in the range of 4000–400 cm\(^{-1}\) and to obtain the data after the treatment. ZnSD was treated with CV dye at optimum conditions, i.e., pH of 9, adsorbent dosage of 0.05 g, contact time of 5 min, and 100 mg/L of dye solution. As shown in Figure 5, the IR peaks at 441, 1124, 1400, 1640, and 3200 cm\(^{-1}\) correspond to the Zn--O stretching bond, S--O stretching, C=O bending mode, C=O stretching, and O--H stretching, respectively.

SEM and EDX Analysis. SEM and EDAX analysis have been carried before and after CV adsorption to identify the surface morphology and elemental composition. The results...
obtained are given in Figure 6a–f. Figure 6a, which is representative of pure ZnO₂, exhibits a spherical shape of the particles; however, upon surface modification with SD, this shape changes to flakes, as presented in Figure 6b. The elemental analysis in Figure 6a,b is presented in Figure 6d,e, respectively. The elemental analysis of pure ZnO₂ shows the presence of Zn and O, while elemental analysis of ZnSD shows zinc, oxygen, sulfur, carbon, and sodium.

It has been noticed that the shape of the ZnO₂ particles changes from spherical to flakes upon surface modification, as shown in Figure 6c. From Figure 6b,c, it is clear that the shape of adsorbent particles changes upon adsorption. Before the adsorption, the adsorbent particles have a flake-type shape; however, after adsorption, the shape of the adsorbent particles becomes bulky and it seems like they accumulate something on their surface, which provides sufficient evidence of the adsorption of CV dye on the surface of the prepared adsorbent. Also, the chemical composition of the adsorbent changes after adsorption, and it is very clear from Figure 6f. Initially, the adsorbent had zinc, oxygen, sulfur, carbon, and sodium; however, after the adsorption of CV dye, the chemical composition changes to zinc, carbon, oxygen, sulfur, and nitrogen. It can be explained by the fact that sodium from the adsorbent combines with chlorine from dye and forms NaCl and escapes out and carbon and nitrogen from the dye were adsorbed on the adsorbent.39

**pH Optimization.** pH is one of the most significant parameters that affect the adsorption of contaminants on the adsorbent.40 In the present study, the pH was varied from 2 to 10 for 25 mL of 100 mg/L CV solution. To each solution of...
different pH values, 0.05 g of ZnSD was added. From Figure 7a, it is clear that the percentage removal of CV increases with increases in the pH and reaches a maximum at pH 10. However, the maximum enhancements were observed when pH changes from 6 to 7. The maximum adsorption (≥99.8%) was noted around pH 10. In the proposed studies, all of the experiments were carried out at a pH of around 10.

ZnSD Dosage Optimization. To find out the optimized adsorbent dosage, experiments were set in which constant concentration and volume of CV solution were taken for different amounts of adsorbent (0.01−0.1 g). The results are shown in Figure 7b, which clearly suggest that the removal of CV dye increases with the increase in the adsorbent amount and reaches a maximum at 0.05 g of adsorbent. This could be explained in such a way that adsorption increases with the increase in the number of active sites available for adsorption.

Contact Time Optimization. Contact time optimization is important to find out the maximum percentage removal of any contaminant from wastewater. The result also indicates the quality of the adsorbent in terms of adsorption efficiency. To know the maximum contact time for the proposed adsorbent, experiments were carried out at different times (1−5 min). The results obtained for different time intervals are illustrated in Figure 7c. Figure 7c reveals that adsorption increases upon increasing the time up to 5 min. The adsorption capacity of the adsorbent was found to be ≥99.8% at 5 min, and further, a plateau was observed.

Initial Dye Concentration Optimization. To optimize the initial concentration of the CV solution, a set of experiments was carried out by taking different initial concentrations of the CV solution at optimized pH and adsorbent dosage. The result of the experiments was plotted in the form of a graph shown in Figure 7d. The figure reveals that ≥99.8% of CV can be removed from 25 mL of initial concentration. However, the removal efficiency decreases with the increasing concentration of the adsorbate. This is because the free site of the adsorbent gets occupied by adsorbate.

Adsorption Isotherm Studies. The ability of an adsorbent to adsorb certain adsorbate can be very well studied by the adsorption isotherm data. To determine the adsorption performance for the optimization of the adsorption pathway, modeling of the adsorption isotherm data plays a significant role. Out of several isotherm models, Langmuir and Freundlich are most commonly used for the modeling of the adsorption data. Graphs plotted for Langmuir and Freundlich are shown in Figure 8. As the value of the correlation coefficient for Freundlich, $R^2 = 0.999$ became
higher than that of the Langmuir adsorption model, which suggests that the uptake of the CV dye on surface-modified sodium docusate zinc peroxide follows the Freundlich adsorption model.

**Kinetics Studies.** Kinetics models for pseudo-first-order and pseudo-second-order kinetics were studied for the determination of the reaction mechanism and the evaluation of the correlation coefficients and rate constants. Graphs were plotted for the pseudo-first-order and pseudo-second-order kinetics and are shown in Figure 9 with their correlation coefficient values. From the plots, the value of the correlation coefficient, $R^2 = 0.995$, of the pseudo-second-order kinetics was found to be higher than that of the pseudo-first-order kinetics, which proves that the adsorption of CV dye over the ZnSD adsorbent follows pseudo-second-order kinematics and suggests that the adsorption of CV dye involves valancy forces through sharing or exchange of electrons between adsorbent and adsorbate.

**Anti-interference Ability.** To further determine the effective adsorption and anti-interference ability of ZnSD in real water, the effects of the coexistence of other competitors (Na$^+$, Mg$^{2+}$, Cl$^-$, and SO$_4^{2-}$) were also examined. In this study, 5 mL of a 0.1 M solution of each competitor was separately added to 30 mL of 100 mg/L CV solutions. Figure 10 describes that the presence of Na$^+$, Mg$^{2+}$, Cl$^-$, and SO$_4^{2-}$ barely affects the adsorption of the CV dye on ZnSD. This means that ZnSD exhibits a strong anti-interference ability for the uptake of CV dye from the wastewater.

**Comparison with Other Reported Adsorbents.** To demonstrate the effectiveness of the present study, we put the data of the adsorption capacity and contact time of different reported adsorbents for CV dye as shown in Table 1. This shows that ZnSD uptakes the CV dye very fast as compared to other reported adsorbents and shows good adsorption capacity.

### Table 1. Different Reported Adsorbents for the Removal of CV Dye and Their Adsorption Capacities

| adsorbent                        | $q_e$ (mg g$^{-1}$) | time (min) | ref  |
|----------------------------------|---------------------|------------|------|
| activated carbon                 | 64.80               | 120        | 52   |
| raw bentonite                    | 131                 | 200        | 53   |
| modified bentonite               | 457                 | 25         | 53   |
| jute fiber carbon                | 28                  | 150        | 54   |
| saw dust                         | 341                 |            | 55   |
| magnetic chitosan beads          | 333.33              | 140        | 56   |
| native cellulose                 | 112                 | 20         | 57   |
| modified cellulose               | 182.85              | 150        | 57   |
| SnFe$_3$O$_4$@activated carbon magnetic | 158.73              | 80         | 58   |
| SDS coated maghemite nanoparticles | 166.7               | 10         | 34   |
| nanoscale zero-valent iron Sargassum swartzii (nZVI-SS) biocomposite | 200                 | 120        | 59   |
| coniferous pinus bark powder(CPBP) | 32.78               | 120        | 28   |
| palm kernel fiber (PKF)           | 78.9                | 30         | 14   |
| ZnSD                             | 123                 | 5          | present study |

### CONCLUSIONS

In the present study, ZnSD was formulated using a simple chemical process for the fast uptake of toxic CV dye from the wastewater. The removal of CV dye, an emerging organic contaminant usually detected in a wide range of industrial wastewater, from wastewater is not an easy job. A typical adsorbent is not very efficient because of its low adsorption capacity, high cost, and long contact time for maximum adsorption, but the proposed ZnSD adsorbent is highly efficient, of low cost, and eco-friendly and can uptake almost all of the CV dye from the wastewater within few minutes of contact time. Various adsorption parameters were adjusted to optimize the conditions for the maximum percentage removal of the CV dye from wastewater such as pH, contact time, initial dye concentration, adsorbent dosages, etc., and it was observed that the maximum percentage removal of 99.8% for a 50 mg/L dye solution and 0.05 g of adsorbent dosage could be obtained at an optimum pH of 10 after 5 min of contact time. The data obtained by analyzing the kinetic and isotherm modeling suggests that the adsorption of the CV dye on the ZnSD adsorbent follows pseudo-second-order kinetics and a Freundlich adsorption model.

The experimental results demonstrate that ZnO$_2$, which was earlier less effective for the removal of CV dye from wastewater, on surface modification with the sodium salt of dioctyl sulfosuccinate as a wetting agent and nonionic surfactant became a highly potent and efficient adsorbent for the uptake of CV dye from wastewater. A comparison of the
adsorption capacity of different adsorbents with that of ZnSD is also shown in Table 1.

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Notes
The authors declare no competing financial interest.

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