Removal of Methylene Violet from Aqueous Solutions Using BaSr$_2$NbO$_{5.5}$

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Abstract

The removals of Methyl violet from aqueous solutions using the double perovskites BaSr$_2$NbO$_{5.5}$ are reported. The oxides were prepared using solid state reaction in which the raw materials were mixed initially by either acetone or water. The X-ray diffraction measurements demonstrated that the preparation methods have influenced the cell volume, crystal size and surface area of the oxides. As consequence, the adsorption properties were also affected. The study showed that the prepared oxides have a cubic structure with crystallite size is less than 82 nm. However, the crystallite size of the oxide obtained by wet method (W) is higher than that of the oxide obtained by dry method (D). Consequently, the amounts of the dye adsorbed by BaSr$_2$NbO$_{5.5}$ (D) were higher than those adsorbed by BaSr$_2$NbO$_{5.5}$ (W). The maximum removal capacities of Methyl violet are found to be 8.71 and 9.39 mg/g using BaSr$_2$NbO$_{5.5}$ (W) and BaSr$_2$NbO$_{5.5}$ (D) respectively. The removals of the dye have positive relationship with pH, temperature, the specific surface area and the mass of the oxide.

Keywords: Removal; Methylene violet; Perovskite oxides

Introduction

Organic dyes play a vital role in industry. They are used in textile dyeing, paper printing, photography, pharmaceutical, leather, food products etc. After usage, dyes are discharged to the water sources like river, seas and oceans etc. [1,2]. The discharge of such substances into the water is dangerous since many of these are toxic, mutagenic and/or carcinogenic to living beings [3]. For instances, methylene blue, organic dye usually used in cotton and wool manufacturing, can cause serious health problems for human such as vomiting, hard breathing and mental disorder. Dyes can also affect biodegradation, light penetration and photosynthesis producing imbalance in the ecosystem [4]. Hence, the development of an effective treatment technique that can remove or convert such pollutants into non-toxic or less harmful materials is highly required. Examples of wastewater treatment methods are filtration, chemical precipitation, electrolysis, sedimentation, oxidation, photo degradation and adsorption. Adsorption is considered as an effective method in term of initial cost, simplicity of construction and insensitivity of toxics. Thus, a wide variety of natural and synthetic materials such as activated carbon, peat, various silica, activated clay, banana pith, natural manganese mineral, oil ash, goat hair, alum sludge, natural zeolite, mixtures of flash, soil and Nano materials have been investigated as dye adsorbents.

Nanomaterials exhibits unusual properties compared to their bulk counterpart due to the large surface area to volume ratio in the nanoscale. Naturally, their material properties and applications largely depend on size, distribution and morphology of the nanomaterial, essentially allowing them to exhibit completely new or improved properties. Nanomaterials find applications to address technological and environmental challenges including of solar energy conversion, catalysis, medicine, and water treatment. Among Nano materials, perovskite oxides have been proven to be of interest due to their efficiency in adsorbing and degrading recalcitrant organic compounds [5]. Generally, perovskite type oxides are containing of two different cations, each surrounded by oxygen anions. The larger cation which can be alkali, alkaline earth, or rare earth has dodecahedral symmetry in their structure are critical in determining the properties of such systems [10,11]. Water can be incorporated into the lattice by occupying either the vacancies or nearby interstitial sites. The site which the incorporated water occupies nearest interstitial sites.

This work investigates the removal of Methyl violet 10 B (MV) from aqueous solutions using the ordered deficient perovskite BaSr$_2$NbO$_{5.5}$. The oxide has been synthesized by solid state reaction but used different slurry media, namely acetone and water. The purpose of the solvents is to enhance the homogeneity of the mixtures, and to create dry (D) and wet (W) media for the initial reaction. The main aim of the study is to examine the impact of an aqueous slurry medium on the adsorption properties of the oxides [7-9].

The ordered defect double perovskites of the type A$_2$B*BO$_{3.5}$ where A and B*=Ca$^{2+}$, Sr$^{2+}$ or Ba$^{2+}$ and B=Sb$^{5+}$, Nb$^{5+}$ or Ta$^{5+}$ are of current interest, since the mechanism of water interaction and the proton diffusion in their structure are critical in determining the physical properties of such systems [10,11]. The title double perovskites exhibit ionic conductivity [12] and can absorb signi cant amounts of water to become proton conductors [13,14]. Unlike stoichiometric ABO$_3$ perovskites, in which all the B-type cations are six coordinates, the effective coordination number of the cations in anion-deficient A$_2$B*BO$_{3.5}$ perovskites are reduced from six, so that locally some B-type cations will be five, or even four, coordinate [15]. Water can be incorporated into the lattice by occupying either the vacancies or nearby interstitial sites. The site which the incorporated water occupies nearest interstitial sites.
will be dependent on the differences in the coordination tendencies of the B\(^+\) and B\(^+\) cations [15].

Methyl violet 10B (MV) is known in medicine as Gentian violet and is the active ingredient in a Gram stain, used to classify bacteria [16]. It is used as a pH indicator, with a range between 0 and 1.6. Compounds related to methyl violet are potential carcinogens. Methyl violet 10B inhibits the growth of many Gram positive bacteria, except streptococci. It is soluble in water, ethanol, diethylene glycol and dipropylene glycol [17]. Methyl violet is a mutagen and mitotic poison, therefore concerns exist regarding the ecological impact of the release of methyl violet into the environment. Methyl violet has been used in the initial stage of the reaction leads to larger crystallites and this is probably the basis for the differences in appearance and texture. Figure 1 demonstrates SEM images for BaSr\(_2\)NbO\(_{5.5}\). The grains are monophasic and apparently free of impurities.

**Experimental**

**Sample preparation**

The preparation of samples involved different stoichiometric compositions of Nb\(_2\)O\(_5\) (Merck, 99.99%) and SrCO\(_3\) or BaCO\(_3\) (BDH, 99.98-99.99%). The mixtures were initially ground, as either an acetone or aqueous slurry, and preheated at 850°C for 12 h, and then reground and heated at 1100°C for 48 h.

**Instrumentations**

The crystallography of the samples was examined by a PANalytical X'Pert X-ray powder diffraction using Cu Ka radiation (1.5400 Å) and a PIXcel solid-state detector. The operating voltage was 40kV and the current was 30 mA. The samples were measured in plate mode at room temperature with a scan range of 10°<\(\theta\)<80° and a scan length of 10 mins were used. The microstructure of the powder samples was examined by scanning electron microscopy using an Intellec tion Quemscan.

The absorbance of solutions was determined using ultraviolet visible spectrophotometer (UV/Vis, model Spect-21D) and (190-900 Perkin-Elmer) at maximum wavelength of absorbance (590 nλ). The concentrations of solutions were estimated from the concentration dependence of absorbance. The pH measurements were carried out on a WTW720 pH meter model CT16 2AA (LTD Dover Kent, UK) and equipped with a combined glass electrode.

**Batch mode**

Batch mode removal studies were carried out by varying several parameters such as contact time, pH, temperature and mass of prepared oxide (adsorbent). Essentially, a 50 ml of dye solution with concentration of 50 ppm was taken in a 250 ml conical flask in which the initial pH was adjusted using HCl/NaOH. Optimized amount of adsorbent was added to the solution and stirred using magnetic stirrer for specific time. The oxide samples were separated from solutions using centrifuge 3500 CPM for 5 minutes.

**Results and Discussion**

**Characterization of oxides**

Visually, it was observed that the colour of the powdered compounds obtained using either acetone or water during the mixing is slightly different. For example, powders of BaSr\(_2\)NbO\(_{5.5}\) are dark yellow when prepared using acetone whereas it is light yellow if water is used in the initial mixing. The hardness of the powders was found to be dissimilar; generally, samples are much smoother after mixing with water. SEM analysis also revealed that the particle sizes were not equal. These surprising observations indicate that the presence of water in the initial stage of the reaction leads to larger crystallites and this probably is the basis for the differences in appearance and texture. Figure 1 demonstrates SEM images for BaSr\(_2\)NbO\(_{5.5}\). The grains are monophasic and apparently free of impurities.

X-ray diffraction measurements showed the oxides had a faceted cubic structure with space group (Fmm). Figure 2 illustrates the XRD patterns of the oxides. The Average Crystallite size \(D_p\), specific surface area \(S\), lattice strain \(\phi\), Lattice parameter \(a\) and Cell volume \(V\) estimated from X-ray diffraction data are summarised in Table 1. The crystallite size can be calculated using shearer formula [19] (Equation. 1) where the specific surface area can be calculated using Sauter formula [20] (Equation.2) in which \(\rho\) is the density of the synthesised material.

\[
D_p = (0.94\lambda)/(\beta f/2\times\cos\theta) \tag{1}
\]

\[
S = 6000 / (D_p \times \rho) \tag{2}
\]
**Effect of contact time:** The removal percentage of dyes over the adsorbents can be calculated as: R%=[(Ci-Ct)/Ci] × 100, where R% is the removal percentage, Ci=50 ppm is initial concentration of dye solutions, Ct is the concentration of dye at contact time estimated from the concentration dependence of absorbance fit. The effect of contact time on the MV removal was observed at the range of (0-120 min). Figure 3 shows the time dependence of MV removal at room temperature. There is no finite time was observed for the dye removal up to 120 min. The removals of the dye increase as the contact time increases. The removals of MV using BaSr$_2$NbO$_{5.5}$ (D) were larger than those using BaSr$_2$NbO$_{5.5}$ (W). This is due to the differences in the crystallite size and the specific surface area of the two oxides. The surface area of BaSr$_2$NbO$_{5.5}$ (D) is found to be larger than that of BaSr$_2$NbO$_{5.5}$ (W) [21].

**Effect of adsorbent mass:** The amount of the dye adsorbed by one gram of the oxides (Q) was calculated as following: Q(mg/g)=[(Ci-Ct)×V]/W, where t=120 min is the contact time, V=50 ml is the volume of dye solution and W is the mass of oxides. As shown in Figure 4. Q decreases as the mass of adsorbents increased.

**Table 1:** Average Crystallite size Dp, Spec ic surface area S, lattice strain φ, Lattice parameter a and Cell volume V estimated from X-ray diffraction data.

|      | Dp (Å) | (g/cm$^3$) | S (m$^2$/g) | φ  | a (Å) | V (Å$^3$) |
|------|--------|-------------|-------------|----|-------|------------|
| BaSr$_2$NbO$_{5.5}$ (D) | 50.24  | 5.419       | 22.04       | 0.0028 | 8.4599(1) | 605.476(2) |
| BaSr$_2$NbO$_{5.5}$ (W) | 72.80  | 5.384       | 15.31       | 0.0019 | 8.4733(5) | 608.554(7)  |

**Figure 3:** The time dependence of MV removal at room temperature. he volume, concentration and pH of the dyes solution are 50 ml, 50 ppm and 7 respectively.

The maximum capacity of adsorbent Qmax can be estimated from the intercept of the liner it of 1/Q at Y axis. It was found that BaSr$_2$NbO$_{5.5}$ (D) has Qmax (57.40 mg/g) higher than that for BaSr$_2$NbO$_{5.5}$ (W) (47.52 mg/g). This result is consisted with the surface area of the oxides (Table 1). Qmax increased as the surface area of the oxides increased. The amounts of MV adsorbed by BaSr$_2$NbO$_{5.5}$ (W) which has the larger crystallite size (72.8 nm) and the smaller spec ic surface area (15.31 m$^2$/g) are much lower than those adsorbed by BaSr$_2$NbO$_{5.5}$ (D) which has the smaller crystallite size (50.24 nm) and the larger spec ic surface area (22.04 m$^2$/g).

**Effect of pH:** To study the effect of pH, experiments were carried out at various pH values, ranging from 2 to 8 for constant dye concentration (50 ppm) and adsorbent mass (0.1 g). Figure 5 shows the removal of dyes as a function of pH. It was observed that the removal of MV on the oxides increases as pH increased. The highest removal of MV was recorded for BaSr$_2$NbO$_{5.5}$ (D) at pH=7 around 59% where the lowest removal of MV was recorded for BaSr$_2$NbO$_{5.5}$ (W) at pH=2 around 21%. The interpretation of pH effects on the efficiency of the adsorption process is a very difficult task, because of its multiple roles. It is related to the acid base property of both the metal oxide and the organic dye. The adsorption of water molecules at metal sites is followed by the dissociation of OH– groups, leading to coverage with chemically equivalent metal hydroxyl groups (M-OH). Due to amphoteric behaviour of both the metal oxide and the organic dye, the equilibrium reactions below are considered. The electrostatic interactions between the positive catalyst surface and dye anions leading to strong adsorption of the last on the oxide support.

\[\text{M-OH} + \text{H}^+ \leftrightarrow \text{M OH}^2;\]
\[\text{M-OH} \leftrightarrow \text{M}^+ + \text{OH}^-;\]
\[\text{Dye OH} + \text{H}^+ \leftrightarrow \text{Dye}^+ + \text{H}_2\text{O};\]
\[\text{H Dye} + \text{OH}^- \leftrightarrow \text{Dye}^- + \text{H}_2\text{O}.\]
Conclusion

The removal of Methyl Violet from aqueous solution by the defected double perovskite BaSr$_2$NbO$_{5.5}$ has been studied. The oxides were synthesised by solid state reaction but using two different slurry media namely water and acetone. The BaSr$_2$NbO$_{5.5}$ (W) oxide obtained by wet method have smaller specific surface area than the BaSr$_2$NbO$_{5.5}$ (D) oxide obtained by dry method. Consequently, the amounts of MV adsorbed by BaSr$_2$NbO$_{5.5}$ (D) were higher than those adsorbed by BaSr$_2$NbO$_{5.5}$ (W).

In general, the study showed no finite time for the two dyes removal up to 120 min. The removals of both MV dyes increased as the physical parameters: time, temperature, pH, adsorbent mass increase. The highest removal efficiency was recorded for MV dye using BaSr$_2$NbO$_{5.5}$ (W) at pH=6 whereas the lowest removal was observed BaSr$_2$NbO$_{5.5}$ (D) at pH=2. The study indicated that the preparation methods has in luenced the texture and adsorption properties of the oxide.

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