

Removal of Neutral Red from Aqueous solutions using Sr₂CaBO_{5.5} (B= Nb⁺⁵& Ta⁺⁵)

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Abstract

Two samples of the defect double perovskites with general formula Sr₂CaNbO_{5.5} and Sr₂CaTaO_{5.5} were synthesized and their capabilities in the removal of neutral red dye investigated. Both samples have faced cubic perovskite-type structure in space group Fm₃m. The replacement

of Nb⁵⁺ by Ta⁵⁺ has influenced both crystal size and density of the two oxides but showed no impact on the removal capacities. The crystallite size of Sr₂CaNbO_{5.5} and Sr₂CaTaO_{5.5} was determined to be 93.56 and 43.69 nm respectively. The maximum removal capacities of Neutral red are found to be 190.5 mg/g using both the two oxides. This result is consistent with the cell volumes which displayed similar values. The removal of Neutral Red has a negative relationship with temperature but steadily increases as pH increased.

Introduction

Organic dyes are considered to be extremely environmental pollutants. Their effluents are, in many cases, carcinogenic and toxic¹. They consist of two main groups: chromophores which are responsible for colour and auxochromes that are responsible for intensity of the colour. Dyes are classified according to chemical structure and type of application. Based on the chromophore, 20–30 different groups of dyes can be discerned, with azo, anthraquinone, phthalocyanine and triarylmethane accounting for the most important groups². The emissions of dyes from industrial activities causes degradation of water quality, thus many methods are reviewed to remove such

organic pollutants. These methods can be divided to physical processes such as adsorption, chemical treatments such as chemical oxidation and other such as biological degradation technique^[3, 4]. Adsorption has become more popular for wastewater treatment due to their efficiency in their removal. It can produce economically high quality water in sufficient time^[5, 6].

Recently, there is a growing interest in developing new adsorbent materials with diverse compositions, properties and functionalities. The physical characteristics of the adsorbents, such as surface area, porosity, size distribution, density and surface charge, all influence the adsorption process. Perovskite oxides with general formula ABO_3 are promising candidates for dyes adsorption. They are highly versatile due to the flexibility in the chemical composition with a large number of cations^[7]. Those cations can fit into both the *A* and *B* positions within the same crystalline structure. Perovskite oxides that contain a lanthanide element at position *A* and a transition metal at position *B* are used more frequently in heterogeneous catalysis, obviously exploiting the catalytic properties of transition metals. Perovskites with oxygen and cation non-stoichiometry can achieve the desired catalytic activity, including multifunctional catalytic properties^[7, 8]. This work investigates the capability of the defect double perovskite $Sr_2CaNbO_{5.5}$ and $Sr_2CaTaO_{5.5}$ in the removal of Neutral Red dye from aqueous solutions. In such double perovskite structure, it is anticipated that the two smallest cations will order in the octahedral sites, this ordering being a consequence of the differences in the size and/or charge between the two cations. The largest cation will then occupy the 12-coordinate (cuboctahedral) site. The corresponding ionic radii of Sr^{2+} (12 coordinate ionic radius, 1.44 Å and 6 coordinate ionic radius, 1.18 Å)^[9]; Ca^{2+} (1.34 and 1.00 Å), Nb^{5+} (6 coordinate ionic radius, 0.64 Å) and Ta^{5+} (0.64 Å) cations suggest that the (Nb^{5+} , Ta^{5+}) and one Ca^{2+} cation will occupy the 6-coordinate sites whereas the Sr^{2+} will occupy the cuboctahedral sites.

Neutral Red is a xanthene dye used for staining in

histology. It is used as a counter stain in combination with other dyes, and for many staining methods. Together with Janus Green B, it is used to stain embryonal tissues and supravital staining of blood^[2].

Experimental

Sample Preparation

The preparation of samples involved different stoichiometric compositions of Ta_2O_5 (Merck, 99.99%) and $CaCO_3$ or $SrCO_3$ (BDH, 99.98-99.99%). The mixtures were initially ground 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 $Cu K\alpha$ 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 flat plate mode at room temperature with a scan range of $10^\circ < 2\theta < 80^\circ$ and a scan length of 10 mins were used. The structures were refined using the program RIETICA^[10].

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 (520 nm). The concentrations of solutions were estimated from the concentration dependence of absorbance fit. 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 10 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.

Result and Discussions

Characterization of Oxides

The preparation of an extensive solid state solution allows us to study the effects of altering the chemical composition on the physical properties. The heating regime described above produced crystalline, yellowish coloured, samples. X-ray diffraction measurements (Figure 1) show the samples to be highly crystalline and the data are consistent with these all having a faced cubic structure with space group ($Fm\bar{3}m$). The solid state chemistry of Ta^{5+} and Nb^{5+} are generally believed to be similar, so it is reasonable to expect $Sr_2CaTaO_{5.5}$ will display similar behaviour to $Sr_2CaNbO_{5.5}$. The cell volume of $Sr_2CaNbO_{5.5}$ (559.49 \AA^3) is found to be similar to that for $Sr_2CaTaO_{5.5}$ (557.67 \AA^3). This reflects the similarity in the ionic radii of both Nb^{5+} (0.64 \AA) and Ta^{5+} (0.64 \AA) cations.

The Average Crystallite size D_p , specific surface area S , lattice strain ϕ , 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 sheerer formula^[11] (Equation. 1) where the specific surface area can be calculated using Sauter formula^[12] (Equation.2) in which ρ is the density of the synthesised material.

$$D_p = (0.94\lambda) / (\beta_{1/2} \times \cos\theta). \quad (1)$$

$$S = 6000 / (D_p \times \rho). \quad (2)$$

Both the shape and the size of particles are defined by the preparation methods; however the ratio of nucleation to growth rates of particles is also important. Each of these processes depends in turn on variations in the reaction conditions such as the temperature, the nature and concentrations of metal and ligand, and the nature of stabilizer and reducer. The differences in the crystallite size, surface area and density of the two oxides (see table) could be attributed to one of these variations.

Batch Mode

Effect of Time

The removal percentage of dyes over the adsorbents can be calculated as: $R\% = [(C_i - C_t) / C_i] \times 100$, where $R\%$ is the removal percentage, $C_i = 10 \text{ ppm}$ is initial concentration of dye solution, C_t is the concentration of dye at contact time estimated from the concentration dependence of absorbance fit. Figure 2. shows the time dependence of NR removal at room temperature. There is no finite time was observed for the dye removal up to 180 min. The removals of the dye increase as the contact time increases. The removal of NR on the surface of $Sr_2CaNbO_{5.5}$ and $Sr_2CaTaO_{5.5}$ were found to be similar ($\sim 94\%$). This result neglects the impact of the crystallite size on the adsorption properties of the two oxides. The removal of the organic dye is likely affected by the chemical compositions of the oxides. The chemistry of Nb^{5+} and Ta^{5+} cations is anticipated to be similar.

Figure 3 illustrates the wavelength dependence of absorbance for NR solutions at room temperature using $Sr_2CaNbO_{5.5}$ and $Sr_2CaTaO_{5.5}$. The maximum wavelength of NR was shifted from 520 nm to 440 nm suggesting organic degradation of the dye probably occurred.

Effect of Adsorbent Mass

The amount of the dye adsorbed by one gram of the oxides (Q) was calculated as following: $Q \text{ (mg/g)} = [(C_i - C_t) \times V] / W$, where $t = 180 \text{ min}$ is the contact time, $V = 50 \text{ ml}$ is the volume of NR solution and W is the mass of oxides. As shown in Figure 4, Q decreases as the mass of adsorbents increased. The maximum capacity of adsorbent Q_{max} can be estimated from the intercept of the liner fit of $1/Q_t$ at Y axis. Both $Sr_2CaNbO_{5.5}$ (50.4 nm , $13.6 \text{ m}^2/\text{g}$) and $Sr_2CaTaO_{5.5}$ (43.7 nm , $24.2 \text{ m}^2/\text{g}$) exhibited a similar value of Q_{max} (190.5 mg/g) at room temperature. This result is consistent with the similarity in the cell volumes of the two oxides which determined to be ($\sim 558 \text{ \AA}^3$). The removal capability of Neutral Red is higher than those recorded for Methyl violet when the perovskite oxides $BaSr_2NbO_{5.5}$ ($\sim 9.3 \text{ mg/g}$)^[13] and $Sr_2CaNbO_{5.5}$ (47.39 mg/g)^[14] were used as adsorbents.

Effect of Temperature

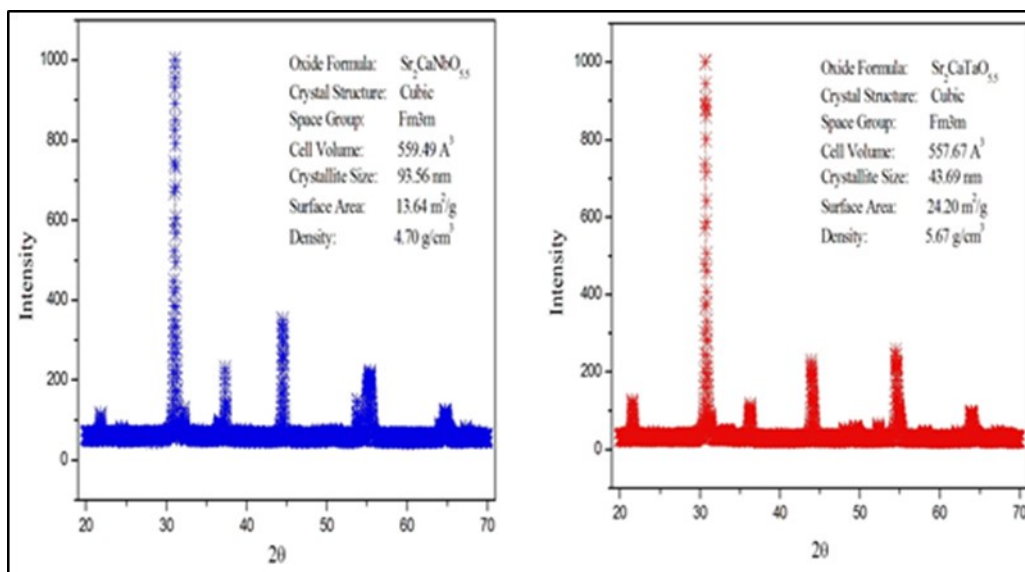


Figure 1. The XRD patterns of Sr₂CaNbO_{5.5} and Sr₂CaTaO_{5.5}.

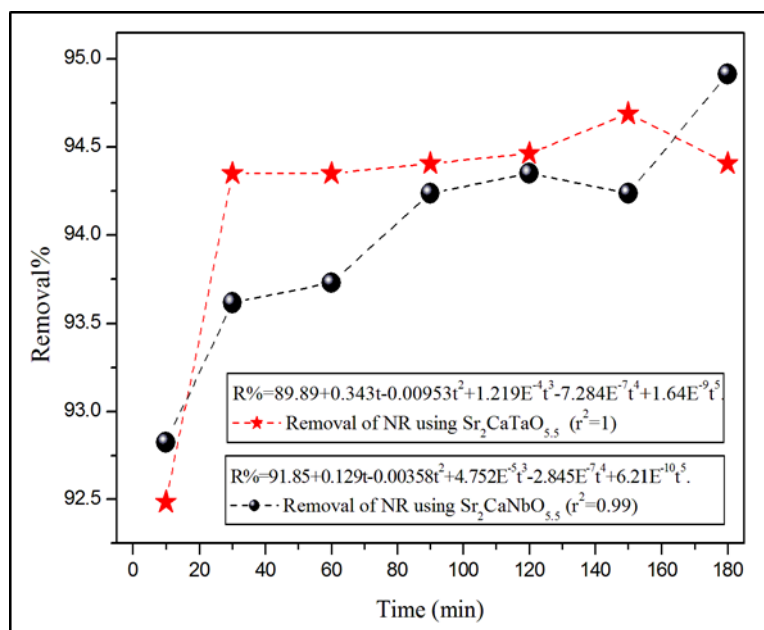


Figure 2. The time dependence of NR removal at room temperature. The volume, concentration and pH of the dyes solution are 50ml, 10ppm and 5.1 respectively.

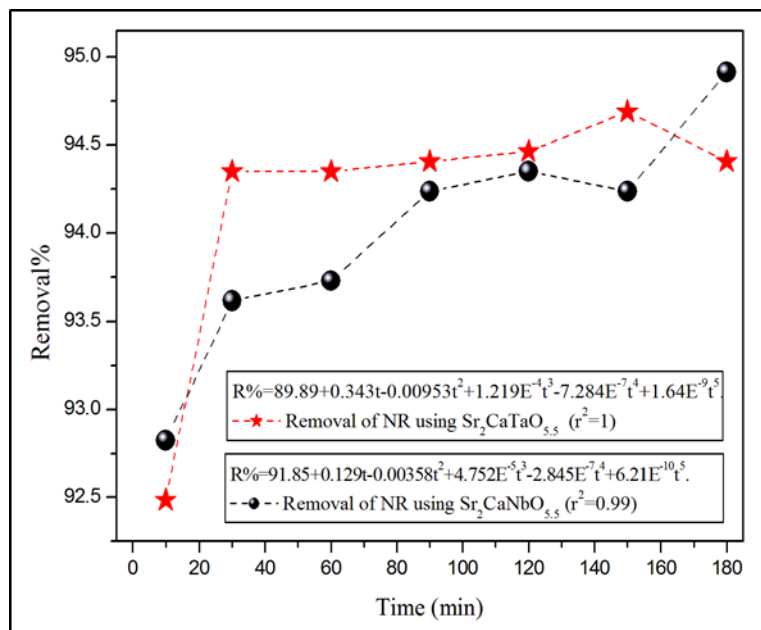


Figure 3. The wavelength dependence of absorbance for NR solution. The time, volume, concentration, adsorbent mass and pH of NR solution are 180 min, 50ml, 10ppm, 0.1 g and 5.1 respectively.

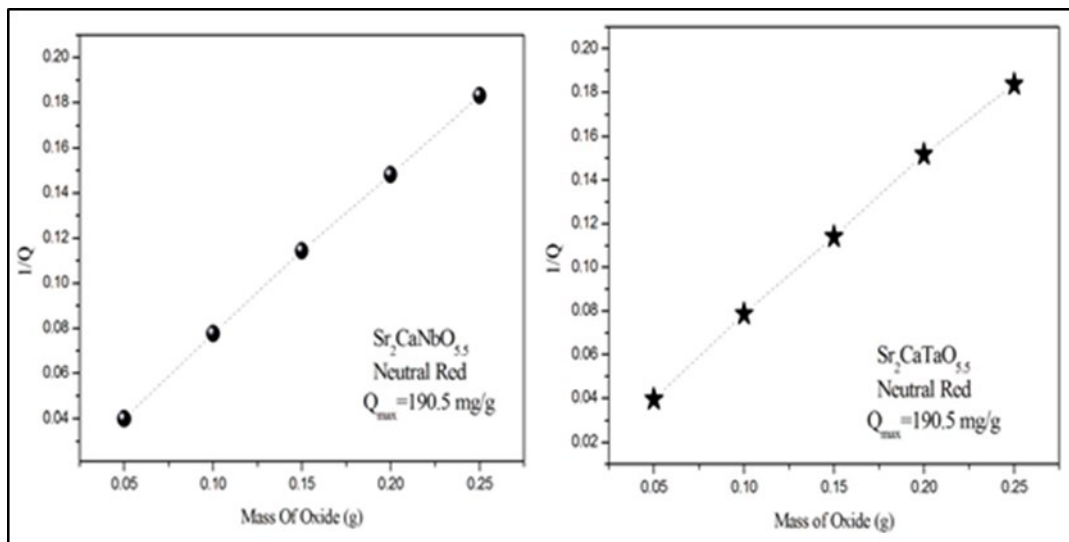


Figure 4. The effect of adsorbent mass on the removal. The time, volume, concentration and pH of dye solutions are 150min, 50ml, 10ppm and 5.1 respectively.

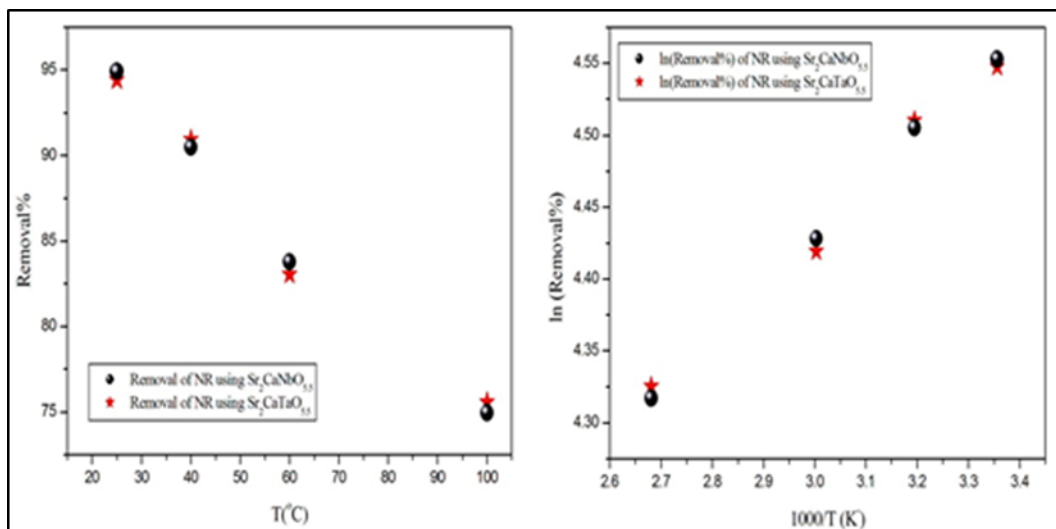


Figure 5. The effect of temperature on the MV removal. The time, volume, pH and concentration of dyes solutions are 150min, 50ml, 5.1 and 10ppm respectively

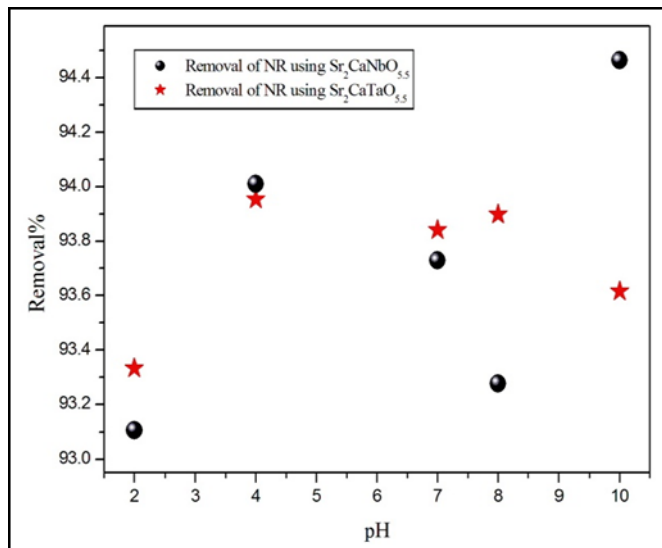


Figure 6. The effect of pH on the removal of NR. The time, volume and concentration of dyes solution are 180 min, 50ml and 10ppm respectively.

Table 1. Average Crystallite size D_p , Specific surface area S , lattice strain φ , Lattice parameter a and Cell volume V . estimated from X-ray diffraction data.

Formula	D_p (ηm)	ρ (g/cm^3)	S (m^2/g)	φ	a (\AA)	V (\AA^3)
$Sr_2CaNbO_{5.5}$	50.45	4.70	13.64	0.0015	8.2401(2)	559.490(1)
$Sr_2CaTaO_{5.5}$	43.69	5.67	24.20	0.0031	8.2300(3)	557.670(1)

Temperature has an important impact on the adsorption process. An increase in temperature helps the reaction to compete more efficiently with e^-/H^+ recombination. The removal of NR dye was investigated at 25, 40, 60 and 100°C. The obtained results are illustrated below in Figure 5. The removal of NR dye decreased as temperature increased. For instance, the removal of NR decreased from ~94% at 25°C to ~74% at 100°C. This result is disagreed with normal expectations, and is probably a consequence of an increase in the thermal energy. It is anticipated that higher temperature induces higher mobility of active sites of adsorbents and the surface area is decreased by increase the temperature^[15]. The energy of activation (E_a), was calculated from the Arrhenius plot of $\ln R$ vs $1000/T$. Arrhenius plot shows that the activation energies of the removal are negative and equal to 2.830 and 2.948 kJ/mole for $Sr_2CaTaO_{5.5}$ and $Sr_2CaNbO_{5.5}$ respectively. This reflects the similarity in the strength of the interaction forces between the dye and the two oxides.

Effect of pH

The pH of solutions is a key parameter in dye adsorption. The magnitude of electrostatic charges which are impacted by the ionised dye molecules is controlled by the solution pH. As a result the rate of adsorption will vary with the pH of the medium used. In general, at low solution pH, the percentage of dye removal will decrease for cationic dye adsorption, while for anionic dyes the percentage of removal will increase. This is due to the increase in the positive charge on the solution interface and the adsorbent surface. In contrast, high solution pH is

preferable for cationic dye adsorption but shows a lower efficiency for anionic dye adsorption. The positive charge at the solution interface will decrease while the adsorbent surface appears negatively charged^[16].

To study the effect of pH, experiments were carried out at various pH values, ranging from 2 to 10 for constant dye concentration (10 ppm) and adsorbent mass (0.1g). Figure 6 presents the removal of dyes as a function of pH. It was observed that the removal of NR using the two oxides slightly increases as pH increased. The highest removal of the dye was recorded at pH= 10 around 94 % where the lowest removal was recorded at pH= 2 around 93%. The removal efficiency of the two adsorbents seems to be similar in the acid media where in the basic media small differences ($\leq 0.9\%$) can be noticed.

Conclusion

The removal of Neutral Red from aqueous solution by the nano particle oxides $Sr_2CaNbO_{5.5}$ and $Sr_2CaTaO_{5.5}$ has been reported. The oxides were synthesised by solid state reaction and characterized by XRD. Despite the differences in crystallite size, the mounts of NR adsorbed by the two oxides were similar. The replacement of Nb^{5+} by Ta^{5+} has showed no influence on the removal capacities. The maximum removal capacities of Neutral red are 190.5 mg/g for the two oxides. Such result could be attributed to the similarity in the cell volumes of the oxides. The removal of dye gradually increased as time and pH increases but decreased as temperature increased.

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