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Adsorptive removal of Congo red dye using nano strontium titanate: A Kinetic approach

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Abstract: The objective of this work is the study of adsorption of dye solution using nano particles. An approach is made for the first time to synthesize the nano Strontium titanate (ST) by self-propagating solution combustion technique using abutilon indicum leaf extract as fuel at low temperature of 450 **ºC**. The synthesized product was calcinated at 600 **ºC** for 2h. The structural and morphological analysis of nano ST were carried out by powder X-ray diffraction (PXRD), and field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM) respectively. The purity of the product is confirmed by fourier transform infrared spectroscopy (FT-IR). Adsorption of Congo Red (CR) on ST was carried out by various adsorption parameters like dosage effect, stirring rate, pH effect, and initial concentration. Adsorption kinetics has also been studied and it follows pseudo second order.
Keywords: Combustion, adsorption, kinetics, Congo red.

1. Introduction

The introduction of waste products in the environment is a big issue of the today's life. This waste product contains colored organic dyes which are produced by many industries like textile, paper, rubber etc [1]. More than 50% of the dyes are hazardous and may affect the aquatic life as well as food chain [2] The removal of these dyes from the aqueous solution remains as a major problem and many methods has been adopted to remove these, such as coagulation [3], oxidation [4], photocatalysis [5], adsorption [6], nanofiltration [7], micellar enhanced ultrafiltration [8] etc.. Adsorption technique is superior to other conventional process because it is ecofriendly and low-cost [9].

Most challenging dyes are anionic in nature like Congo red (CR) as it is soluble in water, bright in color, and shows properties in acidic medium [10]. The structure of the CR is very stable and it is present in the form of sodium salt. Because of this nature, it is very difficult to remove from the aqueous solution; hence it is persisting in the environment [11].

In the present work ST is selected as an adsorbent because, being a perovskite oxide, it has been used in many applications such as water splitting reaction under UV light irradiation [12], electrical applications [13], catalyst [14], superconducting [15],luminescence [16], Solid Oxide Fuel Cells [17] due to its band gap 3.2eV.

Some of the researchers have studied the adsorption of CR using different adsorbents such as rice husk [18] , Seed coat [19] Activated carbon [20], mycelial biomass [21] etc. In the present study adsorption of CR is carried out using nano strontium titanate, because it is a very good charge carrier in the presence of definite pH range, which facilitate the dye adsorption. There is no satisfactory literature relating to the adsorption of CR onto ST nanoparticles. It creates an interest to proceed adsorption of CR using ST as an adsorbent.

In the present study ST is synthesized by combustion method using abutilon indicum lraf extract as a fuel. A phytochemical investigation of abutilon Indicum leaves showed the presence of amino acids, glucose, fructose and galactose [22]. These components help in the combustion process during the synthesis of ST. The adsorption of CR onto ST is studied by varying the various factors like dosage, pH, rate of stirring and initial concentration. The adsorption kinetic is also been studied.

2. Experimental part:

2. a Materials :

The chemicals, strontium nitrate [$Sr(NO_3)_2$ AR99% Nice chemicals], tetra-*n*-butyl titanate[$Ti(OC_2H_9)_4$AR 99% Merck], 1:1 nitric acid [HNO3AR 99% Fischer Scientific] Congo red azo dye [$C_{32}H_{22}N_6Na_2O_6S_2$ Sigma-Aldrich] and distilled water were used without further purification. An Abutilon indicum leaves were collected from the local area.

2. b Method of Synthesize of ST:

2. b.1. Preparation of titanyl nitrate:

The titanyl nitrate was prepared by taking tetra-*n*-butyl titanate as a starting material. First titanyl hydroxide was prepared by adding minimum quantity of double distilled water to tetra-*n*-butyl titanate in a crystalline dish. Further by the addition of nitric acid to this reaction mixture, titanyl nitrate was formed. The corresponding chemical reaction is as follows

$Ti(OC_4H_9)+3H_2O \rightarrow TiO(OH)_2+4C_4H_9OH$----------(1)

$TiO(OH)_2 + 2HNO_3 \rightarrow TiO(NO_3)_2 +2H_2O$ ----------(2)

2. b.2. Extraction of solution from the abutilon indicum leaves:

20g fresh leaves of abutilon indicum were weighed and washed with the distilled water several times to free from the dust. The leaves were boiled with one litre of double distilled water in an electrical heater for 1 hr. The supernatant liquid is filtered through Whatmman filter paper and stored for the further use.

2. b.3. Synthesize of ST nanoparticles:

The different volume of [1ml-5ml] abutilon indicum leaf extract solutions were used as a fuel. The synthesis of ST was optimized by adding 1ml of abutilon indicum leaf extract solution.

The strontium nitrate $Sr(NO_3)_2$, titanyl nitrate $TiO(NO_3)_2$) and 1 ml of abutilon indicum solutions (used as fuel) were dissolved in minimum quantity of distilled water in a crystalline dish with constant stirring on magnetic stirrer about 10-15 min. Then the solution was introduced into the preheated muffle furnace at 450°C. The solution was boiled; it catches flames on the surface and formed white amorphous ST. The amorphous ST was calcinated at 600°C for 2 hr.

2. c Preparation of Congo red azo dye:

Congo red (CR) is an anionic dye with IUPAC name sodium salt of 3,3'-([1,1'-biphenyl]-4,4'-diyl)bis(4-aminonaphthalene-1-sulfonic acid)(formula: $C_{32}H_{22}N_6Na_2O_6S_2$; molecular weight: 696.66 g/mol). 10ppm of dye was prepared by dissolving 10 mg of CR in 1000 ml distilled water.

3. Characterization Techniques

The ST nanoparticles were characterized by PXRD. Powder X- ray diffraction pattern were collected on a Shimadzuxrd-700 X-ray diffractometer with CuKα radiation with diffraction angle range $2\theta = 20^o$ to 80^o, operating at 40 kV and 30 mA. The morphology of ST nanoparticles was studied by recording FE-Sem and TEM. Field emission-scanning electron microscopy (FE-SEM) is carried on a ZEISS ULTRA 55 scanning electron microscope and transmission electron microscope (TEM) was recorded on a Hitachi H-8100

(accelerating voltage up to 200 KV, LaB_6 Filament). FT-IR analysis was studied on a Perkin Elmer Spectrometer (Spectrum 1000) with KBr pellet technique on the range of 400-4000 cm^{-1}.

4. Results and discussion.

4. a Powder X-ray diffraction Spectroscopy.

The phase formation of nano ST powder was confirmed by PXRD. The PXRD patterns of the calcined sample in the Fig.1 shows the presence of small amount of $SrCO_3$ and TiO_2. All the diffraction peaks of the ST were well indexed as cubic and matched with JCPDS card 35-0734 with space group pm-3m (no.221): Lattice parameter (nm) a=0.3905. The average crystalline size was calculated using Debye-Sheerer's formula,

$$d = \frac{k\lambda}{\beta \cos\theta} \quad \text{---------- (3)}$$

Where'd' is the average crystalline dimension$'\lambda'$ =is the X-ray wavelength (0.154056); 'k' is the constant; 'θ' is the Bragg's angel and β is the full width at half maxima (FWHM).The calculated crystallite size was found to be in the range of 10-15nm.

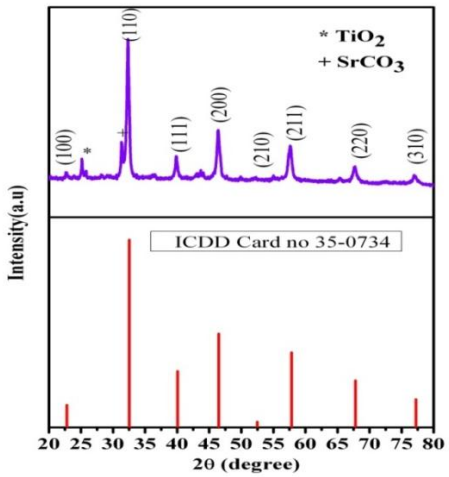


Fig.1 PXRD of $SrTiO_3$ nanoparticles

4. b Morphological analysis:

The morphology of the ST nanopowder was studied by recording FE-SEM and TEM. The Fig.2 shows the FE-SEM image of nano ST powder. It was observed that the particles are spherical in shape with highly agglomeration. This due to the liberation of large volume of gases during combustion reaction. The Fig.3 shows the TEM image of nano ST powder. The image showed that particles were almost spherical in shape and size varied from 10-25nm.

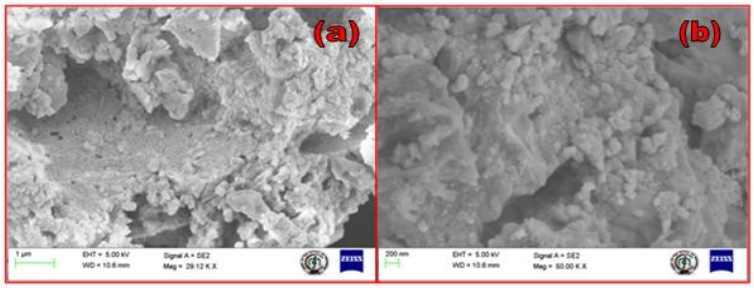


Fig.2 FE-SEM images of $SrTiO_3$nanoparticles

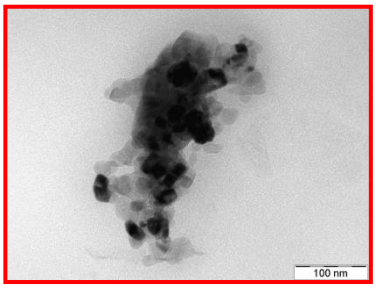
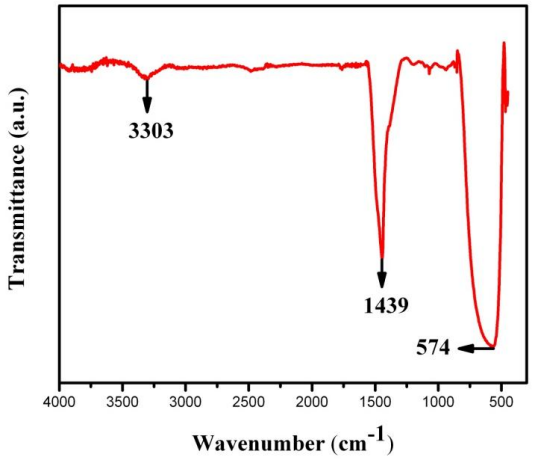


Fig.3 TEM image of $SrTiO_3$nanoparticles

4. c FT-IR analysis

The purity of the product was further confirmed by FT-IR studies and results were depicted in the Fig.4. A strong and broad band at 574cm^{-1} was attributed to the bending mode of Ti–O. The peak at 1439 cm^{-1} was assigned to stretching/bending mode of CO_3^{2-}. A broad band near 3303 cm^{-1} was attributed to the OH^- Stretching mode



5. Adsorption Studies.

5. a Effect of Dosage:

In order to optimize the adsorbent dosage for the removal of CR from the aqueous solution, the adsorption of CR onto ST was carried out by varying the amount of adsorbent from 10 mg to 110 mg is as shown in Fig.5. Before the catalyst addition, almost no change in CR concentration occurred. This indicated that CR was stable in aqueous solution under dark condition. After the addition of catalyst, the rate of adsorption of CR on ST takes place. The result shows that as the amount of adsorbent increases the rate of adsorption is also increases due to the interaction of active site of ST with CR. The maximum adsorption is takes place when the amount of adsorbent was 90 mg. On further increasing the dosage, the amount of adsorption decreases due to the less availability of the surface area of ST. The maximum adsorption was 65% at the dosage of 90mg.

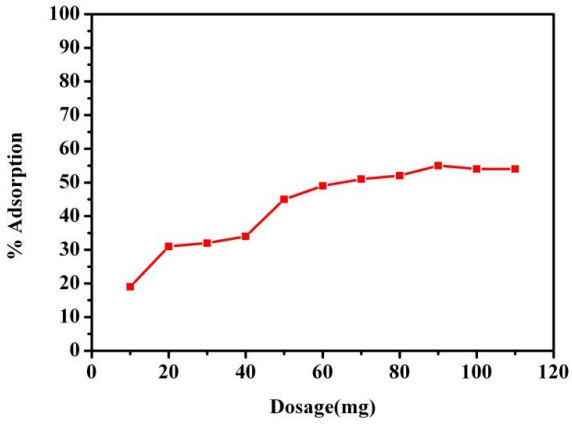


Fig.5. Effect of dosage

5.b Effect of contact time:

By keeping the same dosage as constant, continued the adsorption studies by varying the contact time from 10 min to 35 min. From Fig.6 it is found that rate of adsorption increases with the increase of contact time and reached the maximum 73% when the rate of contact time was 25 min. After this time rate of adsorption decreases due to the saturation of the active site which does not allow further adsorption to take place.

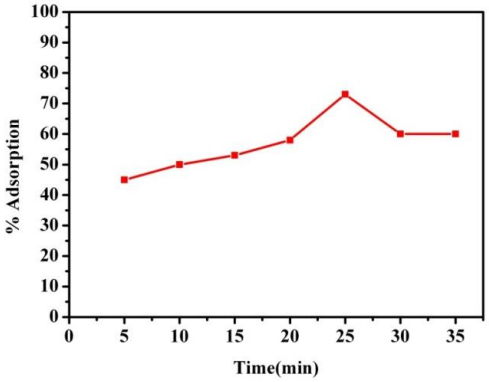


Fig.6. Effect of contact time

5.c Effect of pH:

The pH effect from pH-2 to pH-7 is studied by keeping constant dosage (90 mg) with constant time (25 min). From Fig.7 it was observed that the maximum of 73% adsorption takes place at pH 5 and further it is decreased. At very low pH (i.e. from pH-2 to pH-4); there is an interaction of the positively charged adsorbent with negatively charged adsorbate, which allows the adsorption of CR onto ST nanoparticle. At high pH (beyond pH-5), the highly negatively charged adsorbent surface sites did not favor the adsorption of CR due to electrostatic repulsion.

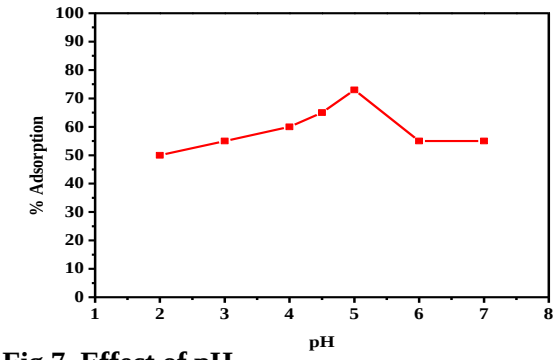


Fig.7. Effect of pH

5.d Initial concentration:

The adsorption studies were carried out by varying the initial dye concentration from 10 ppm-50 ppm. From Fig. 8 it is observed that, as the dye concentration increases the adsorption of CR onto ST nanoparticles decreases from 73% to 35%. This is because; at lower concentrations all the adsorbate present in the solution could interact with the binding sites and thus % adsorption was higher than those higher at initial concentrations. At higher concentration the decrease in % adsorption may be attributed to lack of sufficient surface area to accommodate more adsorbate available in the solution.

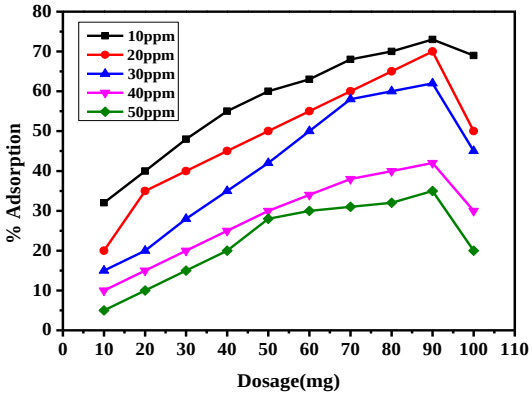


Fig.8. Effect of initial concentration

6. Kinetic Studies

The adsorption of CR on ST is investigated by pseudo-second order kinetic model.

The pseudo second-order kinetic model is given by equation

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad \text{---------- (4)}$$

Where q_e (mg/g) and q_t (mg/g) are the adsorbed amounts of CR at equilibrium and time t (min); K_2 is the adsorption rate constants of Pseudo-second-order equation. The slopes and intercept of the plot t/q_t versus t were used to calculate the pseudo second order rate constants k_2 and q_e. In the Fig.9, a straight line in plot of t/q_t versus t is show good agreement of experimental data with the pseudo second-order kinetic model for different initial adsorbate concentrations. It is found that R^2 is 0.98839 and calculated theoretical q_e values also well agree with the experimental data. These indicate that the adsorption of CR onto ST nanoparticles belongs to the pseudo-second order kinetic model.

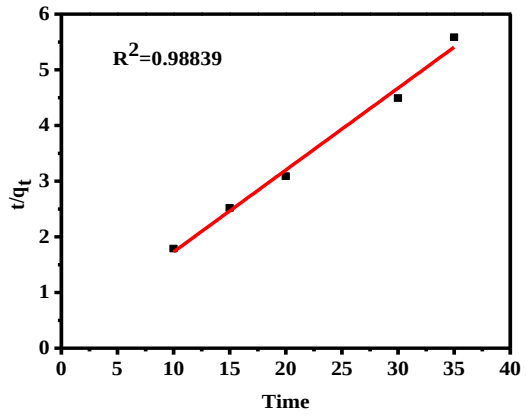


Fig.9. Pseudo-second order kinetic

7. Conclusion.

In this work ST nanoparticle with average crystallite size of 10-15 nm were successfully synthesized by solution combustion method using abutilon indicum plant extract solution as a fuel. The powder X-ray diffraction showed cubic phase and diffraction peaks were well matched to JCPDS file (No. 35-0734). The particles were spherical in shape with high agglomeration was observed by SEM images. Adsorption of CR onto ST was studied and that showed maximum 73% of dye is adsorbed at the rate of 25 min with a dosage of 90 mg. The kinetic adsorption model was revealed to pseudo-second order.

8. Acknowledgements:

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9. References:

1. Jyoti Sharma and Beena Janveja. A study on removal of congo red dye from the effluents of textile industry using rice husk carbon activated by steam,Rasayan J. Chem.,2008,4:936-942.
2. Negrulescu A,Patrulea V,Mincea M, Moraru C, Ostafe V. The adsorption of tartrazine, congo red and methyl orange on chitosan beads, Digest J. Nanomaterials and Biostructures.,2014,9:45-52.
3. Marechal ML,Slokar YM,. Taufer T. Decolouration of chlorotriazine reactive azo dyes with H_2O_2/UV, Dyes Pigments.,1997, 33:181-298.

4. Chen WX, Lu WY, Yao YY, Xu MH. Highly efficient decomposition of organic dyes by aqueous-fiber phase transfer and in situ catalytic oxidation using fiber supported cobalt phthalocyanine, Environ. Sci. Technol., 2007, 41:6240–6245.
5. Fernandez J, Kiwi J, Lizama C, Freer J, Baeza J, Mansilla HD. Factorial experimental design of orange II photocatalytic discoloration process, J. Photochem.Photobiol. A., 2002,151: 213–219..
6. Arami M, Limaee NY, Mahmoodi NM, Tabrizi NS. Removal of dyes from colored textile wastewater by orange peel adsorbent: equilibrium and kinetic studies, J. Colloid Interface Sci., 2005, 288: 371–376.
7. Chakraborty S, Purkait MK, Dasgupta S, De S, Basu JK. Nanofiltration of textilplant effluent for color removal and reduction in COD, Sep. Purif. Technol.,2003,31: 141–151..
8. Purkait MK, DasGupta S, De S. Removal of dye from wastewater using micellar-enhanced ultrafiltration and recovery of surfactant, Sep. Purif. Technol., 2004, 37: 81–92.
9. Senthil Kumar Ponnusamy, Ramalingam Subramaniam. Process optimization studies of Congo red dye adsorption onto cashew nut shell using response surface methodology,Int.J.Ind.Chem.,2013, 4:17.
10. Purkait M K, Maiti A, DasGupta S, Deb S.Removal of Congo red using activated carbon and its regeneration,J. Haz. Mat., 2007,145: 287-295.
11. Gharbani P, Tabatabaii SM, Mehrizad A.Removal of Congo red from textile wastewater by ozonation, Int. J. Environ. Sci. Tech., 2008, 5 :495-500.
12. Troy K, Townsend, Nigel D, Browning E, Frank, Osterloh. Nanoscale strontiumtitanate photocatalysts for overall water splitting, ACS.,2012, 6: 7420–7426.
13. Peter Blennowa, Anke Hagen, Kent K, Hansen A, Reine L, Wallenberg. Defect and electrical transport properties of Nb-doped $SrTiO_3$, Solid. State. Ionics., 2008,179: 2047-2058.
14. TarawipaPuangpetcha, ThammanoonSreethawonga, SusumuYoshikawab, Sumaeth Chavadeja. Synthesis and photocatalytic activity in methyl orange degradation of mesoporous-assembled SrTiO3 nanocrystals prepared by sol–gel method with the aid of structure-directing surfactant, J. Mol. Cataly. A: Che., 2008, 287: 70–79.
15. Makarova M, Dejneka A, Franc J, Drahokoupil J, Jastrabik L, Trepakov V. Soft chemistry preparation methods and properties of strontium titanate nanoparticles, Opt. Mater., 2010, 32: 803–806.
16. Marina Makarova, Jan Drahokoupil, Pavlo Bykov, Alexander Dejneka, Zdenek Dlabacek. Size effect on the structure and optical properties in nanocrystalline SrTiO3, e-J. Surf. Sci. Nanotechnol.,2012, 10: 406-410.
17. Peter Blennowa, Kent K, Hansena, Reine Wallenbergb L, Mogens Mogensena.Strontium Titanate-based composite anodes for solid oxide fuel cells, Electrochem. Soc.,2008, 13: 181-194.
18. Han R, Ding D, Xu Y, Zou W, Wang Y, Li Y, Zou L. Use of rice husk for the adsorption of Congo redfrom aqueous solution in column mode. Biores. Tech., 2008,99: 2938-2946.
19. Oladoja NA, Oladade IA, Idiaghe JA, Egbon EE. Equilibrium isotherm analysis of the sorption of congo red by palm kernel coat. Cent. Eur. J. Chem., 2009,4:760-768.
20. Binupriya AR, Sathishkumar M, Swaminathan K, Ku CS, Yun SE. Comparative studies on removal of Congo red by native and modified mycelial pellets ofTrametes versicolor in various reactor modes. Biores. Tech., 2008,99: 1080-1088.
21. Kannan N, Meenakshisundaram M. (2002). Adsorption of Congo Red on Various Activated Carbons, A Comparative Study, Water, Air, Soil Pollut., 2002,138: 289-305.
22. Vadnere Gautam P, Pathan Aslam R, Kulkarni Bharti U, Abhay Kumar Singhai. Abutilons indicum linn: a phytopharmacological review, Int. J.Res.pharm.Chem., 2013, 3: ISSN: 2231-2781.

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