Preparation of MnO$_2$ nanoparticles for the adsorption of environmentally hazardous malachite green dye

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ABSTRACT

The present study reports preparation of nano sized MnO$_2$ for the adsorptive removal of environmentally hazardous malachite green (MG) dye. MnO$_2$ nanoparticles were prepared by facile solution combustion synthesis using Mn(NO$_3$)$_2$ and urea as oxidizer and fuel respectively at a low temperature of ~ 400 ^{o}C. Phase formation of the prepared sample was analyzed with powder X-ray diffraction (PXRD) studies, scanning electron microscopy (SEM). The PXRD results confirm partial crystallinity and cubic phase and crystallite size of the MnO$_2$ was calculated using Debye- Scherer's formula and it is found to in the range of 25-40 nm. SEM images show the formation of nearly spherical and agglomerated particles. Optical energy band gap was calculated using UV Vis spectroscopy. Adsorption of MG dye onto the MnO$_2$ nanoparticles studies were performed with various parameters such as effect of adsorbent dosage, contact time, initial concentration of the dye and pH of the pollutant. The results suggest that the MnO$_2$ nanoparticles are excellent adsorbent for the removal of MG dye.
Keywords:- Nano MnO$_2$, Solution combustion, Malachite green, Adsorption.

1.INTRODUCTION

The textile industries are the greatest generators of liquid effluent, due to the high quantity of water used in the dyeing processes [1]. Dyes are used in large quantities in many industries including textile, leather, cosmetics, paper, printing, plastic, pharmaceuticals, food, etc. to colour their products. Presently more than 9000 dyes are incorporated in colour index belonging to various chemical application classes. The textile industry alone accounts for two thirds of the total dye stuff production, about 10–15% of the dyes used come out through the effluent [2]. Dyeing and finishing processes from industries do generate large amounts of colored wastewater which are discharged into natural streams with undesirable consequences to the environment and human health. Apart from the unpleasant aesthetic aspects of dye wastewater, its presence in natural streams can cause serious harm to aquatic life by increasing toxicity, chemical oxygen demand, and as well hindering photosynthetic phenomena through reduction of light penetration [3]. Malachite Green (MG) is a cationic dye and widely used for the dyeing of leather, wool and silk, distilleries, jute, paper, as a food-coloring agent, food additive, in medical disinfectant and fish industries. Discharge of MG into the hydrosphere can cause environmental degradation as it gives undesirable color to water and reduces sunlight penetration. The consumption of MG has many adverse effects due to its carcinogenic, genotoxic, mutagenic and teratogenic properties. The carcinogenic properties of MG are due to presence of the nitrogen [4]. Recently greater attention has been committed to the study of removal of dyes and pigments from industrial effluents and waste water by adsorption process using nanostructured materials. Usually organic and inorganic dyes are removed by different chemical and physical techniques, like chemical reaction, electro-coagulation, reverse osmosis, adsorption, flocculation, electro-floatation, ion exchange, membrane filtration, electrochemical destruction, precipitation and many others. Among all these techniques, adsorption technique has been found to be superior to other techniques for waste water treatment in terms of initial cost, simplicity of design, ease of operation and insensitivity to toxic substances [5]. Nano-structured compounds have gained importance in this category due their anticipated high surface area and improved reactive sites [6, 7]. Nano-MnO$_2$ has great potential applications in environment protection field as a new generation of environmental friendly catalyst. There are a number of research results which show that the functional activity of semiconductor materials depends on the structure. Manganese oxide is one of the most interesting materials, which has a wide variety of structure with large surface area. The diverse structures, chemical properties of manganese oxides are

International Journal of Application or Innovation in Engineering & Management (IJAIEM)
Web Site: www.ijaiem.org Email: editor@ijaiem.org
Volume 3, Issue 12, December 2014   **ISSN 2319 - 4847**

taken advantage of in potential applications such as cation–exchange [8]. In this paper, we report a facile, energy saving method to synthesize MnO$_2$ nanoparticles with highly porous structure via solution combustion route and its potential application in removal of malachite green dye from aqueous solution.

2. EXPERIMENTAL

2.1 Materials
Commercially pure manganese nitrate hexa hydrate (Mn(NO$_3$)$_2$ H$_2$O, AR 99% Merck), urea (CO(NH$_2$)$_2$, AR 99% Merck), hydrochloric acid (HCl Fisher scientific), sodium hydroxide (NaOH Fisher scientific), malachite green dye (C$_{23}$H$_{26}$ON$_2$ Sigma-Aldrich), were used as such without further purification.

2.2 Synthesis of MnO$_2$ nanoparticles
The synthesis process involved the combustion of redox mixtures in which manganese nitrate [Mn(NO$_3$)$_2$. H$_2$O] acted as an oxidizing reactant and urea [CO(NH$_2$)$_2$] as a fuel. The initial composition of solution containing manganese nitrate and urea was calculated based on the total oxidizing and reducing valences of the oxidizer and the fuel using the concepts of propellant chemistry [9]. Manganese nitrate and urea were mixed with minimum quantity of doubled distilled water in a crystalline dish and stirred for few minutes until clear solution is formed. The dish was introduced into a muffle furnace maintained at ~ 400 °C. The solution initially undergoes dehydration, followed by decomposition with the evolution of large amounts of gases. The mixture then froths and swells forming foam, very soon the flames spread the entire volume forming black porous product. The entire combustion process is over in 5 min. The foam was grinded to obtain fine powder of MnO$_2$ nanoparticles.

$$3Mn(NO_3)_2 + 4CO(NH_2)_2 \rightarrow 3MnO_2 + 7N_2 + 8H_2O + 4CO_2 \qquad (1)$$

2.3 Instruments used
Solution combustion derived product was characterized by PXRD. Powder X- ray diffraction patterns were collected on a Philips PW/1050/70/76 X-ray diffractometer using CuKα radiation at a scan rate of 2°/min. with diffraction angle range 2θ = 20° to 80°. Product was morphologically characterized by JEOL (JSM-840A) scanning electron microscopy. To calculate optical energy band gap, UV-Vis spectrum was recorded using Elico SL-159 UV-Vis spectrophotometer.

3. RESULT AND DISCUSSIONS

3.1 PXRD studies and crystallite size
Fig. 1 shows the PXRD pattern of the MnO$_2$ powder prepared using urea as fuel in stoichiometric fuel-to-oxidant ratio at 400 °C. The PXRD results confirm the partial crystallinity of cubic phase. The crystallite size is calculated [using (131) peak] from the full width at half maximum (FWHM (β)) of the diffraction peaks using Debye- Scherer's method [10] using the following equation,

$$d = \frac{k\lambda}{\beta \cos \theta} \qquad (2)$$

Where '*d*' is the average crystalline dimension perpendicular to the reflecting phases, '*λ*' is the X-ray wavelength, '*k*' is Scherer's constant (0.92), '*β*' is the full width at half maximum (FWHM) intensity of a Bragg reflection excluding instrumental broadening and '*θ*' is the Bragg's angle. The calculated average crystallite size of the sample is found to be 15-20 nm.
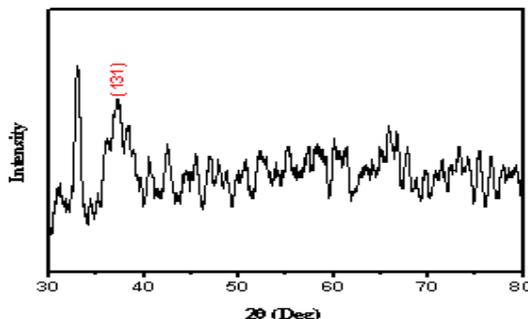

Fig. 1 PXRD pattern of MnO$_2$ nanoparticles

3.2 Morphological analysis
SEM micrograph (Fig.2) reveals the overall appearance of the combustion derived product. The particles are nearly spherical in shape has uniform size and distribution with varying sizes, might be due to non uniform distribution of temperature during combustion. It can be observed that product aggregation is constituted by many irregular particles with a variety of pores voids due to the evolution large amount of gases during synthesis. This type of structure is

International Journal of Application or Innovation in Engineering & Management (IJAIEM)
Web Site: www.ijaiem.org Email: editor@ijaiem.org
Volume 3, Issue 12, December 2014   **ISSN 2319 - 4847**

typical of combustion derived samples. Highly porous nature of MnO_2 nanoparticles facilitates and enhances the adsorption characteristics.
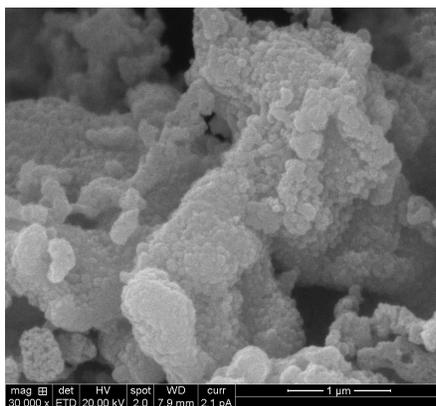

Fig. 2 Scanning Electron Micrograph

3.3 UV-Vis spectroscopy studies

In order to determine the optical energy band gap of MnO_2 nanoparticles the UV-Vis absorption spectrum was recorded. The sample shows a strong absorption peak (λ_{max}) at 467 nm at the UV region. Fig. 3 (a) shows the UV-Vis absorption spectrum of MnO_2 nanoparticles. This can be attributed to photo excitation of electron from valence band to conduction band. The optical energy band gap (E_g) was estimated (Fig. 3 (b)) by the method proposed by Wood and Tauc [11] according to the following equation,
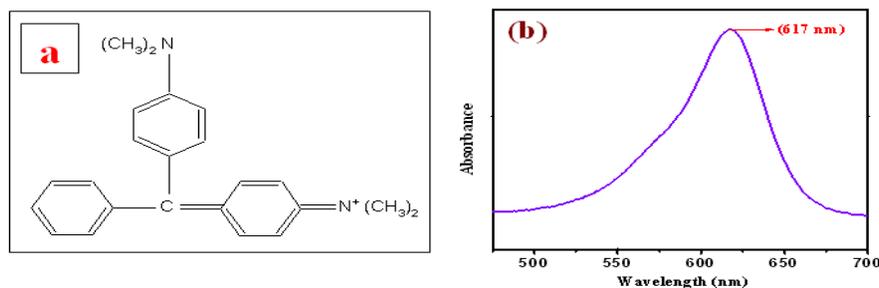
$$(h\nu\,\alpha)\,\alpha\left(h\nu - E_g\right)^n \qquad (3)$$

where 'α' is the absorbance, 'h' is the Planck constant, 'ν' is the frequency, '$E_g^{'}$' is the optical energy band gap and 'n' is a constant associated to the different types of electronic transitions ($n = 1/2, 2, 3/2$ or 3 for direct allowed, indirect allowed, direct forbidden and indirect forbidden transitions, respectively). E_g value for MnO_2 nanoparticles is ~ 5.1 eV.
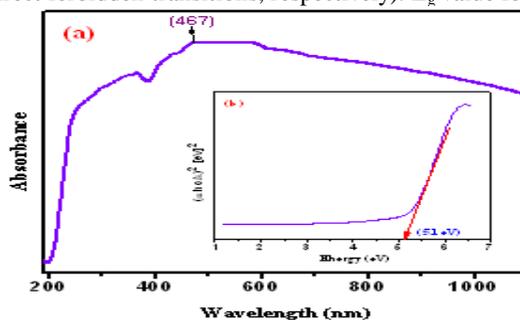
Fig. 3(a) UV-Vis Spectrum, 3(b) Optical energy band gap plot

4. ADSORPTION STUDIES

Adsorption experiments were performed using organic hazardous cationic Malachite green dye. Malachite green is a basic triphenylmethane dye with a molecular weight 327. IUPAC name of MG is [4-[(4-dimethylaminophenyl)-phenylmethyidene]-1-cyclohexa-2,5-dienylidene] dimethylazanium with molecular formula $C_{23}H_{25}N_2^+$. Malachite green has a high solubility in acidic organic solvents but less in water [12]. Chemical structure and UV-Vis spectrum of malachite green dye are shown in Fig. 4a and 4b.

Fig. 4(a) Chemical structure, 4(b) UV-Vis spectrum of Malachite green dye

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Web Site: www.ijaiem.org Email: editor@ijaiem.org
Volume 3, Issue 12, December 2014   **ISSN 2319 - 4847**

4.1 Batch experiments

Batch experiments were carried out at different time, dose, and pH 100 ml of dye solution of concentration was mixed with different dose (5 to 65 mg) of adsorbent in 250 ml beaker. Dye solution containing MnO_2 adsorbent was stirred magnetically (in absence of light) to increase the contact between the dye solution and the adsorbent. After desired time the adsorbent was separated from the solution by centrifugation at 2000 rpm for 10 min. Residual concentration of dye in supernatant was estimated spectrophotometrically by monitoring the absorbance at 617 nm (λ_{max}) using a UV–Vis spectrophotometer.
The % Adsorption was calculated as follows

$$\% Adsorption = A_o - A_t / A_o \times 100 \quad (4)$$

Where A_o is the initial optical density and A_t is the optical density of the dye solution after adsorption at 't' min.

4.2 Effect of contact time

Effect of contact time on the adsorption of malachite green dye onto MnO_2 nanoparticles was studied. It can be observed from the Fig. 5 that the dye adsorption increases with the increasing of stirring time of 30 min. The rate of adsorption is initially quite rapid with most of the compound being adsorbed within the first 30 min. It was found that more than 96% adsorption of dye occurred in the first 30 min; thereafter the rate of adsorption was found to be slow. This shows that equilibrium can be assumed to be achieved after 30 min. It is basically due to saturation of the active site which does not allow further adsorption to take place.
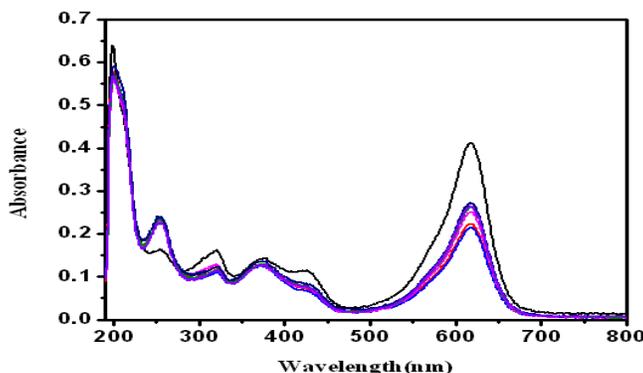
Fig. 5 Effect of contact time on adsorption of MG on MnO_2

4.3 Effect of dose of adsorbent

Adsorption of dye is strongly influenced by the quantity of the adsorbent. Adsorption of malachite green onto MnO_2 nanoparticles was studied with changing the amount of adsorbent from 5 mg to 65 mg/L at a constant stirring rate of 30 minutes with optimum dye concentration of 10 ppm. It is observed from the Fig. 6 that with increase in the dose, adsorption of malachite green increases upto optimum quantity of adsorbent. Maximum of 96% dye adsorbed at the dose of 45 mg of adsorbent. Further increase in adsorbent dose, decreases the adsorption percentage. This might be attributed to over-lapping or aggregation of adsorption sites resulting in decrease in total adsorbent surface area available to malachite green and increase in path length [13].
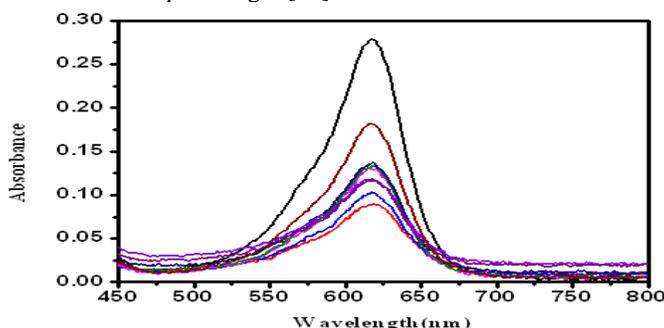
Fig. 6 Effect of dose on adsorption of MG on MnO_2

4.4 Effect of pH

The pH of system has a great effect on the adsorption efficiency of organic dyes. Effect pH on malachite green adsorption onto the MnO_2 nanoparticles was carried out at 10 ppm of initial dye concentration with 45 mg mass of adsorbent at 30 min of stirring rate at lab temperature. As given in the Fig. 7, MnO_2 nanoparticles show maximum of 96% dye adsorption at the pH of 9 which decreased to 3% at pH of 2. This confirms that the low pH (2–5) was unfavourable for malachite green adsorption by MnO_2 nanoparticles.
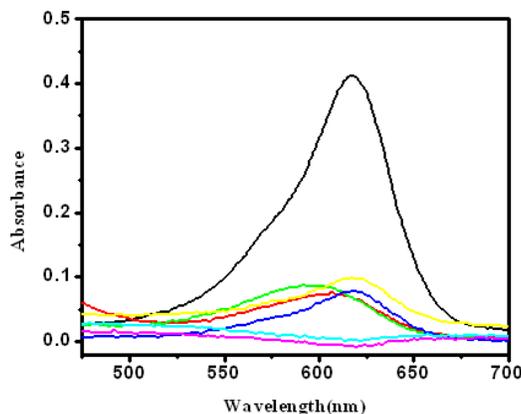
Fig. 7 Effect of pH on adsorption of MG on MnO$_2$

5. CONCLUSION

MnO$_2$ nanoparticles were successfully prepared by the simple solution combustion synthesis method and its adsorption capacity for Malachite green dye was investigated. The result showed that the parameters like effect of pH and contact time will play a very important role on the adsorption.

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