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Sustainable nano composite of mesoporous silica supported red mud for solar powered degradation of aquatic pollutants

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ABSTRACT

Potent utilisation of a huge amount of red mud generated from aluminium industries is a threat to the environment. In the present work the red mud is successfully utilised as an effective photo catalyst for removal of Cr (VI) and malachite green from waste water. A series of red mud/MCM-41composite (RMCM) is developed by simple sol-gel method. The materials are characterised by N_2 ads-des studies, XRD, FTIR, UV–vis DRS, PL and electrochemical studies. From the XRD study it is confirmed that red mud contains both hematite (α-Fe_2O_3) and goethite (α-FeOOH) phases of iron. Their synergetic effect develops a *p-n* junction and expedites the photo catalytic activity of the material. The structural advantages of MCM-41 plays a vital role for suppressing the e^-/h^+ recombination which is confirmed from the PL study. The RMCM (1:1) exhibits the maximum reduction (85%) of 20 mg L^{-1} of Cr (VI) solution and oxidation of malachite green (97%). The oxidation and reduction processes provide beneficial method for purification of the waste water and environmental restoration. Further the applications of the RMCM can be extended for absorption of heavy metals, generation of H_2 energy by splitting water and photo catalytic organic transformation reactions. The current work will be beneficial for the researchers working in this field.

1. Introduction

Sustainable development is gaining immense importance in the chemical industry. It comprises of the three P's i.e. people, planet and profit for social, environmental and economical developments. According to a current report, sustainable development has been interpreted into four basic categories i.e. resources, waste, hazards and costs. Reduction, reuse, and neutralization are the three strategies for reducing the impact of waste. In this sense, new efforts must be made and the use of industrial wastes would not only be limited to their re-utilization as mere substitutes of standard raw materials. Moreover, new value added materials could be developed from the wastes through an appropriate treatment of the reused wastes.

Red mud, a solid waste residue formed after the caustic digestion of bauxite ores during alumina production, is highly alkaline ($p^H = 10-13$) owing to its large content of sodium hydroxide. About 120 million tons per year red mud was generated during the alumina production. Generally red mud contain different metal oxides like $Fe_2O_3 = 30-60\%$, $Al_2O_3 = 10-20\%$, $TiO_2 = \text{trace}-25\%$, $SiO_2 = 3-50\%$, $CaO = 2-8\%$ and $Na_2O = 2-10\%$ [1]. Consequently, the management of these large quantities of red mud is a major problem. At present, most of the red mud is disposed by landfill, which may pose a huge impact on the environment, including water and soil pollution and also decreases the useful land area. Apart from that red mud disposal and reuse is also a big concern. Therefore, developing novel techniques for the utilisation of red mud is a big challenge to the scientists. Red mud is utilised for environmental remediation in order to achieve the purpose of treating wastes with wastes.

Excessive discharge of industrial wastewaters into the water bodies has created a great problem worldwide. Either the organic pollutants, dyes (e.g. Phenol, Rhodamine B, Methylene blue, Malachite green) or the heavy metal ions (e.g. Cr (VI), Cd (II), and Hg (II)) from waste waters will induce serious harms to the environment as well as to humanity [2–4]. Specifically Cr (VI) attacks DNA, proteins and membrane lipids there by disrupting cellular integrity and functions. Also the dyes are carcinogenic in nature [5]. Currently many literatures are available for Cr (VI) adsorption using waste materials [6–8]. Most of the industrial waste waters contain both the heavy metals and organic pollutants at the same time. Therefore the coherent design of materials to achieve the simultaneous removal of these two pollutants becomes an imperative requirement. In past few decades much attention has been paid to the photo-catalytic degradation of heavy metal pollutants and organic dyes. A wide range of photo-catalytically active metal oxides i.e. TiO_2, CdS, ZnO and Fe_2O_3 have been studied for photo

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degradation of organic pollutants [9–11].

A lot of work has been done on nano α-Fe_2O_3 modified MCM-41 and for catalytic and photo-catalytic applications [12]. Vasile et al. [13] synthesized nanosized magnetic α-Fe_2O_3/MCM-41 composite for photo-catalytic degradation of methylene blue. They have utilised H_2O_2 in the reacting system and followed the photo Fenton like mechanism. A silica coated α-Fe_2O_3 material has been synthesized by Deb et al. [14] for removal of heavy metals from waste water. Extensive work has been done by Parida et al. on Fe and Fe_2O_3 doped oxides like CeO_2, Al_2O_3/MCM-41, RGO, MnO_2/MCM-41 for photo catalytic applications [15–20].A few work has been done on composites of red mud in literature. Abbasi et al. [21] has synthesized red mud and carbon nano tube composite in CVD method and utilised it as an efficient adsorbent for Pd (II) adsorption. The acid activated red mud was used as an effective catalyst for oxidative removal of CO by Batra et al. [22]

The acid activated red mud being a visible light active material can act as efficient catalysts for photo catalytic oxidation of MG as well as Cr (VI) reduction. In photo-catalytic process surface area of the material plays a vital role. The active surface area of red mud is around 60 m^2/g. Hence to enhance the surface area of the material the activated red mud needs to be made composite with such a material which has wide surface area. The mesoporous silica MCM-41 is an excellent support for all most all type of materials. It provides large surface area (1000 m^2/g), tunable pore size and enormous pore volume for the metal oxides. Hence the photo-catalytic properties of red mud and surface properties of MCM-41 together can be an effective photo-catalytic material.

In the present work for the first time we have synthesized the composites of red mud and mesoporous MCM-41 for photo-catalytic Cr (VI) reduction and malachite green oxidation simultaneously. The active surface area of MCM-41 and the presence of both α-Fe_2O_3 and α-FeOOH phases are the key factors for the excellent photo-catalytic activity of the catalyst.

2. Experimental

2.1. Activation of red mud by H_2SO_4

The red mud collected form aluminium industry at Damanjodi, Odisha, is treated with H_2SO_4 to make it activated and to reduce the alkalinity. 5 g of the red mud was taken in a conical flask and 15 mL of 5 M H_2SO_4 was added to it. The solution was stirred at 80 °C for 30 min followed by addition of 100 mL of water to each of them. The solution was then stirred for 2 h and then centrifuged to collect the solid material. The material was then dried in an oven at 80 °C overnight and then ground and collected in sample tube. Further the material is designated as RM.

The Fe quantity in RM is estimated by volumetric analysis method and the value is found to be 2.25 gm.

2.2. Synthesis of acid activated red mud/mesoporous MCM-41 composites

2.4 g of cetyl trimethyl ammonium bromide (CTAB) was dissolved in 120 mL of deionized water. Different weights of RM (1.36 g, 2.71 g and 4.04 g) are made solutions with water and added to the above CTAB solution. After 20 min 8 mL of NH_3 solution and 10 mL of tetraethyl ortho silicate (TEOS) were added to it. The resultant solution was kept under stirring for an additional 2 h. Obtained solid mass was recovered by filtration, washed with deionized water,dried at 110 °C overnight and finally calcined in muffle furnace at 550 °C for 5 h. The materials are further termed as RMCM (1:2), RMCM (1:1) and RMCM (2:1). The ratios indicate the molar ratio of RM: SiO_2 in TEOS.

2.3. Characterization techniques

The X-ray diffraction patterns in both wide angle (10–80^0) and small angle (1–5^0) range of the powdered samples are measured by Rigaku Miniflex using CuKα as the radiation source. The FTIR spectra of the samples are recorded by the help of Varian-800 FTIR instrument. KBr matrix is used and spectra are recorded in the wave number range of 4000 cm^{-1}–400 cm^{-1}. The BET surface area, average pore size and pore volume are measured by ASAP 2020 (Micromeritics) using N_2 adsorption and desorption method. The co-ordination environment of the samples were examined by UV–vis diffuse reflectance spectroscopy. The spectra were recorded in JASCO V-750 UV–vis spectrophotometer in the wave length range of 200–800 nm. The PL spectra are recorded by a JASCO FP-8300 spectrofluorometer. The photo electrochemical measurement was performed using a potentiostat/galvanostat under illumination conditions ($\lambda \geq 420$ nm). The current voltage was measured using a conventional pyrex electrochemical cell consisting of the prepared electrode as the working electrode, and a platinum wire and a Ag/AgCl electrode were used as the counter and reference electrodes, respectively. The potential of the working electrode was controlled by a potentiostat. The cell was filled with an aqueous solution of 0.1 M Na_2SO_4 and the pH of the solution was adjusted to 6.

2.4. Photocatalytic study

Photocatalytic reduction of Cr (VI) was carried out by taking 25 mL of 20 mg L^{-1} of freshly prepared $K_2Cr_2O_7$, 0.02 g of catalyst for 60 min. The pH was adjusted by dilute 0.1 M H_2SO_4 and 0.1 M NH_4OH (Merck) in the entire reaction process. All the experiments were done in the summer season from 12 pm to 2 pm at Bhubaneswar, Odisha. The average light intensity was around 10 40,000 ± 20 Lx measured using an LT lutron Lx-101. The resulting solution was taken in a pyrex flask and stirred in dark for 10 min to attain the adsorption-desorption equilibrium between the composite and the Cr (VI) before light irradiation. Then the solution was kept under visible light for rest 20 min the solution mixture was centrifuged and the catalyst and the substrate was separated. The concentration of Cr (VI) was detected by diphenyl carbazide (DPC) and the colored solution was analysed quantitatively by using JASCO V-750 UV–vis spectrophotometer with absorption band at 348 nm. Similarly the photocatalytic oxidation of organic dye was carried out with 100 mg L^{-1} MG, 0.02 g of catalyst in 60 min time with variable pH (3, 5, 7 and 11). After analysis the final solution was analysed in the spectrophotometer with absorption band around 621 nm.

3. Result and discussion

3.1. Surface properties

The BET surface area, pore size and pore volume of the acid treated RM and the RMCM composites are studied by N_2 adsorption-desorption method and the data is given in Table 1. Activated red mud possess a low surface area of 61 m^2/g whereas RMCM (1:1) composite shows an enhanced value of 465 m^2/g. The parent MCM-41 possesses a surface area of 878 m^2/g [23].The red mud particles are well dispersed on the MCM-41 surface. Hence there is a decrease in the surface area of the parent MCM-41 [24]. The N_2 adsorption desorption isotherm of the composite shows a type IV hysteresis loop (Fig. 1). Hence it is confirmed that the mesoporous nature of the MCM-41 remain intact after

Table 1
Surface properties of the materials.

Sl. No.	Sample name	BET surface area (m^2/g)	Pore size (A^0)	Pore volume (cm^3/g)
1	RM	61	10.7	0.01
2	MCM-41	878	35.0	0.65
3	RMCM (1:2)	480	30.4	0.19
4	RMCM (1:1)	465	32.1	0.29
5	RMCM (2:1)	455	31.5	0.12