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Selective sorption and subsequent photocatalytic degradation of cationic dyes by sonochemically synthesized nano $CuWO_4$ and $Cu_3Mo_2O_9$

Dimple P. Dutta[a]*, Anjali Rathore[b], Anand Ballal[c], A. K. Tyagi[a]

[a]Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

[b]Indian Institute of Science Education and Research, Bhopal, Madhya Pradesh 462 066, India

[c]Molecular Biology Division, Bhabha Atomic Research Centre, Mumbai 400 085, India.

Phone: +912225592308; email: dimpled@barc.gov.in

Abstract

Sorption of harmful organic pollutants from industrial effluent and their concomitant photodegradation by the sorbent under visible light can be an effective method for wastewater remediation. In this work, we report the facile synthesis of $CuWO_4$ and $Cu_3Mo_2O_9$ nanoparticles via a simple sonochemical approach. The materials exhibit superior selective sorption of cationic dyes. The uptake of cationic dyes like rhodamine B (RhB), methylene blue (MB) and malachite green (MG) have been studied along with their adsorption kinetics. The sorption plots have been fitted to various isotherms and the results have been discussed in detail. Removal of the dye from the sorbent has been carried out via mechanical agitation as well as via photocatalysis. The dye sorbed nanosorbents have been subjected to photocatalytic degradation under visible light and they show promising results. The sorbents can be completely removed from the system by simple centrifuging. The reusability of the sorbents has also been tested and they have been

found to retain their efficiency after several consecutive runs. Thus, these materials show promise as effective remediators for industrial dye effluents.

1. Introduction

Environmental degradation has been the prime fallout of burgeoning population and rapid industrialization during the modern era. The pollution caused by the industries are taking a heavy toll on the environment by spoiling soil quality and releasing unwanted toxins in air as well as water bodies, which adversely affects flora and fauna. The lack of proper waste disposal by the industries contributes immensely to air, soil and water pollution. Particularly, the leather, cosmetics, paper, printing and textile industries use various synthetic complex organic dyes as coloring material. The textile industries generally require a lot of water for different processes which results in contamination of the water with these dyes. Untreated or poorly treated effluents from these industries lead to large scale water pollution as dyes are generally toxic in nature and are mostly not amenable to microbial degradation.[1] Anaerobic degradation of certain dyes has been reported to form carcinogenic compounds that can end up in the food chain.[2] The highly colored dyes also endanger aquatic life by increasing the chemical oxygen demand (COD) and reducing the penetration of sunlight and oxygen in water.[3] Hence, proper treatment of these dye effluents is imperative in reducing water pollution.

The dyes are generally resistant to light, detergent, soap, sweat and common oxidizing agents and hence, conventional water treatment procedures are generally ineffective to treat these effluents.[4] Over the years, various methods like chemical treatment, membrane separation, ultrachemical filtration, coagulation and flocculation have been developed for treatment of industrial effluents.[5] However, most of the commonly used dyes are completely soluble in water and hence the above techniques are rendered useless for their removal. Hence, considerable emphasis has been laid in recent years to processes like photocatalysis and sorption for treatment of dye effluents.[6] The simplicity, reliability and effectiveness of the process of adsorption of dyes on solid sorbents, makes it a preferred method of choice. Activated carbon has been extensively studied as sorbents for various dyes but they have high production and regeneration costs which limits its practical utility.[7,8] Various cheap natural adsorbents like clay, zeolites, agricultural/biomass wastes, minerals and ores have also been studied for dye sorption.[9] However, it is difficult to compare their relative performance since the efficiency of the sorption process depends critically on the specific physical and chemical characteristics of the sorbent such as porosity, surface area and physical strength. Apart from the inherent advantages and disadvantages of each individual sorbent in wastewater treatment, their adsorption capacities also vary according to the experimental conditions.[10] Hence, there is a constant quest for novel adsorbents having high sorption capacity, fast kinetics of adsorption/desorption, easy separation and regeneration. In this context, nanomaterials have the potential to make a big foray in developing more cost effective and environmental acceptable water purification processes due to their small size and high surface area. Nanostructured sorbents offer the opportunity of higher sorption capacity and can be designed to target specific contaminants. Very recently surface functionalized TiO_2 nanoparticles synthesized via sol gel method has been shown to exhibit high adsorption affinity for MB dye which is a prerequisite for its efficient photodegradation.[11] Also a lot of recent research has been directed towards development of metal organic frameworks (MOF) with nanosized pores which has shown promise in selective adsorption of dyes.[12-15] However, the synthesis of such MOFs is an involved process rendering complication in the industrial dye effluent treatment which is always on the lookout for simple solutions. Hence there is a lot of renewed interest in inorganic materials like metal tungstates and molybdates which are considered to be functional materials having diverse potential applications in scintillation counters, lasers and optical fibers, humidity sensors, catalysts, low-dimensional magnetism and photoelectrocatalytic water oxidation.[16-24] Tungstates and molybdates with metal ions having radius < 0.77Å adopt the wolframite structure where the divalent metal ions and W^{6+}/Mo^{6+} ions gets stabilized in octahedral sites.[25] $CuWO_4$, with its narrow band gap (E_g) of ~ 2.3–2.4 eV, has been studied extensively as material for photoanode in photolectrochemical cells for splitting of water.[26-30] $CuMoO_4$ finds application as potential cathode material for lithium ion batteries.[31,32] Micropompons of $Cu_3Mo_2O_9$ synthesized hydrothermally have been reported to exhibit appreciable photocatalytic activity for the degradation of congo red under visible light irradiation.[33] Recently, we have reported the sorption affinity of $MnWO_4$/$MnMoO_4$ nanostructures for common dyes and heavy metal ions such as copper.[34] However, to the best of our knowledge, sorption behaviors of copper tungstates and molybdates have not yet been explored. Hence, it was of interest to synthesize nanoforms of these materials which can act as sorbent for organic pollutants and subsequently photodegrade them under exposure to light.

In this work, we report the superior sorption ability and photocatalytic properties of $CuWO_4$ and $Cu_3Mo_2O_9$ nanomaterials synthesized using a sonochemical technique. In sonochemical synthesis, the ultrasonic waves generate high temperature and pressure cavitation hotspots which enhance the chemical reactions. The synthesis has been carried out in the absence of any capping agent and it is also a surfactant as well as template free technique which ensures easy recovery of the final product. The products obtained from the sonochemical synthesis have been characterized using powder XRD and TEM. For the sorption studies, common dyes like rhodamine B, methylene blue, malachite green and methyl orange were selected. These are triphenylmethyl /azo dyes which are extensively used in textile and food industries as coloring agents. Human exposure to these dyes is detrimental to health causing skin, eyes and respiratory tract irritation.[35-37] The presence of these dyes in the industry effluents is a matter of great concern and nanosorption followed by photocatalytic degradation can be an effective technique of remediation. The experimental results indicate that our sonochemically synthesized as-prepared $CuWO_4$/ $Cu_3Mo_2O_9$ nanostructures are expected to be new promising materials for cationic dye effluent remediation.

2. Experimental

2.1 Materials and method

The reactions were carried out under air at room temperature and pressure. High purity (≥ 99%) AR grade copper nitrate [$Cu(NO_3)_2.xH_2O$], sodium tungstate [$Na_2WO_4.2H_2O$] and sodium molybdate [$Na_2MoO_4.2H_2O$] were obtained from commercial sources.

Synthesis of $CuWO_4$

In a typical reaction, an aqueous solution (20ml) of [$Na_2WO_4.2H_2O$] (4.47 g, 13.57 mmol) was added dropwise to an aqueous solution (20ml) of [$Cu(NO_3)_2.3H_2O$] (3.28 g, 13.57 mmol) under pulse sonication. After the addition was complete, the beaker was subjected to high intensity (100 W/cm^2) ultrasonic radiation under air for 1.5h using an ultrasonicator (Oscar Ultrasonics) operating at 40 kHz. The external temperature of the contents in the beaker rose upto 65°C. After sonication, the precipitate was washed with water and centrifuged. The light green precipitate obtained was dried in air.

Synthesis of $Cu_3Mo_2O_9$

To an aqueous solution (20ml) of [$Cu(NO_3)_2.3H_2O$] (3.35 g, 13.86 mmol), an aqueous solution (20ml) of [$Na_2MoO_4.2H_2O$] (3.36 g, 13.88 mmol) was added under sonication. Immediate precipitation was observed. The high intensity sonication was continued for 1.5h and the resultant solution was centrifuged to separate the precipitate. The sea green precipitate was washed twice with distilled water and air dried.

2.2 Dye sorption experiments

The sorption studies on $CuWO_4$ and $Cu_3Mo_2O_9$ samples for each individual dyes viz. Rhodamine B (RhB), Methylene blue (MB) and Malachite Green (MG) was carried out in the batch mode as reported by us previously.[34] In these experiments, an accurately weighed amount of the sorbent was equilibrated at room temperature with a known concentration of the dye maintained at a particular pH for a known period of time (actual values given later during the discussion of each sorption experiment). Once the equilibration was complete, the amount of dye left behind in solution was measured spectrophotometrically at 546, 668 and 617 nm for RhB, MB and MG respectively. The various experimental conditions of pH, amount of sorbent and initial dye concentration were varied to get a complete understanding of the sorption process. To ensure reproducibility of the results, all the experiments were done in triplicate and the mean values have been reported.

2.3 Dye desorption experiments

Approximately 50mg of spent adsorbent was centrifuged out of 20ppm dye solution (RhB, MB and MG) and was dried in a hot air oven for 2h at 50°C. The dye loaded adsorbent was suspended in 50 ml distilled water and sonicated for 1h at 40kHz. The suspension was centrifuged at regular intervals and the supernatant was analyzed spectrophotometrically for the desorbed dye concentration.

The adsorption desorption experiments were done repeatedly to ascertain the reusability of the $CuWO_4$ and $Cu_3Mo_2O_9$ adsorbents.

2.4 Photocatalytic degradation of dye to regenerate the sorbent

50mg/L of RhB, MB and MG dye was individually adsorbed on 50mg $CuWO_4$ and $Cu_3Mo_2O_9$ samples. The efficient and fast sorption of the dyes on the nanoparticles surface rendered the solution completely colorless. Hence, the dye sorbed sorbent was centrifuged out and kept in the form of an aqueous paste on a glass petridish and irradiated with a 150 W xenon lamp (15V, 3300K) to simulate daylight. Absorbance spectrum of the irradiated sample was recorded after every 15min interval and the extent of photocatalytic degradation of the dye was monitored by measuring the decrease in its absorbance value.

2.5 Characterization

Powder XRD of $CuWO_4$ and $Cu_3Mo_2O_9$ samples were recorded on a PANalytical X-Pert Pro powder x-ray diffractometer. The CuK_α (k = 1.5406 and 1.5444Å) radiation was used and diffraction was measured over 2θ range of 10°–80°. The conventional TEM micrographs of the particles dispersed on carbon coated copper grids were recorded using a Libra 120 KeV Electron Microscope (Carl Zeiss). The Brunauer–Emmett–Teller (BET) surface area was determined by high purity nitrogen sorption using a Bel Japan Inc., Belsorp II surface area analyzer. The samples were degassed under flowing argon at 100°C for 10h before the nitrogen adsorption. The diffuse reflectance spectra were determined with a UV–vis spectrophotometer (Varian Cary 5000) with $BaSO_4$ as the reference standard.

3. Results and Discussion

Characterization of $CuWO_4$ and $Cu_3Mo_2O_9$

$CuWO_4$ and $Cu_3Mo_2O_9$ have been synthesized using a simple sonochemical method. The XRD pattern of the as prepared $CuWO_4$ and $Cu_3Mo_2O_9$ samples revealed its amorphous nature. Furnace heating of the as synthesized powders at 500°C for 1h yielded crystalline $CuWO_4$ and $Cu_3Mo_2O_9$ as is evident from their powder XRD patterns shown in Figure 1a and 1b, respectively. The XRD pattern in Figure 1a is consistent with standard data for the scheelite triclinic phase of $CuWO_4$ with $P\bar{1}$ space-group symmetry (PCPDF file no. 80-1918).[38] The calculated lattice parameters of a = 4.690Å, b = 5.824Å, c = 4.881Å, $\alpha = 91.63°$, $\beta = 92.41°$ and $\gamma = 82.91°$ are very close to that of the reported values. The average crystallite size calculated using the Debye-Scherrer equation from the FWHM (full width half maxima) of the XRD peaks was found to be ~35 nm. In previous reports on sonochemical synthesis of $CuWO_4$, CTAB was used as surfactant and the as synthesized powder had to be heated at 500°C for 5h to achieve proper crystallinity in the sample. [38] In our case, the method is surfactant free and a shorter time of 1h is required to get crystalline $CuWO_4$ nanoparticles. Figure 1b confirms the formation of orthorhombic $Cu_3Mo_2O_9$ with space group $Pna2_1$ (PCPDF 702493). The average size of the particles was found to be ~15 nm using the Debye Scherrer equation. Incidentally, there are no reports on the sonochemical synthesis of $Cu_3Mo_2O_9$ nanoparticles in the literature.

TEM studies have been done to further investigate the microstructure and topography of the thermally treated $CuWO_4$ and $Cu_3Mo_2O_9$ samples (Figure 2a and 2c). The representative TEM image of $CuWO_4$ shows formation of spherical particles with diameters ranging between ~20-85 nm (Figure 2a). The $CuWO_4$ nanoparticles are not monodispersed and the agglomeration seen in the TEM image is due to the thermal treatment of the as synthesized product to develop crystallinity in the final sample. The histogram depicting the size distribution of the $CuWO_4$ nanoparticles as observed from the TEM image is given in Figure 2b. The average diameter of the nanospheres was found to be 36.6 ± 12.2 nm which is in good agreement with the size obtained from powder XRD. In case of the furnace heated $Cu_3Mo_2O_9$ sample, the TEM image confirms formation of mostly spherical nanoparticles with sizes ranging between 10 to 30 nm (Figure 2c). The corresponding histogram in Figure 2d gives an average diameter of 15.1 ± 1.6 nm for the $Cu_3Mo_2O_9$ nanoparticles which matches well with the size obtained via Scherrer calculation on the powder XRD pattern of the same sample.

The surface area of the nanoparticles plays an important role in justifying their application as sorbents. In order to assess the specific surface area of our sonchemically synthesized $CuWO_4$ and $Cu_3Mo_2O_9$ nanoparticles, their N_2 adsorption-desorption isotherms were recorded at -195.75°C. A classical Type III isotherm was obtained in each case suggesting the presence of mesoporous structures. Using the B.E.T. equation, the specific surface area was found to be ~77.84 ± 0.18 m^2/g and ~85.79 ± 0.25 m^2/g for the $CuWO_4$ and $Cu_3Mo_2O_9$ nanoparticles, respectively (Figure 3a and 3b). The increase in specific surface area in case of copper molybdate is probably due to the decrease in their particle size compared to that of copper tungstate. The specific surface area obtained in case of our sonochemically synthesized $CuWO_4$

nanoparticles is much higher than that reported for $CuWO_4$ nanorods.[34] Similar observations have been reported in case of nanocrystalline WO_3 synthesized via wet chemical route.[39]

Effect of pH on adsorption

The effect of pH on the dye adsorption capacity of the $CuWO_4$ and $Cu_3Mo_2O_9$ nanoparticles has been studied. A change in pH can alter the surface charge on the nanosorbent as well as the degree of dissociation of the dye molecule. 10mg of $CuWO_4$/$Cu_3Mo_2O_9$ nanoparticles was added to 10ml of 20 mg/L dye solution (RhB, MB and MG) maintained at various pH (2, 3, 5, 7, 9) using hydrochloric acid or sodium hydroxide. The pH was measured by using a portable pH meter (Mettler Toledo, FG2- FiveGo pH). The adsorption of the dye over the sorbent was studied by checking absorbance for each dye through a UV-vis spectrophotometer. The dye concentration was measured after every 3 minutes until constant or zero absorbance was seen. From Figures 4a-c, it can be observed that the fastest and complete sorption of the dyes occurs at pH 3 for the $CuWO_4$ nanoparticles. RhB sorption was effective exclusively under acidic pH whereas MB dye sorption occurred under both acidic and alkaline pH. This was tested by adding 10mg of the sorbent to a 20 mg/L mixture of all three dyes maintained at pH 9 and selective sorption of the MB dye was observed (Supplementary Figure S1). Also, among the three dyes, the shortest time for complete sorption was seen for MB which was 3 min. However, in case of $Cu_3Mo_2O_9$ nanoparticles, the sorption occurred only under acidic conditions for all the three dyes and the fastest sorption was seen at pH ~3 (Figure 4d-f). Both RhB and MB was completely adsorbed on the $Cu_3Mo_2O_9$ nanoparticles within a short time span of 3 min. At neutral pH, none of the dyes were sorbed on the $Cu_3Mo_2O_9$ nanoparticles. Since there is a strong dependence of the dye sorption properties of $CuWO_4$ and $Cu_3Mo_2O_9$ nanoparticles on the pH of the medium, it can be inferred that the ion exchange plays a roles in this sorption process. The same set of experiments were carried out with 10ml of 20 mg/L methyl orange (MO) solution which is an anionic dye. It was observed that both $CuWO_4$ and $Cu_3Mo_2O_9$ nanoparticles did not adsorb the anionic dye under acidic, basic or neutral pH.

Effect of concentration of dye on adsorption

For 20 mg/L concentration, the time taken for the complete sorption of RhB, MB and MG dye at pH~3 by our $CuWO_4$ nanoparticles was 9 min, 3 min and 9 min, respectively. The effect of the concentration of the dye solution on the time of uptake for all the dyes was studied within a range of 20 to 200 mg/L. All the experiments were done using 10 mg $CuWO_4$ nanoparticles and pH of the dye solution was maintained at 3. It was observed that even for 200 mg/L concentration, complete sorption of all the three dyes occurred on the $CuWO_4$ nanoparticles with no further increase in time. On increasing the amount of $CuWO_4$ nanoparticles from 10 to 20mg, the time taken for complete sorption of 200 mg/L RhB solution decreased from 9 min to 3 min (Figure 5a and 5b). In case of the $Cu_3Mo_2O_9$ nanoparticles, the time taken for complete sorption of various concentrations of the dyes (20 to 200 mg/L) at pH~3, is given in Table 1. On increasing the concentration of dye to 200 mg/L, MB adsorption is the slowest. However, on increasing the amount of $Cu_3Mo_2O_9$ nanoparticles from 10 mg to 30 mg, 200 mg/L MB dye was completely sorbed in 3 min.

The amount of dye adsorbed on per gram of the adsorbent ($CuWO_4$/ $Cu_3Mo_2O_9$ nanoparticles) has been calculated using the mass balance equation

$$q_e = \frac{(C_0 - C_e)\,V}{m} \qquad (1)$$

where q_e is the equilibrium concentration of the dye on the adsorbent (mg/g), m is mass of sorbent (g), V is the volume of the solution (L), C_0 represent the initial concentration of dye (mg/L) and C_e is the equilibrium concentration of the dye solution. Figure 6a and 6b indicates that the extent of sorption exhibited by the $CuWO_4$ and $Cu_3Mo_2O_9$ nanoparticles, respectively, is a function of the initial dye concentration. In case of $CuWO_4$, for all the three dyes, the sorption amount keeps increasing with the initial concentrations of the dye indicating that even 10mg of the sorbent is capable of adsorbing dyes of concentration higher than 200mg/L. Similar observations had been noted in case of sonochemically synthesized $MnWO_4$ nanoparticles.[34] To study the maximum sorption capacity, the initial dye concentration of MB was increased to 500mg/L and it was observed that the limiting value of q_e obtained experimentally was ~367mg/g (Supplementary Figure S2). In case of $Cu_3Mo_2O_9$ nanoparticles, the amount taken up by the sorbent keeps on increasing for the MB dye within the concentration range of 10 to 50 mg/L and almost saturates when the concentration of dye is increased to 200 mg/L. The limiting value of q_e obtained in this case is ~ 80 mg/g. The q_e value improves from 19.86 to 70.51 mg/g as the MG dye concentration is increased from 50 to 200 mg/L. For RhB dye, the q_e value increased linearly with increase in the dye concentration from 20 to 200mg/L. Higher initial concentration of the dyes have been reported to enhance the adsorption process by providing a driving force to overcome the mass transfer resistance of the dyes between the aqueous and solid phases.[40]

Adsorption Isotherm Study

The adsorption isotherms of both $CuWO_4$ and $Cu_3Mo_2O_9$ nanoparticles for all the three dyes have been tested with the Langmuir and Freundlich models in order to establish the correlation for the equilibrium data in the design of the sorption system. This indicates the distribution of the adsorbed molecules between the liquid phase and the solid phase when the adsorption process reaches equilibrium state. A better regression coefficient (R^2) value gives an indication of the applicability of the isotherm models. The Langmuir isotherm equation is based on the assumption that monolayer adsorption of solute molecules occurs on a fixed number of localized surface sites present on the sorbent.[41] In Freundlich isotherm equation, non-ideal sorption is taken care of by considering heterogenous surface energy systems.[42] The linear form of the Langmuir and Freundlich equations are given below

$$\frac{C_e}{q_e} = \left(\frac{1}{bQ_0}\right) + \left(\frac{1}{Q_0}\right) C_e \qquad (2)$$

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \qquad (3)$$

where Q_0 and b are Langmuir constants related to adsorption capacity and rate of adsorption, respectively, K_F (mg/g (L/mg)$^{1/n}$) is roughly an indicator of the adsorption capacity and $1/n$ is the adsorption intensity constant that varies with the heterogeneity of the adsorbate. For $CuWO_4$ nanoparticles, the Langmuir and Freundlich plots corresponding to the adsorption of all the three dyes are shown in Figures 6c and 6d, respectively. From the fitting parameters listed in Table 2, it can be inferred that the adsorption data fits both Freundlich and Langmuir models as they have almost comparable R^2 values. Initially monolayer adsorption of the dyes occurs on $CuWO_4$ nanoparticles followed by multilayer adsorption. In case of Langmuir adsorption isotherm, a dimensionless constant separation factor (R_L) is used to determine the favorability of the adsorption process.[35]

$$R_L = \frac{1}{1+bC_0} \qquad (4)$$

where C_0 (mg/L) is the highest initial concentration of adsorbent, and b (L/mg) is Langmuir constant. The type of isotherm is indicated by the R_L values, $R_L = 0$ (irreversible), $0 < R_L < 1$ (favorable), $R_L = 1$ (linear) and $R_L > 0$ (unfavorable). For our sonochemically synthesized

$CuWO_4$ nanoparticles, the R_L values have been found to be 0.588, 0.641 and 0.625 for RhB, MB and MG, respectively, indicating that the adsorption is a favorable process. In case of Freundlich isotherm, value of $n>1$ indicates favorable adsorption condition. From Table 2 it can be seen that for $CuWO_4$ nanoparticles, the n values are ~1 indicating predominance of monolayer adsorption. The maximum sorption capacity of $CuWO_4$ for RhB, MB and MG dye as calculated from the Langmuir model was found to be ~303, 370 and 333 mg/g, respectively. This is much higher than that reported in case of $MnWO_4$ nanoparticles.[34] For the $Cu_3Mo_2O_9$ nanoparticles, the Langmuir and Freundlich plots corresponding to the adsorption of all the three dyes are shown in Figures 6e and 6f, respectively and the fitting parameters are given in Table 2. For RhB and MG adsorption, the Freundlich isotherm fits the data better than the Langmuir isotherm. This is confirmed by the higher value of R^2 obtained in the former case. This suggests that the adsorption process of RhB and MG on $Cu_3Mo_2O_9$ nanoparticles is multilayer in nature and should be better represented by the Freundlich isotherm rather than the Langmuir model. In case of MB, better R^2 value for Langmuir model and R_L of 0.270 indicates monolayer sorption. However, the maximum sorption capacity of the $Cu_3Mo_2O_9$ nanoparticles for MB was ~99 mg/g which is much less than that observed in case of $CuWO_4$.

Adsorption kinetics

The physicochemical process of adsorption involves the transfer of the dye from the liquid phase to the surface of the nanoparticles. The study of the kinetics of the sorption process at different time intervals gives an idea about the mechanism of adsorption. Rapid sorption of all three dyes has been observed in case of our sonochemically synthesized $Cu_3Mo_2O_9$ nanoparticles. The average time required by 10mg of $Cu_3Mo_2O_9$ for sorption of all three dyes (10ml, 50ppm) was between 3 to 6 min. Hence, kinetic modeling studies could not be done since it was not possible to measure various points within such small time periods. However, kinetic modeling studies on RhB and MG dye adsorption by $CuWO_4$ nanoparticles was carried out. Here, we have analyzed the sorption kinetic data using Lagergren's first order and pseudo-second order models. The equation for Lagergren's first order model is given as

$$log(q_e - q_t) = log\ q_e - \frac{k_1}{2.303} t \qquad (5)$$

where q_t and q_e represent the amount of dye adsorbed (mg/g) at any time t and at equilibrium time, respectively, and k_1 represents the adsorption rate constant (min^{-1}).[43] The k_1 values can be obtained from the slope of the plot of log (q_e - q_t) vs. t. The pseudo second order kinetic equation is given as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (6)$$

where k_2 = rate constant of pseudo-second-order (g/mg/min) and can be obtained experimentally from the intercept of plot of t/q_t vs. T.[33] The parameters of pseudo-first and pseudo-second order kinetic models obtained for RhB and MG adsorption by $CuWO_4$ nanoparticles have been given in Table 3 and Table 4, respectively. It can be seen that for RhB adsorption, the regression coefficient (R^2) values are between 0.8517 – 0.9984 and 0.9778 – 0.9993 for the pseudo-first and pseudo-second order kinetic models, respectively (Table 3). The higher R^2 values indicate that the pseudo-second order kinetic model fit quite well with the experimental data and moreover the calculated and experimentally obtained q_e values show a better match in this case. Similarly, in case of MG adsorption, better R^2 values have been obtained in case of the pseuso-second order kinetic model. The calculated q_e values obtained from the pseudo-first order kinetic model are erratic whereas they match with the experimentally obtained q_e values in case of the pseudo-second order kinetic model. The sum of error square analysis (SSE%) has been done to prove the validity of the pseudo-second order kinetic model for the adsorption process. The SSE was calculated using the following equation

$$SSE(\%) = \sqrt{\frac{\sum\left(q_{e,exp} - q_{e,cal}\right)^2}{n}} \qquad (7)$$

where n is the number of data points. From Table 3 and Table 4, it can be seen that the SSE% value is lower in case of pseudo-second order model compared to the pseudo-first order model. Thus, it can be inferred that the adsorption of RhB and MG dyes on our sonochemically synthesized $CuWO_4$ nanoparticles was best fitted to the pseudo-second order kinetic model which indicates the possibility of chemisorption as the rate limiting step.[44]

To get a better idea about the adsorption mechanism, the intraparticle diffusion model suggested by Weber and Morris has been used to further analyse the kinetic results.[45]

$$q_t = k_{id} t^{1/2} + C \qquad (8)$$

The slope of the plot of q_t vs $t^{1/2}$ gives the value of k_{id} which is the intraparticle diffusion rate constant (mg/g $min^{0.5}$). A linear plot with an intercept equal to zero indicates that pore diffusion is the rate limiting step. However, in case of RhB and MG adsorption by $CuWO_4$ nanoparticles, a multilinear plot is obtained having at least two linear segments (Figure 7a,b) suggesting the occurrence of both external mass transfer as well as pore diffusion of the solute.[46] The steep rise in the plot for all concentrations of RhB and MG dye solution suggests rapid external surface adsorption of the dye on the nanoparticle surface during the initial period. The gradual rise in the second stage suggests that at this point intraparticle diffusion becomes the rate limiting step. Thus, it can be inferred that in case of RhB and MG adsorption on $CuWO_4$ nanoparticles, the intraparticle diffusion is not the rate limiting step exclusively.[47]

Selective sorption of cationic dyes by $CuWO_4$ and $Cu_3Mo_2O_9$ nanoparticles

The selectivity of our sonochemically synthesized $CuWO_4$ and $Cu_3Mo_2O_9$ nanoparticles for cationic dyes have been demonstrated by the following experiment. 10mg of $CuWO_4$ /$Cu_3Mo_2O_9$ was added to 10 ml of 20ppm mixture of RhB, MG, MB and MO solution. The pH of the dye solution was adjusted to 3 as the nanoparticles exhibits highest sorption efficiency at that pH. Figure 8a and 8b shows the change in the absorbance values of the dye solution with the passage of time, in presence of $CuWO_4$ and $Cu_3Mo_2O_9$ nanoparticles, respectively. The sorption of the cationic dyes is complete within 10 minutes while the peak at 515nm persists even after 5h. This peak is due to the azonium ions formed in the MO dye in acidic pH.[48] Thus, the selective sorption of cationic dyes from a mixture of cationic and anionic dyes is possible using these $CuWO_4$ /$Cu_3Mo_2O_9$ nanoparticles.

Desorption study

For its practical application in industry, it is essential that the sorbent materials can be removed easily from the system and has considerable reusability. We have tested the reusability of our $CuWO_4$ and $Cu_3Mo_2O_9$ samples by conducting desorption experiments using mechanical vibrations from ultrasonic waves to dislodge the dye ions from the surface of the nanosorbents. In case of the dye loaded $Cu_3Mo_2O_9$ samples, ~98% desorption was observed for MB dye within a short time span of 45 min. For RhB and MG, the time taken for ~97% desorption was 65 and 70 min, respectively. Such fast desorption indicates physisorption of the dyes on $Cu_3Mo_2O_9$ surface. Similar observations have been reported in case of MB sorption on alumina nanoparticles.[35] The regenerated sorbent was centrifuged, separated from the supernatant water, dried in air and used for further sorption studies. The absorption desorption experiment was repeated thrice. The thrice regenerated sorbent was tested with a mixture of all three dyes

(20ppm) and ~98% removal was observed within 3min (Figure 9). However, in case of $CuWO_4$ sorbent, only ~40% desorption was observed for RhB, MG and MB dyes after 3h, 3.5h and 2.5h, respectively. This indicates that the dyes bind more tenaciously on the $CuWO_4$ surface compared to $Cu_3Mo_2O_9$ surface and the process may be that of chemisorption. Thus the desorption experiments supports the results obtained from kinetic studies which indicated that RhB and MG dye adsorption on $CuWO_4$ nanoparticles best fitted the pseudo-second order kinetic model.

Mechanism of sorption

The zeta potentials of $CuWO_4$ and $Cu_3Mo_2O_9$ nanoparticles have been measured and they were found to be negative (Table 5). RhB, MB and MG are all cationic dyes and hence they get attracted to this negative surface charge on the nanomaterials whereas MO being an anionic dye is not adsorbed. An increase in the zeta potential values has been observed on addition of each of the cationic dyes which indicates the occurrence of charge neutralization due to mutual electrostatic attraction. The zeta potential of our sonochemically synthesized $Cu_3Mo_2O_9$ nanoparticles is more negative than $CuWO_4$ nanoparticles and probably this result in the faster adhesion of the cationic dyes to the former compared to the later. It is well known that in aqueous solutions, the basic dyes exist in cationic form. At lower pH compared to the pK_a value of RhB (3.7), the carboxylic group of the cationic form of RhB^+ stays protonated and does not lose proton to form zwitterions.[49-51] The cationic form has more affinity towards the negatively charged tungstate and molybdate surface and hence the maximum adsorption of RhB occurs at a pH value of ~2 - 3. A pH value between 2 to 5 has been found to exhibit maximum sorption of cationic dyes like MB and MG on the negatively charged $CuWO_4$ and $Cu_3Mo_2O_9$ surface. However, when the pH of the solution is lowered, a decrease in the number of negative sites on the sorbent surface is expected which should lower the amount of sorption. This indicates that electrostatic interaction is not the only mechanism operating in this case. With decrease in pH, more hydrogen ions gets bonded on the surface of the tungstate and molybdate nanosorbent which increases the possibility of hydrogen bonding with the nitrogen atoms present in MB and MG.[52]

Photocatalytic degradation of adsorbed dye

The utility of a sorbent for dye remediation from wastewater increases manifold if the adsorbed dye can be degraded photocatalytically. To assess the photocatalytic activity of our sonochemically synthesized $CuWO_4$ and $Cu_3Mo_2O_9$ nanoparticles, their band gaps have been obtained from the diffused reflectance spectra recorded for these samples by using the Kubelka Munk function. $CuWO_4$ and $Cu_3Mo_2O_9$ are indirect band gap materials and the band gap can be obtained by the following equation:

$$(F(R_\propto)\, h\nu)^{1/2} = A(h\nu - E_g) \qquad (9)$$

where $F(R_\propto)$ is called the remission or Kubelka–Munk function, diffuse reflectance ($R_\propto$) of the examined samples is $R_\propto = R_{sample}/R_{standard}$ and A is a constant that is dependent on the transition probability of the optical absorption process. The variation of $(F(R_\propto)\, h\nu)^{1/2}$ versus ($h\nu$) has been plotted (Figure 10a and 10b) and by extrapolating the linear portions of these plots to the x-axis (photon energy) i.e. $h\nu = 0$, values of theoretical band gap for the samples could be obtained. $CuWO_4$ has an indirect band gap of 2.20 ± 0.02eV which is similar to that reported in literature.[53,54] The $Cu_3Mo_2O_9$ nanoparticles have a slightly higher band gap of 2.32 ± 0.03 eV. Thus both $CuWO_4$ and $Cu_3Mo_2O_9$ have their absorption edge in the visible range of the spectrum. The photocatalytic activity have been probed by irradiating 50mg of 20ppm dye sorbed (RhB, MB, MG) nanopowders under a 150W Xe lamp. The degradation curves for the various dyes obtained with the $CuWO_4$ and $Cu_3Mo_2O_9$ nanosorbents are shown in Figures 10c and 10d, respectively. $CuWO_4$ displays a better visible light photocatalytic activity with ~100% dye degradation within 130min, 180min and 240min for MG, MB and RhB, respectively. The results can be compared with that reported for $CuWO_4$ nanoparticles synthesized via polyol method. Approximately 100% MB degradation (7ppm) under visible light occurred within 240min in solution phase.[55] In contrast, only partial degradation of the dyes is observed in case of our $Cu_3Mo_2O_9$ sorbent even after 240min of exposure to visible light. The apparent first order rate constant for the visible light photodegradation kinetics has been calculated in each case and the results are given in Table 6. It is observed that the reaction rates are one magnitude higher for the $CuWO_4$ nanosorbent compared to that of $Cu_3Mo_2O_9$. It should be noted that ~100% sorption of dyes occurred on both the sorbents. Hence, hindrance of direct photon absorption for photocatalytic degradation due to complete blockage of the surface will not lead to such varied result.

The band positions of $CuWO_4$ can be predicted using the electronegativity concept, and its CB and VB potentials at the point of zero charge can be calculated by the following equation:

$$E_{VB} = \chi - E^e + 0.5E_g \qquad (10)$$

$$E_{CB} = E_{VB} - E_g \qquad (11)$$

where χ is the absolute electronegativity of $CuWO_4$ (6.315 eV), E^e is the energy of free electrons on the hydrogen scale (~4.5 eV), and E_g is the bandgap (2.20 eV).[56] Based on the above equations, E_{VB} and E_{CB} of $CuWO_4$ were calculated to be +2.915 eV and +0.715 eV, respectively. The positions of valence band and conduction band of semiconductor reflect the oxidation ability of hole and reduction ability of electron, respectively. Since the valence edge potential of

$CuWO_4$ is more positive than ($E_{(\bullet OH/H2O\bullet)}$ = +2.68 eV vs. NHE), the trapped holes in the valence band of $CuWO_4$ can oxidize H_2O to yield $^{\bullet}OH$. $^{\bullet}OH$ is considered to be one of the main reactive species during photocatalytic reaction and to be responsible for oxidation decomposition of many organic dye pollutants.The favourable band edge positions of $CuWO_4$ make it an ideal candidate to generate $OH^{\bullet}$ radical via oxidation of water which is regarded as the principal oxidant for dye photodegradation.[57] The E_{VB} and E_{CB} of our sonochemically synthesized $Cu_3Mo_2O_9$ nanoparticles were also calculated and they were found to be 0 eV and -2.32 eV, respectively. In this case, the photogenerated electrons in the CB of $Cu_3Mo_2O_9$ could be captured by adsorbed O_2 to generate $O_2^{-\bullet}$ radicals. This might be the probable reason for the partial degradation of all three cationic dyes sorbed on our sonochemically synthesized $Cu_3Mo_2O_9$ nanoparticles. It is to be noted that $Cu_3Mo_2O_9$ has been reported to exhibit selective photodegradation of anionic dyes like Congo Red and very low degradation ability for cationic dyes. [33] Further studies with simple dye solutions need to be done to understand the photocatalytic selectivity exhibited by $Cu_3Mo_2O_9$.

Regeneration of the sorbents

An important aspect to be considered for commercial viability of sorbents is its easy and economic regeneration. The $Cu_3Mo_2O_9$ nanosorbent could be regenerated by simple mechanical agitation in an ultrasonic bath and its efficiency remained practically unchanged after three consecutive runs. In case of $CuWO_4$, the sorbent recovered after photocatalytic degradation was also subjected to dye sorption and photocatalytic degradation for three consecutive cycles. The nanoparticles retained its sorption efficiency and the sorbed MG dye could be effectively photodegraded as is evident from Figure 11a. The crystalline structure of the sample obtained after three consecutive cycles was studied using powder XRD (Figure 11b). The patterns obtained matched exactly with that of the starting sample which confirms its stability. The photostable property of $CuWO_4$ was also checked by recording the FTIR spectra of the MB sorbed starting compound and that obtained after photocatalytic degradation of the MB dye under visible irradiation (Figure 11c). The $CuWO_4$ sample obtained after photocatalysis was dried in air before recording the FTIR spectrum. The MB dye sorbed sample showed broad peak between 2600 to 3700cm^{-1} due to O-H stretching vibrations of the hydroxyl groups. The relatively sharp peak at ~1625 cm^{-1} is attributed to the H-O-H bending vibrations of the water molecules.[58] The strong IR band at 1380 cm^{-1} is due to $\nu_s(CH_2)$ vibration. The broad band in the range of 1000 to 500 cm^{-1} is due to the various stretching and bending modes of the WO_4^{2-} lattice.[59] It can be clearly seen from Figure 11c that the characteristic absorptions of the tungstate lattice have not changed throughout the photocatalytic degradation process indicating the photostability of the $CuWO_4$ nanoparticles.

4. Conclusion

Here we have demonstrated the efficient selective cationic dye sorption property of sonochemically synthesized $CuWO_4$ and $Cu_3Mo_2O_9$ nanoparticles. The kinetic studies on the dye sorption ability of both materials could be best fitted to a pseudo second order kinetic model. Though the sorption of dyes was faster on nano $Cu_3Mo_2O_9$ compared to nano $CuWO_4$, the sorption capacity of the latter was higher than the former. The adsorbed dye could be desorbed completely from the $Cu_3Mo_2O_9$ nanosorbent via simple mechanical agitation in an ultrasonic bath. However, only partial desorption of the dyes occurred from nano $CuWO_4$ using the same technique. The photocatalytic degradation of the adsorbed dyes and concomitant regeneration of both the nanosorbents has been tested under visible light. It was seen that almost 100%

photodegradation of the MB, MG and RhB dyes occurred within 130 to 240 min of visible irradiation in case of nano $CuWO_4$. Thus easy recovery of both sorbents could be demonstrated and they also exhibit good multicyclic efficiency. Hence, these materials can find application in the field of cationic dye effluent remediation in the industries.

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Table 1: Time taken for complete sorption of various concentrations of the dyes at pH~3 by $Cu_3Mo_2O_9$ nanoparticles

Concentration of Dye (mg/L)	Time taken for complete sorption (min)		
	RhB	MB	MG
20	3	3	6
30	6	3	6
40	6	3	6
50	6	3	6
100	6	15	6
200	10	30	10

Table 2: Langmuir and Freundlich isotherm constants and correlation coefficients of $CuWO_4$ and $Cu_3Mo_2O_9$ nanoparticles for the three dyes

Sample	Dye solution	Langmuir			Freundlich		
		Q_0 (mg/g)	b	R^2	K_F	n	R^2
$CuWO_4$	RhB	303.2 ± 2.65	0.0035 ± 0.0001	0.9982	0.981 ± 0.0032	0.994 ± 0.0015	0.9998
	MB	370.1 ± 3.30	0.0028 ± 0.0002	0.9913	0.968 ± 0.001	1.002 ± 0.0031	0.9997
	MG	333.5 ± 1.54	0.0030 ± 0.0001	0.9989	0.991 ± 0.0025	1.004 ± 0.0012	0.9998
$Cu_3Mo_2O_9$	RhB	3719.5 ± 9.32	0.0002 ± 0.0023	0.6826	1.006 ± 0.0021	1.008 ± 0.0005	0.9988
	MB	99.6 ± 1.23	0.0135 ± 0.0014	0.9844	4.553 ± 0.0054	1.831 ± 0.0122	0.8867
	MG	840.3 ± 7.43	0.0012 ± 0.0009	0.8221	1.318 ± 0.0043	1.095 ± 0.0011	0.9983

Table 3: Pseudo-first and second-order kinetic models for different concentrations of RhB dye adsorption on $CuWO_4$ nanoparticles.

C_0 (mg/L)	$q_{e,\ exp}$ (mg/g)	Pseudo-first order kinetic model				Pseudo-second order kinetic model			
		$q_{e,\ cal}$ (mg/g)	k_1 (min^{-1})	R^2	SSE (%)	$q_{e,\ cal}$ (mg/g)	k_2 (g/mgmin)	R^2	SSE (%)
20	19.81	17.63 ± 0.015	0.4111 ± 0.0047	0.9724	1.091	19.53 ± 0.016	0.1691± 0,0039	0.9893	0.140
30	29.13	28.26 ± 0.007	0.5343 ± 0.0013	0.9994	0.435	29.41± 0.009	0.1101± 0.0041	0.9889	0.280
40	39.44	43.59 ± 0.002	0.4905 ± 0.0011	0.9907	2.075	39.82 ± 0.010	0.0477± 0.0046	0.9778	0.190
50	49.30	32.66 ± 0.021	0.4606 ± 0.0058	0.8517	8.320	48.57 ± 0.007	0.1835± 0.0023	0.9973	0.365
100	99.10	63.53 ± 0.056	0.5688 ± 0.0042	0.9272	17.784	98.91 ± 0.005	0.1278± 0.0017	0.9993	0.190
200	198.20	191.24 ± 0.021	0.6517 ± 0.0031	0.9553	3.479	198.41 ± 0.011	0.0349± 0.0014	0.9976	0.210

Table 4: Pseudo-first and second-order kinetic models for different concentrations of MG dye adsorption on $CuWO_4$ nanoparticles.

C_0 (mg/L)	$q_{e,\ exp}$ (mg/g)	Pseudo-first order kinetic model				Pseudo-second order kinetic model			
		$q_{e,\ cal}$ (mg/g)	k_1 (min^{-1})	R^2	SSE (%)	$q_{e,\ cal}$ (mg/g)	k_2 (g/mgmin)	R^2	SSE (%)
20	19.81	37.57 ± 1.234	0.7139 ± 0.083	0.7690	8.879	20.01± 0.014	0.1000 ± 0.0016	0.9684	0.095
30	28.85	35.77 ± 1.045	0.6674 ± 0.045	0.9137	3.459	29.15± 0.009	0.1509 ± 0.0003	0.9943	0.150
40	38.06	30.08 ± 0.746	0.6816 ± 0.014	0.9630	3.989	38.46 ± 0.001	0.3381 ±0.0003	0.9992	0.200
50	49.25	32.18 ± 0.935	0.5688 ± 0.021	0.9402	8.535	49.26 ± 0.001	0.2289 ± 0.0001	0.9991	0.005

Table 5: Zeta potential measurements for $CuWO_4$ and $Cu_3Mo_2O_9$ nanoparticles with RhB, MB, and MG dyes at various pH.

Sample	ξ(mV) at pH 3	ξ(mV) at pH 5	ξ(mV) at pH 7
$CuWO_4$	-20.23	-15.43	-15.61
$CuWO_4$ + RhB	-11.74	-14.64	-15.25
$CuWO_4$ + MB	-10.34	-11.25	-12.21
$CuWO_4$ + MG	-14.32	-14.15	-15.02
$Cu_3Mo_2O_9$	-36.43	-32.11	-31.56
$Cu_3Mo_2O_9$ + RhB	-28.42	-30.65	-29.32
$Cu_3Mo_2O_9$ + MB	-27.67	-29.84	-29.11
$Cu_3Mo_2O_9$ + MG	-28.34	-30.25	-30.78

Table 6: Apparent first order kinetic constant for visible light photodegradation of dye sorbed $CuWO_4$ and $Cu_3Mo_2O_9$ nanoparticles

Sample	Sorbed dye	1st order kinetic const. (min^{-1})	R^2
$CuWO_4$	RhB	$1.42x10^{-2}$	0.9825
	MB	$2.01x10^{-2}$	0.9858
	MG	$3.28x10^{-2}$	0.9825
$Cu_3Mo_2O_9$	RhB	$2.59x10^{-3}$	0.9810
	MB	$4.42x10^{-3}$	0.9829
	MG	$4.17x10^{-3}$	0.9838