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Degradation of Dyes (Methylene Blue and Congo Red Dye) Using Phosphomolybdic Acid

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Abstract: ***The phosphomolybdic acid (PMA) has been used as an adsorbent for the removal of dyes (Methylene blue and Congo red dye) from synthetic aqueous solution. Different factors of the adsorbent, like, contact time, pH of the sorption medium, concentration of the dye solution, were investigated by the batch sorption experiment. The adsorption equilibrium data was best fitted by the Langmuir isotherm model. The maximum adsorption capacities were found to be 99.6, 99.4 and 1g of phosphomolybdic acid for dyes (Methylene blue and Congo red dye).***

Keywords: Adsorption isotherm; Phosphomolybdic acid (PMA); Dyes (Methylene blue and Congo red dye);Fourier Transform Infrared Spectra (FT-IR); Ultra-Violet spectra (UV); Scanning Electron Microscopy (SEM).

1. Introduction

Water pollution can be defined as any physical, chemical, or biological alteration in water quality that effected living organisms. Chemical industries and human communities are the example of point sources, which mainly cause the pollution of surface waters like rivers, lakes and seas. The waste water of textile dye draining in to the river without treatment would bring out serious pollution of water resource and threatening of ecology environment and human health[1-5]. Azo dyes are a versatile class of colored organic compounds that have extensively been used in industry for applications such as textiles, paper, leathers, additives and analytical chemistry [6]. The presence of heavy metals in the aquatic ecosystem poses human health risks and cause harmful effects to living organisms in water and to their consumers [7]. The oxidative modification of Biolignim (BL) has been investigated to make it more suitable as an adsorbent for transition/ heavy metals [8]. In addition, many elements of the oxidant are incorporated into the final product (atom economy). On the other hand, for sustainable economic development, preventing waste, rather than treating it or cleaning it up is the key requirement. Thus, one of the most imperative issues for chemists is the search for green chemical transformations. In particular, waste reduction is a key requirement in the development of new attractive industrial processes. In this context, a variety of metallodendritic compounds used as recoverable catalysts have been reported[9]. A limited studies on degradation of dyes (methylene blue and congo red dye)usingphosphomolybdic acid, $H_3 [PMo_{12}O_{40}]$ have been reported in the literature. Polyoxometalates (POMs),are anionic metal oxide clusters formed primarily from early transition metals, mainly vanadium, molybdenum and tungsten. The cluster assembly proceeds in solution by oligo-condensation reactions between reactive fragments, often by using templates to control the final cluster architecture. Polyoxometalates have attracted wide interest from researchers working in chemistry, biology, catalysis, molecular electronics and materials science[10]. In this present work, themolecular natures, morphology, FTIR, UV-Vis and SEM of phosphomolybdic acid and phosphomolybdic acid with dyes have been discussed. The effect variable factors like contact time, concentration of dye, adsorbent dose, pH and the degradation rate of dye solution have been examined. The Langmuir and Freundlich models were used in the adsorption studies.

2. Materials and apparatus

All the chemicals in the present work are of analytical grade and are used as such without further purification. The test solution of dye was prepared for (Merck, Nice, Germany) by serial dilution of stock solution (1000 ppm) using deionized distilled water. Purified sample of phosphomolybdic acid was employed with the adsorbent. Elico CL 157 Colorimeter and Metrohm E-632 pH meter with glass combination electrode were used throughout this study.

2.1 Preparation of the adsorbent

The phosphomolybdic acid was prepared as per the literature method [11]. The ammonium heptamolybdate, $(NH_4)_6Mo_7O_{24}.4H_2O$ (3g) was added to 10ml of H_2O, dissolved well and then conc.HNO_3 (2ml) was added. The phosphomolybdic acid was recrystalized in hot water. The sample was used as an adsorbent.

2.2 Analytical Measurements

Infrared (IR) spectra were recorded on KBr pellets using a PerkinElmer spectrometer. The UV spectra of the samples were recorded using JASCO V-630 UV-Visible spectrometer and JEOL-JSM 6390 Scanning electron microscope (SEM).

3. Method- Adsorption Experiment

All the starting materials were obtained from M/s Fluka and used as received. The Phosphomolybdic acid with dyes was stirred at room temperature at 500 and 400 rpm. After the required time their content was filtered through 0.40 mm membrane filter using a vacuum pump. The adsorption was assessed by determining the residual concentration of dye in the sample solution of Methylene Blue and Congo red in phosphomolybdic acid at 248 and 340 nm respectively. The removal percentage of dye from aqueous solution was calculated using the following equation[6]

$$R = \frac{Co - Ce}{Co} \times 100$$

Where, Co= Initial concentration of dye
Ce= concentration of dye after degradation.

$$qe = \frac{Co - Ce}{m} \times V$$

Where, V = volume of solution (L)
m = mass of adsorbent (g).
The reported value of dye adsorbed by the adsorbent in each test was averaged of at least three measurements.

4. Results and Discussion

4.1 Effect of contact time

The rate of removal of dyes (Methylene blue and Congo red dye) is shown in Fig.1.From this it can be seen that adsorption of dyes (Methylene blue and Congo red dye) reached equilibrium after a contact time of 60 min, while the removal efficiency for dyes at equilibrium was 99.0, 99.4 and 99.6 respectively. The fractional adsorption is low in high concentration due to dyes that present in lower concentration adsorption medium could interact with the adsorption sites, in order to obtain a higher adsorption yields. Hence, at higher concentration, lower adsorption yields were observed because of the saturation of the adsorption sites. As is shown Fig.1, desorption occurred after saturation. Therefore, considering technical and economic aspects, a contact time of 60 min was chosen for dye removal from aqueous solution by the adsorbent phosphomolybdic acid.

4.2 Effect of the amount of adsorbent

Adsorbent dosage is an important parameter because this factor determines the capacity of an adsorbent for a given initial concentration of the adsorbent shown in Fig.2. It is clear that the removal of the dye increased with increasing weight of adsorbent.

4.3 Effect of pH

To study the effect of pH on the decolorisation of dye, experiments were carried out at various pH values, ranging from 1-6, at which values the chemical precipitation was avoided. It is clear from the results shown in Fig.3, that the methylene blue and congo red dye adsorption is more favorable at higher pH condition due to the less competition of H^+ ions. The optimum pH for the removal of dye was found to be in the range of 2-4 for methylene blue and1-4 for Congo red respectively.

4.4 Infrared spectral studies

FTIR spectra of the synthesized sample of phosphomolybdic acid with Congo red dye and phosphomolybdic acid with Methylene blue are shown in the Fig.4. The IR spectral data of phosphomolybdic acid is given in table 1. The IR spectrum of phosphomolybdic acid sample shows three modes of vibrations observed at 955, 881 and 798 cm^{-1}, which corresponds to v_{sym}M - O, v_{asym} M - O_b, and v_{asym} M - O – X modes respectively. The mode of vibration at 1062 cm^{-1} attributed to P-O asymmetric stretching frequency, Methylene blue and Congo red dye with phosphomolybdic acid samples are observed three vibration modes P-O asymmetric stretching at 1045 and 1047 cm-^{1}, v_{sym}M-O_t 976 and 957 cm^{-1}, v_{asym}M-O_b 874 and 892cm^{-1}, v_{asym} M-O-X 789cm^{-1} and 773cm^{-1} respectively. The downward shift of stretching frequency of phosphomolybdic acid with dyes indicating that the phosphomolybdic acid has a large distorting effect owning to the interaction between the phosphomolybdic acid and dyes[12-15].

4.5 Ultra-Violet spectral studies

The rate of decolorisation was recorded with respect to the change in intensity of absorption peaks at 248 nm for Methylene blue and 340 nm for Congo red dye respectively. The absorption peaks were diminished and disappeared during the reaction, indicating that the dye has been degraded is shown in Fig.4.

4.5 Decolorisation of dye using the catalyst Phosphomolybdic acid

Investigation was carried out using the catalyst, Phosphomolybdic with Methylene Blue and Congo Red dye. The degradation of dye in solution is due to photo excitation of the PMA, followed by the formation of electron – hole pair on the surface of catalyst[16]. The high oxidation potential of the hole ($h+_{vb}$) in the catalyst permits the direct oxidation of the dye to reactive intermediates.

$$(MO/MO_2) + h\nu \rightarrow (MO/MO_2)\,(e^-_{cb} + h^+_{vb}) \qquad ....1$$

Metal oxide

$$h+_{vb} + \text{dye} \rightarrow \text{oxidation of the dye} \qquad ....2$$

Another reactive intermediate which is responsible for the degradation is hydroxyl radical (OH*). It is either formed by the decomposition of water or by reaction of the hole with OH^-.The hydroxyl radical is an extremely strong and non selective oxidant (E^0=+3.6V) which leads to the partial or complete mineralization of several organic chemicals

$$h+_{vb} + H_2O \rightarrow H^+ + OH^* \qquad ....3$$

$$h+_{vb} + OH \rightarrow OH^* \qquad ....4$$

$$OH^* + \text{Dye} \rightarrow \text{Degradation of the dye} \qquad ....5$$

During this the colour of phosphomolybdic acid was changed from yellow to green for methylene blue and yellow to red for Congo red respectively. The colour change of phosphomolybdic acid is confirmed from UV-vis spectra, shown in Fig.5.

4.6 Scanning electron microscopy (SEM)

The morphology and microstructure of the dye adsorbed phosphomolybdic acid was further investigated by scanning electron microscopy (SEM). Typical SEM image of the phosphomolybdic acid with dyes is shown in Fig. 6 . The SEM micrographs show that the PMA material has got successfully embedded in the phosphomolybdic acid matrix.

5. Conclusions

The preceding experiments disclosed that polyoxometalates could be effectively used for removal of dyes (Methylene blue and Congo red dye) from aqueous solution. The developed adsorption studies show that the optimum pH for the removal of dye was found to be in the range of 2-4 for methylene blue and for Congo red 1-4 respectively. The equilibrium adsorption data was very well fitted by the Langmuir model. The maximum adsorption capacity for dyes (Methylene blue and Congo red dye) was found to be 99.4 and 99.6 mg g^{-1}. The results show that polyoxometalates may be used successfully for the removal of dyes (Methylene blue and Congo red dye) from aqueous solution for ecological clean out reason. This technique can be improved to remove the dyes from the aqueous solution.

6. Acknowledgements

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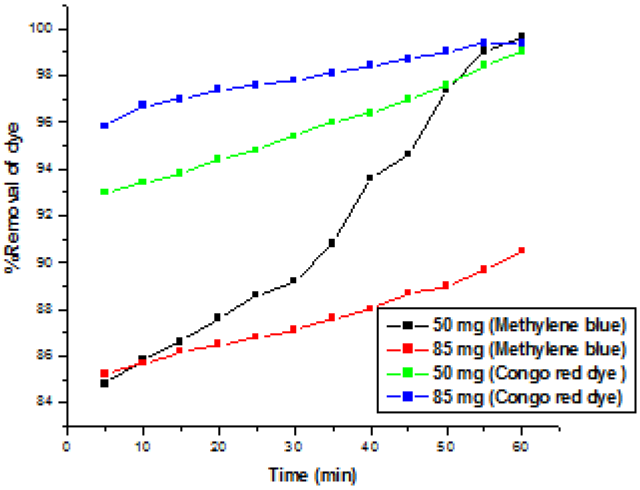

Figure 1: Effect of contact time on the adsorption of dye removal by phosphomolybdic acid. Conditions: 50ml concentration 50, and 85 mg/L, stirring speed=500, 400 rpm; contact time=1h, pH=2, adsorbent dose 1000 mg.

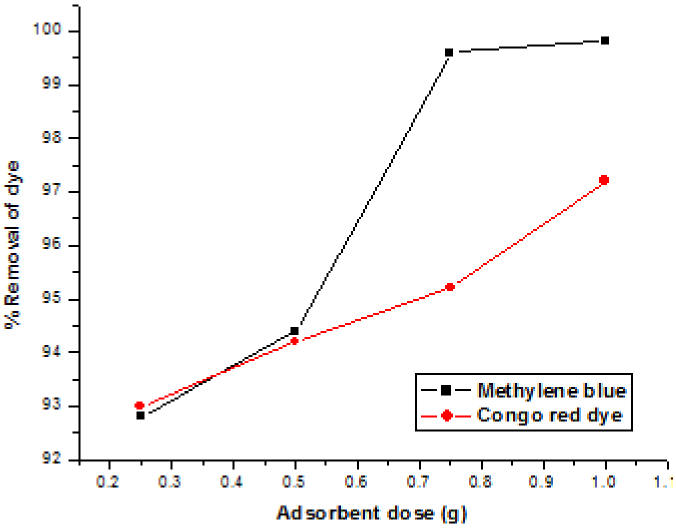

Figure 2: Effect of adsorbent dose on the adsorption of dye removal by phosphomolybdic acid. Conditions: 50ml concentration 50, and 85 mg/L, stirring speed=500, 400 rpm; contact time=1h, pH=2, adsorbent dose 250- 1000 mg.

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List of tables

Table 1: IR spectral data for the phosphomolybdic acid and phosphomolybdic acid with dyes

$H_3PMo_{12}O_{40}$	$H_3PMo_{12}O_{40}$ with *Methylene blue*	$H_3PMo_{12}O_{40}$ with *Congo red dye*	*Tentative assignment*
1062	1045	1047	v_{asym}(P - O)
955	976	957	v_{sym} (M - O_t)
881	874	892	v_{asym}(M - O_b)
798	789	773	v_{asym}(M - O – X)

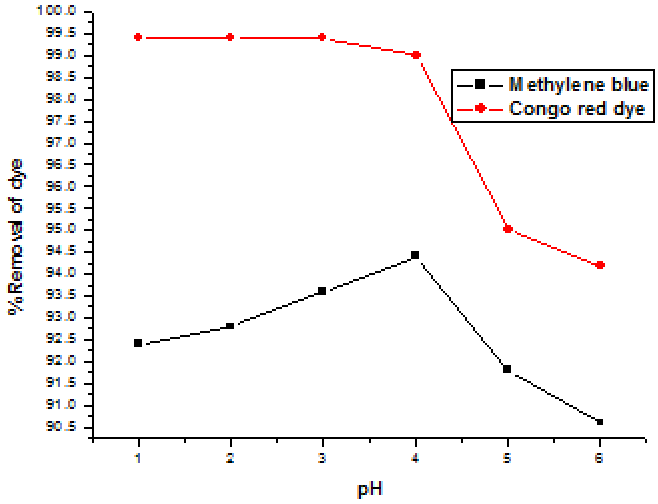


Figure 3: Effect of pH on the adsorption of dye removal by phosphomolybdic acid. Conditions: 50ml concentration 50 mg/L, stirring speed=500, 400 rpm; contact time=1h, adsorbent dose 1000 mg.

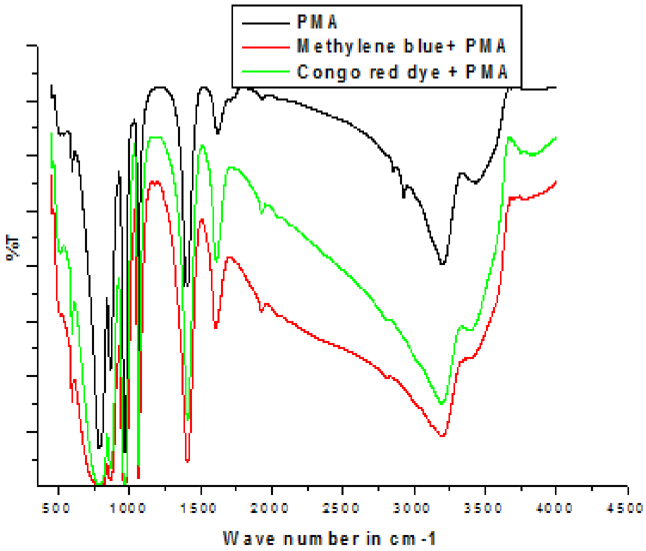


Figure 4: FTIR spectrum of phosphomolybdic acid with Congo red dye sample and Methylene blue

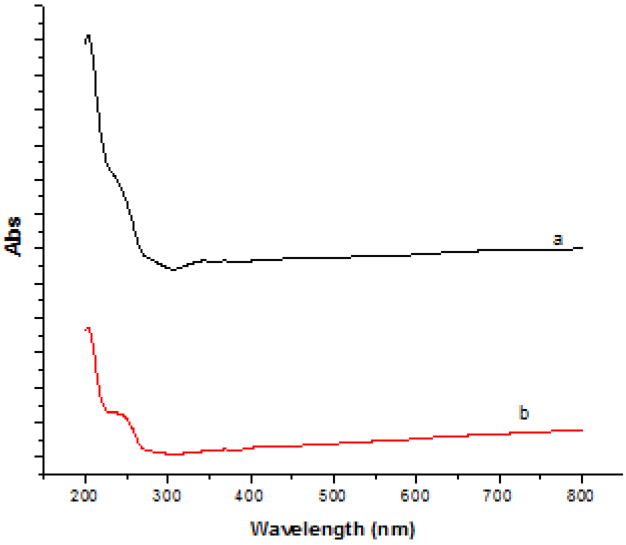
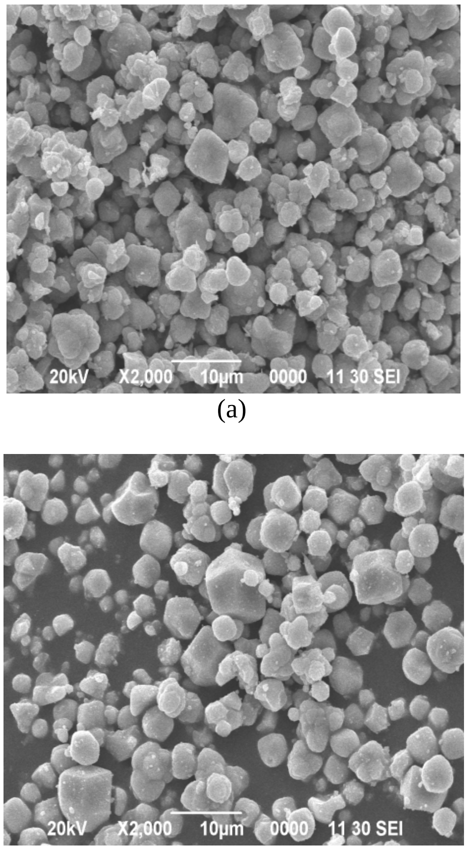


Figure 5: UV-Visible spectrum of phosphomolybdic acid with (a) Congo red and (b)methylene blue



(a)

(b)

Figure 6: SEM of phosphomolybdic acid loaded with dyes (a) Congo red dye and (b) Methylene blue

References

[1] Yao L, Lua S K, Zhang L, Wang R, Dong Z L, *J. Hazardous. Mat*, 271, 10, 2014.
[2] Chen W H, Mi J X, *J. Polyhedron*, 80, 15, 2014.
[3] Taleb M F A, *J. Carbohydrate Poly*, 144, 65, 2014.
[4] MeetiMehra, Sharma T R, *Adv. Appl. Sci. Res*, 3, 849, 2012.
[5] Tong K S, Azraa A, Jain Noordin A, *Int. J. Enverol. Sci. and Devlop*, 3, 656 , 2012.
[6] Hassan ZavvarMousavi, AbdorrahmanHosseinifae, VahdatJahed, *J. Serb.Chem Soc*, 77 393, 2012.
[7] Madhavan Nair, LekshmyHarikumaran Nair, DevakiammaThankamani, *J. Serb. Chem. Soc*, 76, 846, 2011.
[8] Xiu-Li Wang, QiangGao, Guo-Cheng Liu, *Inorg.Chem. Comm*, 14 ,745, 2011.
[9] Weiping Wang, Shuijin Yang, *J. Water Resource Pro*, 2, 1, 2010.
[10] Dey K C, Sharma V, *Int. J. Chem. Tech Res*, 2 ,1, 2010.
[11] Smith D P, So H, Bender J, Pope M T, *Inorg. Chem*, 12, 685, 1973.
[12] Kazanaskii L P, Torchenkova V, Spitsyn V I, *Russ Chem. Rev*, 43, 37,1974.
[13] Kozhevnikow I V, Mattveev K I, *Russ Chem. Rev*, 51, 1075, 1982.
[14] Murugesan R P, Sami, Jeyabalan T, Shanmugasundaram, *Transition Met. Chem*, 23, 001, 1998.
[15] Rocciodli-Deltcheff C, Fournier M, Frank R, Thouvenot R, *Inorg. Chem*, 22, 207,1983.
[16] Movahedi M, Mahjoub A R, Janitabar-Darzi S, *J. Iran. Chem. Soc*, 6 ,570, 2009.