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MOLYBDENUM VERSUS TUNGSTEN BASED POLYOXOMETALATES FOR HIGHLY EFFECTIVE METHYLENE BLUE REMOVAL

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1. INTRODUCTION

Water, the linchpin of all known life forms, necessitates rigorous safeguarding from the myriad pollutants that arise from human activities, including the effluents from industrial processes. The discharge of untreated wastewater into the environment, particularly those containing synthetic dyes, poses a significant threat to aquatic ecosystems and human health. These dyes, with their complex aromatic molecular structures, are not readily biodegradable and can be toxic, carcinogenic, or mutagenic (Hameed et al., 2009). Approximately, 10-20% of dyes are formed as waste during the dyeing process. These dyes are chemically stable, resistant to natural remediation, toxic, and even carcinogenic, posing complications to both the environment and human health (Bazrafshan et al., 2014). Their presence in water bodies not only impedes light penetration, affecting photosynthesis in aquatic plants, but also compromises the aesthetic and potable quality of water. Therefore, the treatment of wastewater, with a focus on dye removal, is of paramount importance. Among the dye pollutants, methylene blue (MB) stands out as a notorious heterocyclic aromatic compound that can cause breathing hazards, vomiting, hyperhidrosis and mental disorders (Balu et al., 2018).

Common approaches for the removal of dyes from industrial wastewaters are chemical oxidative modification, reverse osmosis, biological treatment, and photocatalytic degradation amongst others. Accordingly, these methods are used to remove organic dyes from water on the basis of their physical, chemical and biological properties. In the last years, adsorption technologies have become a very important tool for removing dyes from industrial wastewater pertaining to their low cost, high efficiency, and simple operation (Liu et al., 2015).

Recently, polyoxometalates (POMs) have emerged as a promising solution for water treatment due to their combination of unique physical and chemical properties. POMs continue to gain exponential popularity that started in the early 1990s as a result of a review by Pope and Müller (Long et al., 2010). POMs is class of anionic metal-oxygen clusters that can offer advantages such as simple preparation, low cost, high reactivity, non-corrosiveness, non-polluting nature and excellent stability (Taghdiri, 2017; Ivanova, 2014). POM chemistry research is a key emerging area in the treatment of water from many pollutants (Omwoma et al., 2015). Water treatment removes contaminants and undesirable components, or reduces their concentration so that the water becomes fit for its desired end-use. Dyes are one major water pollutant that can be removed with POMs.

This study focuses on testing the efficiency of two POMs compounds, namely $[SiW_{12}O_{40}]^{4-}$ (SiW_{12}) and $[Mo_8O_{26}]^{4-}$ (MO_8) (Figure 1), for the removal of methylene blue from aqueous solutions. Hence, the two adsorbents were synthesized according to classical procedures and characterized in the solid state by FTIR spectroscopy to assess purity. The effect of various parameters on the efficiency of dye removal by POMs were evaluated.

$[SiW_{12}O_{40}]^{4-}$ $[Mo_8O_{26}]^{4-}$

Fig.1: Polyhedral representation of POMs used as adsorbents in this study.

2. Experimental Section

2.1. Chemicals and reagents

$Na_2MoO_4 \cdot 2H_2O$, sodium metasilicate (Na_2SiO_3), sodium tungstate (Na_2WO_4), anhydrous potassium bromide, and methylene blue were purchased from Sigma Aldrich and used as received without further purification. Ultrapure water was used in all experiments.

2.2. Equipment and Apparatus

Ultrapure water was obtained from BOECO water purification system. Absorption spectra were collected on UV/Vis spectrophotometer (Thermo Heliosγ). Fourier Transform Infrared (FTIR) spectra were recorded using KBr pellets on a NICOLET 4700 IR spectrometer.

2.3. Synthesis of K4[α-SiW12O40].17H2O (SiW12)

$[SiW_{12}O_{40}]^{4-}$ was prepared according to the procedures reported in literature (Ginsberg, 1990). In brief, sodium metasilicate (5.5 g) was dissolved with magnetic stirring at room temperature in 50 mL of distilled water (Solution A). Sodium tungstate (91 g) was dissolved in 150 mL of boiling distilled water (Solution B). To the boiling Solution B, a solution of 4 M HCl (92.6 mL) was added dropwise over 5 min with vigorous stirring to dissolve the local precipitate of tungstic acid. Solution A was then added, followed by immediate addition of 25 mL of 4 M HCl. The solution was kept at 100 °C for 1 h. A solution of 1 M sodium tungstate (25 mL), and immediately thereafter, 40 mL of 4 M HCI were added. After cooling to room temperature, the solution was filtered. To obtain the potassium salt, the pH was adjusted to 2 with aqueous 1 M KOH, and 25 g of solid KCl was added. The potassium salt was collected by filtering, and was dried in air.

2.4. Synthesis of Na4Mo8O26 (Mo8)

$[Mo_8O_{26}]^{4-}$ was also prepared according to the procedures reported in literature (Ginsberg, 1990). In brief, $Na_2MoO_4 \cdot 2H_2O$ (5 g) was dissolved in water (12 mL), followed by the addition of 6 M HCl (5 mL) with vigorous stirring, and the solution was then filtered. Addition of 20 mL of 95% ethanol resulted in the precipitation of $Na_4Mo_8O_{26}$ as a yellow solid, which was isolated by filtration and air-dried.

2.5. Assessment of MB Removal by POMs

Methylene blue stock solution (1000 ppm) was prepared by dissolving accurately weighed 0.1 g MB dye in 100 mL of ultrapure water. The experimental solutions used were prepared by serial dilutions from the stock solution. All dye solutions were then properly wrapped with aluminum foil and stored in dark to prevent direct sunlight exposure and dye decolorization.

2.5.1. Effect of contact time

0.1 g of each POM compound was mixed with 25 ppm dye solution at room temperature for various intervals of time (55 min for SiW_{12} and 50 min for MO_8). The optimum contact time was detected according to the high adsorption efficiency as determined by UV/Vis spectrometry where the absorbance of the residual dye in the solution was measured at the dye's maximum wavelength (λ_{max} = 664 nm).

2.5.2. Effect of adsorbent dose

The effect of the adsorbent dosage on the adsorption efficiency of each POM compound for the removal of MB was evaluated by varying the adsorbent dose from 0.01-0.2 g in 25 ppm solution of MB. The mixture was shaken for a period of time according to the optimum contact time already chosen. The adsorption efficiency was then determined by UV/Vis spectrophotometry.

2.5.3. Effect of initial dye concentration

The effect of initial dye concentration on the adsorption efficiency of MB removal was determined by conducting a series of experiments at different initial dye concentrations ranging from 2-35 ppm. The mixture was agitated with the optimum adsorbent dose for the optimum contact time already selected.

2.5.4. Effect of pH

Adsorption experiments were carried out at pH range from 1-10. The pH of the reaction was maintained by adding the required amounts of dilute HCl or NaOH in aqueous medium, as well as the use of buffer solutions. The optimum adsorbent dose and contact time already chosen for 25 ppm MB solution were used. The pH meter was calibrated with pH 4, 7, and 10 buffers. Similarly, the adsorption efficiency was then determined by UV/Vis spectrophotometer.

2.5.5. Effect of temperature

The adsorption experiments were performed at five different temperatures (20, 25, 30, 35, 40 ºC) in a thermostat-controlled shaker. MB solution (25 ppm) was mixed with the optimum adsorbent dose for the chosen contact time. Likewise, the adsorption efficiency was then determined by UV-Vis spectrophotometry.

2.5.6. Dye concentration and percentage of removal

The MB dye concentrations were determined by examining the absorbance at its maximum wavelengths (λ_{max} = 664 nm) at which the molecules existed as ions in aqueous medium. The percentage of dye removal was calculated according to the following equation (Bazrafshan et al., 2014):

$$\textbf{Removal efficiency (\%)}\ \ R=(C_0-C_t/C_0)*100$$

where C_0 is initial dye concentration, and C_t is the concentration of dye after exposure to POM for time *t*.

3. RESULTS AND DISCUSSION

The highly negatively charged POMs SiW_{12} and Mo_8 were tested in the current study for their ability to remove the cationic methylene blue dye. Using polyoxometalates to reduce water pollution has received a special attention from the scientific community due to the high reactivity and unique properties of these inorganic frameworks. The ability of SiW_{12} and Mo_8 under study to remove methylene blue from water systems relies on the strong electrostatic attraction forces between the negatively charged oxygen atoms in the polyoxometalates and the positively charged ammonium ions in MB dye.

3.1. Characterization of POMs by FTIR

The successful synthesis of the POMs was inferred from the corresponding FTIR spectra. The peaks in FTIR spectrum of MO_8 in the range of 573-960cm^{-1} were ascribed to ν(Mo-O-Mo) and ν(Mo=O) vibrations (Figure 2a). The broad IR band centered around 3410 cm^{-1} and the signal at 1609 cm^{-1} can be attributed to the stretching and bending vibrations respectively of the –OH moiety of lattice water. A band around 3492 cm^{-1} was also involved with water molecules. The IR spectrum also consists of peaks arising for various Mo–O stretching vibrations at around 725, 672, 543, 452 cm^{-1}. On the other hand, the main characteristic features of the Keggin structure for SiW_{12} (Figure 2b) can be discerned from the fingerprint region from 1500 cm^{-1} to around 400 cm^{-1}. For example, Si-O vibrations were observed at 917cm^{-1}, while the signal corresponding to W–O symmetric stretching appeared at around 800 cm^{-1}.

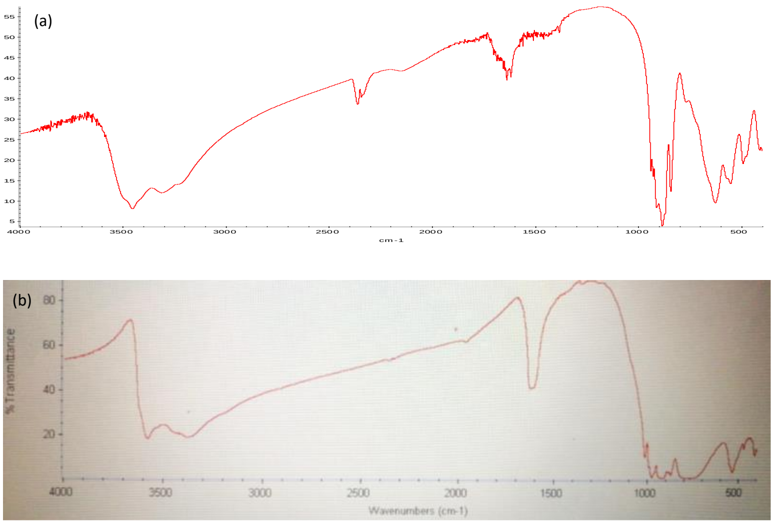

Fig.2: FTIR spectra of (a) MO_8 and (b) SiW_{12}.

3.2. Effect of various parameters on the removal of MB with MO8

3.2.1. Effect of contact time on the removal of methylene blue with MO_8

The removal percentage of MB by MO_8 as a function of contact time is shown in Figure 3. Rapid and highly efficient removal of the dye molecules from the aqueous solution by the POM was attained only after 5 min where a maximum recovery of 94% was reached. The remarkable rapid removal of the dye might be due to the abundancy of active sites and the larger surface area of the adsorbent (POM). An equilibrium state was reached after 5 min where no further increase in the removal efficiency was recorded, indicating that all active sites on the adsorbent $[Mo_8O_{26}]^{4-}$ were occupied by the dye. Hence, the chosen optimum contact time was 10 min to allow the strong ionic attractions between the anionic adsorbent and the cationic dye to reach equilibrium (Liu et al., 2015).

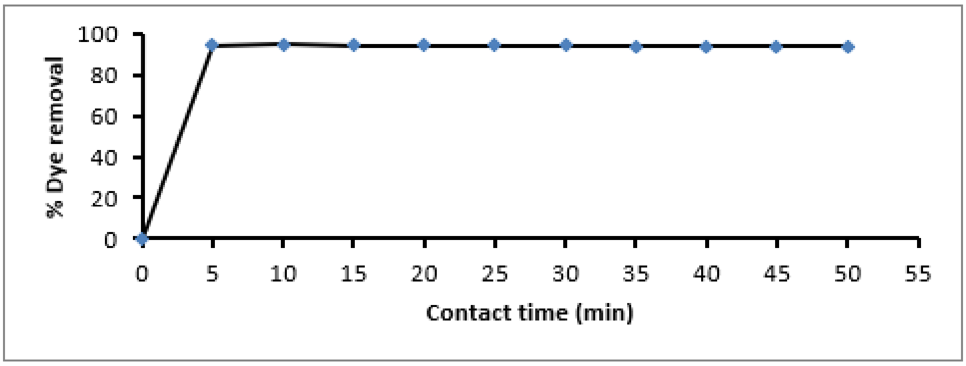

Fig.3: Effect of contact time on the adsorption efficiency of MO_8 for MB dye removal.

3.2.2. Effect of adsorbent dose on the removal of methylene blue with MO8

The effect of adsorbent dosage has been studied by varying the amount of adsorbent added over a range of (0.01-0.2 g) for $[Mo_8O_{26}]^{4-}$ at fixed initial MB dye concentration (25 ppm), and at the optimum contact time of 10 min. Results are summarized in Figure 4. An efficient removal of MB dye (95%) was obtained at 0.02 g for $[Mo_8O_{26}]^{4-}$. A further increase in the dosage of the adsorbent did not have any significant influence on the dye removal from the solution over the studied POM range because all available adsorption sites were almost saturated with MB. Such result patterns have been reported in prior studies for other dyes (Liu et al., 2015; Li et al., 2015; Mani et al., 2017; Ibrahim et al., 2017; Gong et al., 2005; Azhar et al., 2005; Anwar et al., 2012; Teka and Enyew, 2014; Yi et al., 2015).

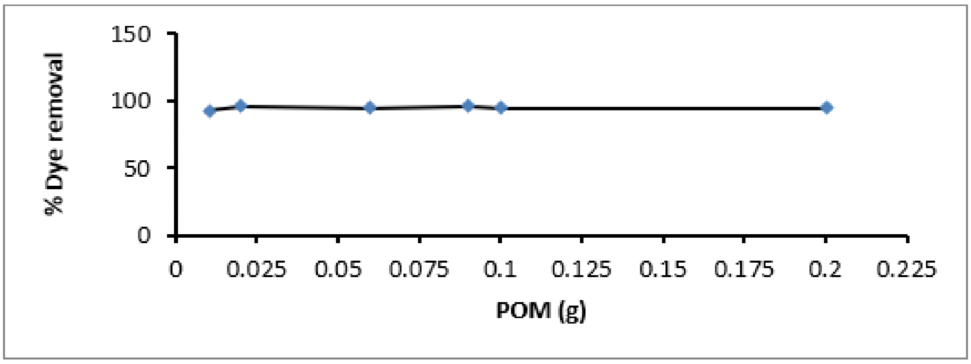

Fig.4: Effect of adsorbent dose on the adsorption efficiency of MO8 for MB dye removal.

3.2.3. Effect of initial dye concentration on the removal of methylene blue with MO8

The effect of initial MB dye concentration on the removal efficiency shown in Figure 5 was tested at the optimum adsorbent dose (0.02 g) and contact time (10 min) determined in previous experiments. The removal efficiency of MB dye decreased as the initial MB dye concentration increased from 2 to 35 ppm for MO_8. At low concentration, the ratio of initial number of dye molecules to the available adsorption sites is low contrary to that at high concentration, where the available sites become saturated which leaves behind a higher residual dye concentration (Liu et al., 2015; Umoren et al., 2013).

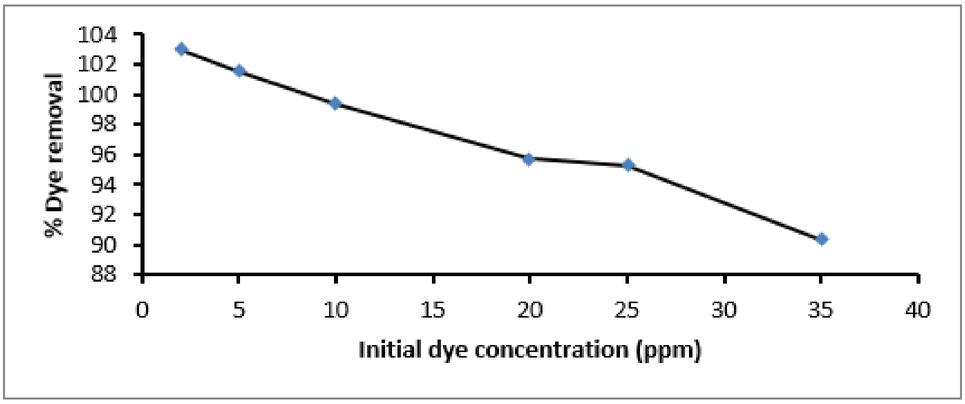

Fig.5: Effect of initial dye concentration on the adsorption efficiency of MO8 for MB dye removal.

3.2.4. Effect of pH on the removal of methylene blue with MO8

The solution pH is a very important parameter for dye adsorption studies. The effect of pH on MB dye removal has been studied by varying the pH over a range (1-10) at constant initial dye concentration of 25 ppm. Experiments were conducted using the optimum adsorbent dose (0.02 g POM) and at the optimum contact time (10 min) and results are depicted in Figure 6. The highest dye removal efficiency was observed in a pH range 2-9. MB is a cationic dye that exists in the positively charged form in highly acidic aqueous solution. At acidic pH, the presence of excess H^+ ions compete with the MB dye cation for the adsorption sites on the adsorbent causing a decline in the percentage MB removal. A similar result was also reported elsewhere for the adsorption of MB (Badii et al., 2010).

At pH=9, the alkaline condition could place the hydroxide ion on the adsorbent surface and the electrostatic repulsions between the adsorbent and the positively charged basic dye would be less, thereby increasing the extent of adsorption. However, with the increase of pH above 9, the chloride anion in MB is exchanged with NaOH via a displacement reaction, forming NaCl. Unfortunately, NaCl salt might result in the deactivation of the adsorbent and the percentage removal decreased again from 93.96 to 48.60% for $[Mo_8O_{26}]^{4-}$ (Ibrahim et al., 2017; Ndi Nsami and Ketcha Mbadcam, 2013; Jirekar et al., 2014; Jeyabalan and Peter, 2014; Tang et al., 2017).

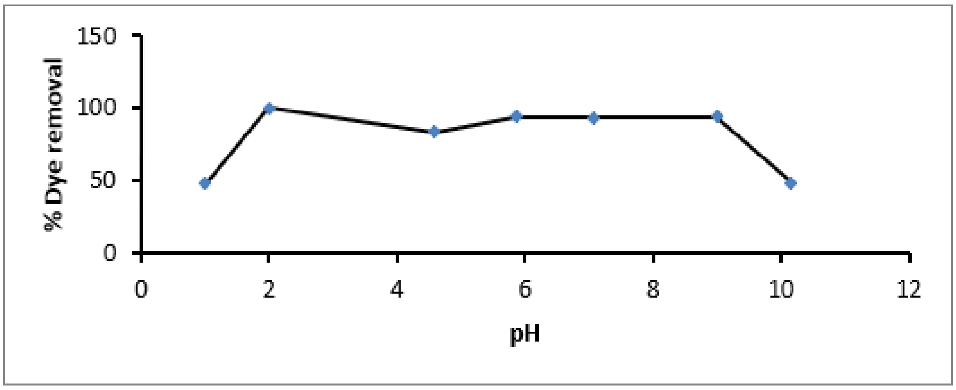

Fig.6: Effect of pH on the adsorption efficiency of MO_8 for MB dye removal.

3.2.5. Effect of temperature on the removal of methylene blue with MO8

Temperature is an important parameter to investigate when studies adsorption interactions. The effect of temperature on MB adsorption efficiency onto MO_8 was monitored at different temperatures 293-313 K at an initial dye concentration of 25 ppm, and results are shown in Figure 7. Interestingly, the rise in temperature did not significantly affect the adsorption of the dye molecules onto the active sites of the adsorbent. Comparable dye removal efficiencies were observed at the lowest (293 K) and highest (313 K) tested temperatures, thus highlighting the strong affinity of MB to MO_8. Increasing the temperature of the reaction mixture did not reverse the removal efficiency suggesting that the adsorption process is exothermic in nature (Patil et al., 2011; Geçgel et al., 2012; Liu et al., 2016).

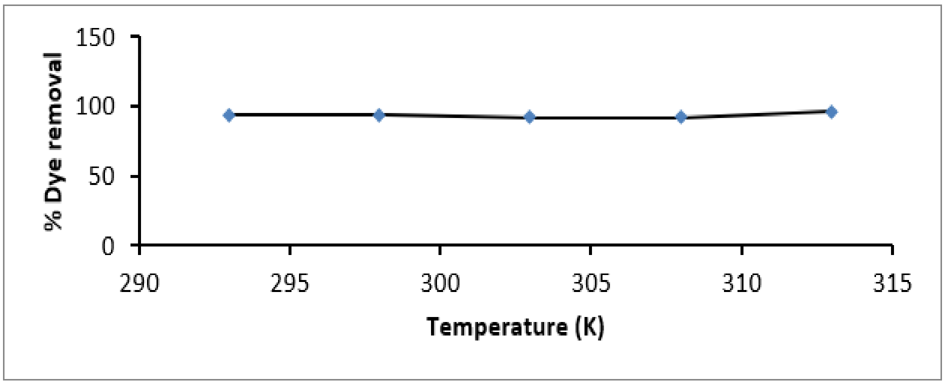

Fig.7: Effect of temperature on the adsorption efficiency of MO_8 for MB dye removal.

3.3. Effect of Various Adsorbent Factors on the Removal of MB with SiW12

3.3.1. Effect of contact time on the removal of methylene blue with SiW_{12}

The optimal time that is sufficient for the maximal removal of the MB dye from the aqueous solution by the adsorbent (SiW_{12}) was determined by mixing fixed amounts of the dye solution SiW_{12}, and monitoring the absorbance of the reaction mixture at 664 nm. As can inferred from Figure 8, SiW_{12} proved to be an efficient adsorbent of MB dye where the highest removal (74%) was achieved only after 5 min. Incubating the reaction mixture for longer times did not improve the removal efficiency further. This phenomenon is due to the fact that upon initial mixing, all the active sites on the surface of the adsorbents were empty and available to receive MB molecules (Gan et al., 2018; Yan et al., 2014). After 5 min, all the active sites were occupied, and therefore, an increase in the reaction time did not translate into improved removal of the dye. SiW_{12} POMs were less efficient than MoO_8 in MB dye removal (74% vs. 94% dye removal).

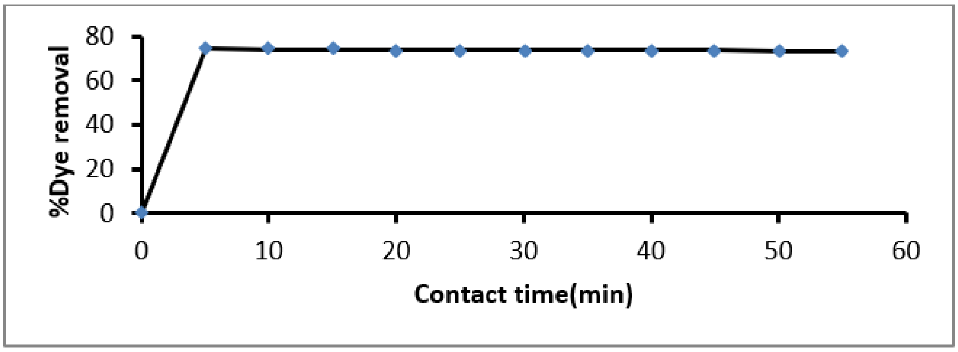

Fig.8: Effect of contact time on the removal of methylene blue with SiW_{12} compound

3.3.2. Effect of adsorbent dose on the removal of methylene blue with SiW12

The effect of the amount of SiW_{12} on the removal of MB dye was studied by mixing different doses of the adsorbent (0.01-0.2 g) in 25 ppm dye solution. At these experimental conditions, the highest removal of the dye molecules (74%) was achieved at 0.01 g of the adsorbant (Figure 9). Increasing the levels of the adsorbent to 0.2 g did not result in enhanced removal of the dye. It is possible that at adsorbent quantities beyond the optimum value, MB particles start to agglomerate on the surface (Salman et al., 2016; Rani et al., 2016).

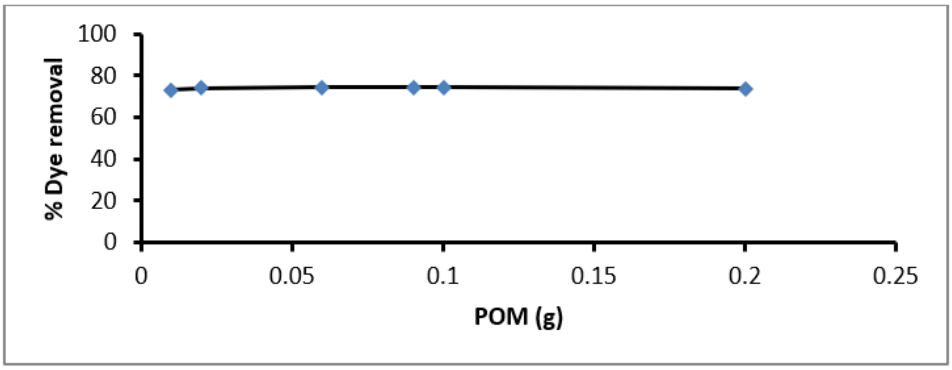

Fig.9: Effect of adsorbent dose on the removal of methylene blue with SiW12 compound.

3.3.3. Effect of initial dye concentration on the removal of methylene blue with SiW12

The initial concentration of the dye can affect the overall removal efficiency of the dye molecules. Therefore, the percentage of dye removal was evaluated at a fixed dose of the adsorbent, and varying concentrations of the dye (2-35 ppm). Results are showen in Figure 10. As expecetd, the removal efficieny of the dye molecules by was higher at lower initial concentrations (100% at 2 ppm of dye), indicating that the ratio of the adsorbent to the dye is adequate for maxiaml recovery of the dye. As the initial concentration of the dye increases, the percent recovery decreases steadily, reaching 61% for 35 pm of the dye. As mentioned above, the active sites of the adsorbent were saturated at 2 ppm of the dye. Therefore, the adsorbent molecules cannot tolerate excess dye molecules which remain dissolved in the solution (unrecovered) leading to diminished overall recovery. Similar results were found in (Yan et al., 2014; Salman et al., 2016).

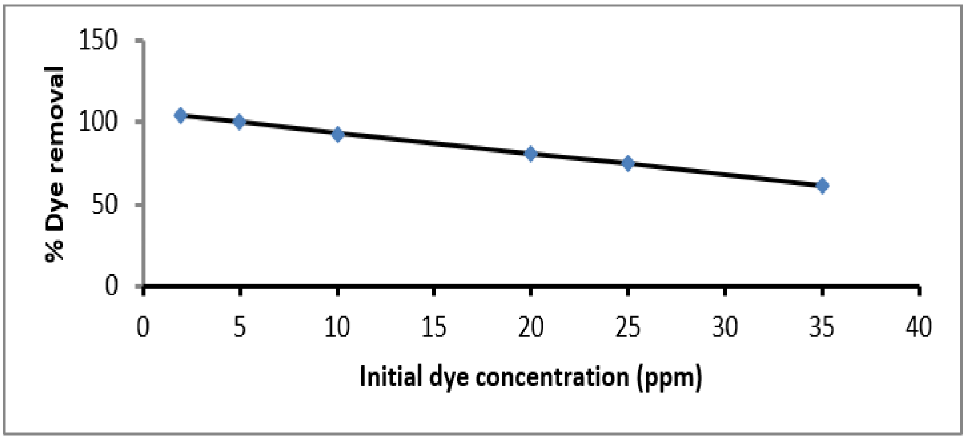

Fig.10: Effect of initial dye concentration on the removal of methylene blue with SiW12 compound.

3.3.4. Effect of pH on the removal of methylene blue with SiW12

The overall charge of the dye molecules and the adsorbent, and therefore the recovery efficiency of the dye, is strongly influenced by the pH of the solution. In this study, the removal of MB molecules by SiW_{12} was tested at a different pH values ranging from 1-10. The experiment were conducted using the optimum adsorbent dose and contact time already selected (Figure 11). Maximal recovery of the dye (89%) was observed at pH 4. At other pH values, the percent recovery was 74%. It seems that at the optimal pH of 4, MB molecules are positively charged and can interact through electrostatic interactions with an overall negatively charged SiW_{12} resulting in maximal removal of the dye (Rani et al., 2016). The high removal percentage for SiW_{12} in acid conditions is also due to the stability of these complexes at lower pH values. In highly acidic media (pH<4), the positive hydrogens ions can interfer with dye cations for the available adsorption sites on the adsorbent leading to lower recovery values of the dye (Salman et al., 2016).

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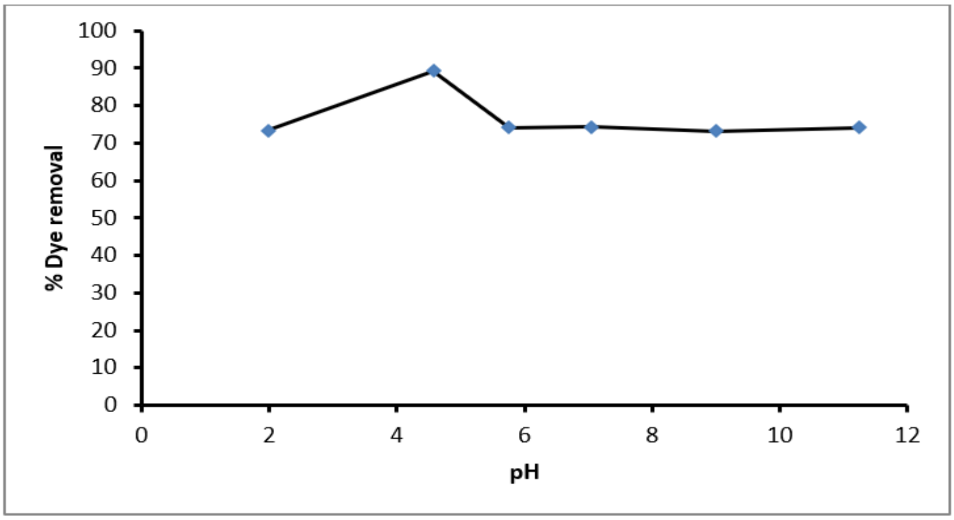

Fig.11: Effect of pH on the removal of methylene blue with SiW12 compound.

3.3.5. Effect of temperature on the removal of methylene blue with SiW12

To understand the effect of temperature on the removal of the dye by POMs, the ability of SiW_{12} to remove MB was tested at five different temperatures (293, 298, 303, 308 and 313 K) at a dye solution of 25 ppm. It has been reported that if the percentage of removal of MB increases with temperature, then the adsorption process is classified as endothermic (Gan et al., 2018). In this study, increasing the temperature did not result in a considerable change in the percentage of dye removal, indicating that the attractive interactions between the dye molecules and the adsorbent are remarkbly strong (Figure 12). It is also possible that The high percentage of removal is also due the large pore sizes in the adsorbent facilitates the penetration of the dye molecules deep into the adsorbent, and prevents its detachement even at high temperatures. Such stability at high temperatures expands the scope of application of the POMs as adsorbents in different industrial settings.

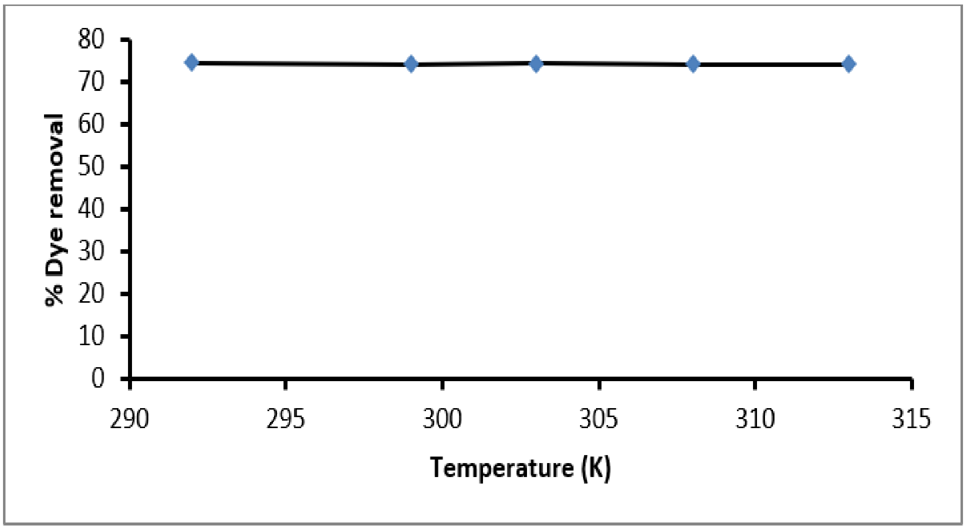

Fig.12: Effect of temperature on the removal of methylene blue with SiW12 compound.

4. CONCLUSION

Two polyoxometalates, namely MoO_8 and SiW_{12}, were investigated for their effectiveness in removing MB from aqueous solutions and the effect of several parameters on the efficiency of the adsorption process. The study found that $[Mo_8O_{26}]^{4-}$ exhibited high adsorbent efficiency towards the removal of methylene blue, a common cationic dye, from water. Although $[SiW_{12}O_{40}]^{4-}$ was good adsorbent for the removal of MB, it was less efficient compared to MoO_8. Overall, both POMs compounds demonstrated good overall adsorption efficiency. The results of his work showed that the chosen adsorbents that were prepared via a cheap and facile synthetic pathway can be explored as eco-friendly effective adsorbents for the removal of types of organic dyes and other pollutants.

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