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REMOVAL OF METHYLENE BLUE DYE IN AQUEOUS SYSTEM USING POLYVINYL ALCOHOL AND CHEMICALLY MODIFIED-ALUMINIUM FOIL BLEND

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ABSTRACT

Aqueous solution containing different concentrations of methylene blue dye was treated with chemically modified aluminium foil/PVA blends. There have been impressive decolourisation of the dye molecules in the aqueous system treated with the blends. Contact time and amount of composite facilitate more decolourisation of the dye solution. 97 % dye removal has been recorded at optimum conditions of the experiment. Energy dispersive X-ray fluorescence (EDXRF) analysis was used to determine the elemental composition of the aluminium foil and FTIR analysis was used to ascertain the composite formation between the foil and PVA. The blends have shown an impressive swelling property in aqueous system and poor to moderate in other organic solvents.

1 INTRODUCTION

Composites are often produced to have superior characteristics than their parent materials. The physico-chemical changes that come along the blend formation provides some additional properties to the starting materials. The component materials in the composites may be described as having synergistic effects that provide better and desirable properties in the final product [1]. Mixing of different materials to construct materials of targeted applications have been a common breakthrough in different industries today. Polymers, both synthetic and natural are widely used with different materials to construct new products with impressive properties [2,3]. Nanocomposites from polymers and metal ions, biomolecules and other materials are impressively used in healthcare system and tissue engineering [4,5].

Polyvinyl alcohol (PVA), being a synthetic polymer with remarkable properties such as good chemical resistance low price and hydrophilicity, is widely used in different industrial applications such as textile, adhesives, agricultural and pharmaceuticals. The polymer is also used in food industry for packaging purposes and in medical industry for drug delivery, cancer therapeutics and wound healing [6,7,8,9]. The structural features of PVA such as the presence of OH groups in its molecule and small molecular size (Figure 1) are responsible for most of the properties that identify the polymer. For instance, hydrophilicity and impressive mechanical stability [10]. PVA blends with alginate (natural polymer) are reported to be used in waste water treatment, dye absorption and in bioremediation [11,12,13,14].

Water contamination due to human activities and population expansion have become an issue of great concern to environmentalists. Different techniques are employed in waste water remediation and purification. Cost, limited-hazard and recyclability are among the important factors that are being considered in making the choice. Aluminium is one of the common elements that are found in almost every urban household in form of kitchen wires, cans, doors, pie plates and wrapping packages [15]. Among the most common source of aluminium contamination into the environment is aluminium foil (Al-foil). It’s widely used today in many industries, households and eateries. The foil is not easily degradable or easy to recycle, it can only be disposed of using an incinerator or disposed in landfills. Water contamination from organic dyes usually comes from industries such textile, leather, cosmetics or ink industry. The presence of colourants in water can be hazardous when the dye molecule is toxic on its own or by releasing toxic molecules when it is degraded. Moreover, even when the colorants are made from non-toxic substances, their presence may lead to poor sunlight penetration and low oxygen level in the water. These may lead to termination of life activities in the water environment [16].

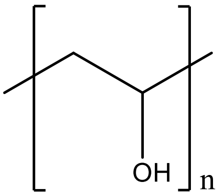

***Figure 1**. Structure of polyvinyl alcohol.*

2 EXPERIMENTAL MATERIALS

2.1 Chemical Modification of Aluminium Foil Sample

Procedure reported by Narayana and Shafirovich (2014) [17] was used with little modification. Aluminium foil waste was obtained from domestic sources in the waste bins, the samples were washed, dried, and then shredded to an average 10 × 10 mm size. 5.0 g of the small pieces of aluminium waste was accurately weighed and transferred into 500 cm^3 beaker. 250 cm^3 of 1.5 M KOH was added to the 500 cm^3 beaker containing the aluminium pieces. The mixture was heated to 200 °C for 30 minutes. Bubbles of hydrogen was observed from the reaction of aluminium and aqueous KOH. The reaction was observed to be complete when the hydrogen evolution ceased and there were no visible pieces of aluminium metal. The solution was filtered to remove solid residue. The clear filtrate was transferred into a clean 500 cm^3 beaker and allowed to cool. 100 cm^3 of 9.0 M H_2SO_4 was added to the solution and stirred gently. The reaction beakers were set into the ice-water bath to chill for about 30 minutes. As the mixture became cold, crystals of aluminium salts began to form in few minutes. Further crystallization of the mixture was carried out using 50% ethanol/water mixture. The crystals formed was filtered from the solution and dried for 48 hours in an oven at 50 °C. The modified aluminium foil was obtained and labelled as M-Al-foil. The overall reaction is represented in the scheme 1.

$$2Al_{(s)} + 2KOH_{(aq)} + 4H_2SO_{4(aq)} + 22H_2O_{(aq)} \text{-------->} 2KAl(SO_4)_2\ .12H_2O_{(s)} + 3H_{2(g)}$$

Scheme 1: *Production of M-Al-foil from aluminium foil.*

2.2 Preparation of PVA/ M-Al-foil Blend Hydrogel via Freezing and Thawing Method

0.2 g of synthesized aluminium salts crystals were weighed and transferred into a 100 mL beaker labelled as A. Distilled water (10 mL) was added into the beaker and stirred gently for 1hr at ambient temperature. PVA (1 g) was transferred into a 100 mL beaker and labelled as B. Distilled water (10 mL) was added to the beaker and heated to 80 °C for 1hr. After allowing the mixture to cool, the two solutions (A and B) were combined and gently mixed at room temperature using a magnetic stirrer until homogeneity was achieved. The mixture was then poured on a petri dish and exposed to the atmospheric pressure to degas. The Hydrogel formed was frozen for 12 hrs and then thawed. The mass of dried blend was measured.

2.3 Characterization

2.3.1 Ultraviolet spectroscopy

UV-VIS Pye Unicam Spectrophotometer Type Sp 8- 200 was used in this experiment. All spectrophotometric measurements were carried out at ambient temperature.

2.3.2 Energy dispersive X-Ray florescence (EDXRF)

A Jeol 5400 (Japan) scanning electron microscope with energy dispersive X-ray (EDX) attachment was used to determine the uptake of the different elements by different substrates.

EDXRF analysis is designed to analyze groups of elements simultaneously. This type of XRF instrumentation separates the characteristics x-rays of different elements into a complete fluorescence energy spectrum which is then processed for qualitative or quantitative analysis.

2.3.3 FTIR analysis

FTIR spectrophotometer model Mattson 100, made by Unicam, (UK) was used for the FTIR measurements over the range 500-4000 cm^{-1}. The FTIR spectra of the samples were obtained using ATR mode.

The Thermal properties and structural characterization were carried out using TGA and SEM analyses respectively.

2.4 Solvents Absorption and Retention of the Blend

20 mg of the sample was soaked in 25 mL of different solvents for 24 h at room temperature. The samples were then removed and blotted on filter paper to remove excess water/solvent on the surface. The swelling (%) was calculated according to the following equation:

$$\text{Swelling } \% = {}^{W2}/_{W1} \times 100 \tag{1}$$

where W1: initial weight of the sample and W2: final weight of the swollen sample.

2.5 Adsorption of Methylene Blue Dye

Procedure reported by Karaoglu and Ugurlu (2010) [18] was used with little modifications. Methylene blue dye stock solution was prepared by dissolving 1 g of the dye in 1000 cm^3 distilled H_2O. Different targeted concentrations were obtained in the experiment by diluting the stock solution prepared. Different operating conditions such as contact time, dose of blend, dye concentration and pH were respectively studied. The pH adjustments were made by the controlled addition of 1 M, NaOH and 1 M HCl. The varying amounts of methylene blue concentration (5 mg/L to 100 mg/L) were prepared. 100 mL of the dye solution was used in each batch experiment at ambient temperature. In each case the dye uptake was determined by measuring the light absorption of the residual dye solution after contact with the blend. The dye sorption by samples was determined according to equation (2):

$$\text{Dye uptake\%} = \text{Dye conc. on sample / initial dye conc. X } 100 \tag{2}$$

3 RESULTS and DISCUSSION

3.1 FT-IR Analysis

Figure 2 shows the FT-IR spectroscopy of pure PVA sample before blending with the aluminium crystals. The IR spectrum showed absorption bands at 3265 cm-1 and at 1699 cm-1due to OH stretching and bending modes respectively. Absorption bands at 2907 and 1080 cm-1 are due to C-H stretching and bending respectively. In Figure 3, the FTIR spectrum of the PVA/M-Al blends show reasonable adjustment of peaks. The OH stretching vibration at around 3265 cm-1 has now been shifted to 3324 cm-1 and C-H bending vibration has changed from 1699 to 1658 cm-1 in the blend. This changes in absorption peaks are associated with the presence of other substances from the alum in the blend.

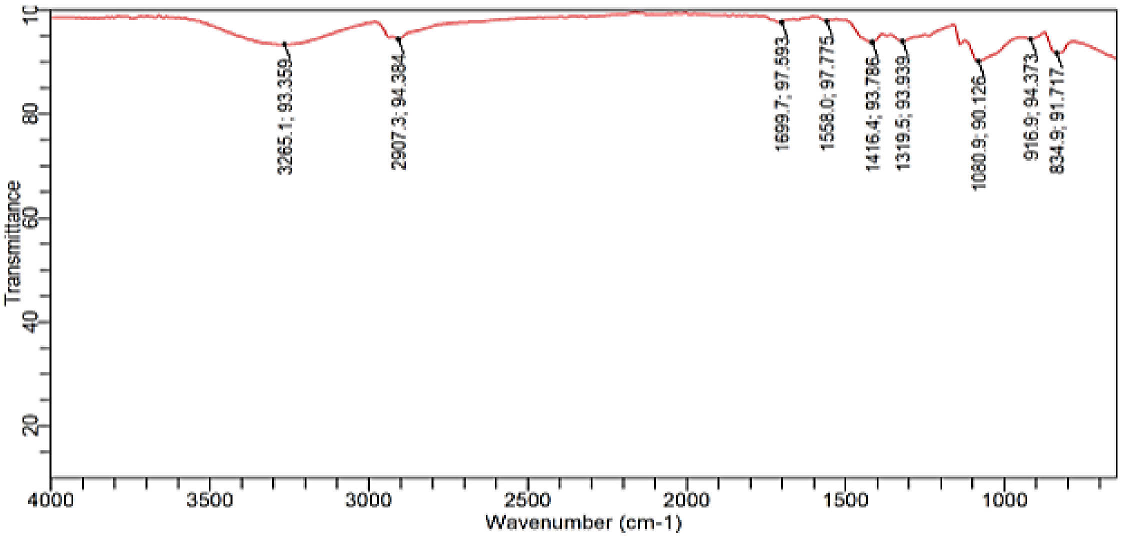

Figure 2. *FTIR spectra of PVA virgin sample.*

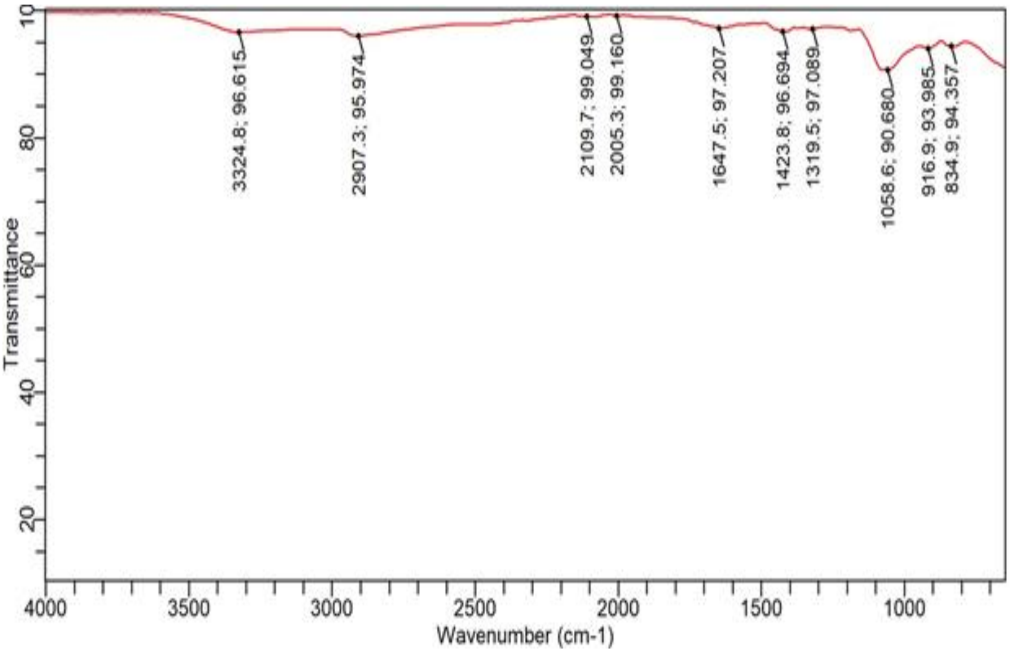

Figure 3*. FTIR spectrum of PVA/M-Al blend.*

3.2 EDXRF Analysis of Alum Crystals

Table 1 shows the elemental composition and oxides present in the extracted alum from the aluminium foil. The results showed high amount of aluminium, Sulphur and potassium and their respective oxides. Presence of these elements further confirms that aluminium salt (alum) has been successfully prepared from aluminium foil. Other elements and their oxides that are in a negligible quantity are also presented.

Table 1*. EDXRF results showing the composition of some elements present in alum crystals.*

Elements	%Elements	Oxides	% Oxides
Fe	0.02375	Fe_2O_3	0.03396
Na	0.136	Na_2O	0.183
Al	6.605	Al_2O_3	12.480
Si	0.7736	SiO_2	1.655
P	0.1338	P_2O_5	0.3067
S	19.098	SO_3	47.688
K	8.452	K_2O	10.181

3.3 Swelling Properties of the Blend

The swelling property of the blend in water and other solvents was carried out by immersing the blend in different solvent for 24 hours. The swelling property of the blend in each solvent is shown in Table 2. From the result it can be observed that the blend has a high tendency to swell in water and moderately in other solvents with high polarity and dielectric constants than in nonpolar solvents [19]. The trend goes in the following order: water >DMF>ethylacetate>n-hexane>benzene.

Table 2. *Swelling of PVA/M-Al blend in organic solvent and water after 24hours.*

Solvents	%Swelling
Water	236
Benzene	75
Dimethylformamide	146
Ethylacetate	97
n-hexane	78

3.4 Studies on Dye Removal from Waste Water

3.4.1 Effect of contact time

Figure 4 shows the trend in dye adsorption by the blend in percentage with contact time. The results obtained showed the highest dye adsorption at 35 minutes. However, there wasn’t significant dye adsorption with further increase of time. This can be attributed to the fact that, at the initial stage the number of free adsorption sites was higher and the slow or constant adsorption rate in the later stage was due to slower diffusion of solute into the interior of the adsorbent.

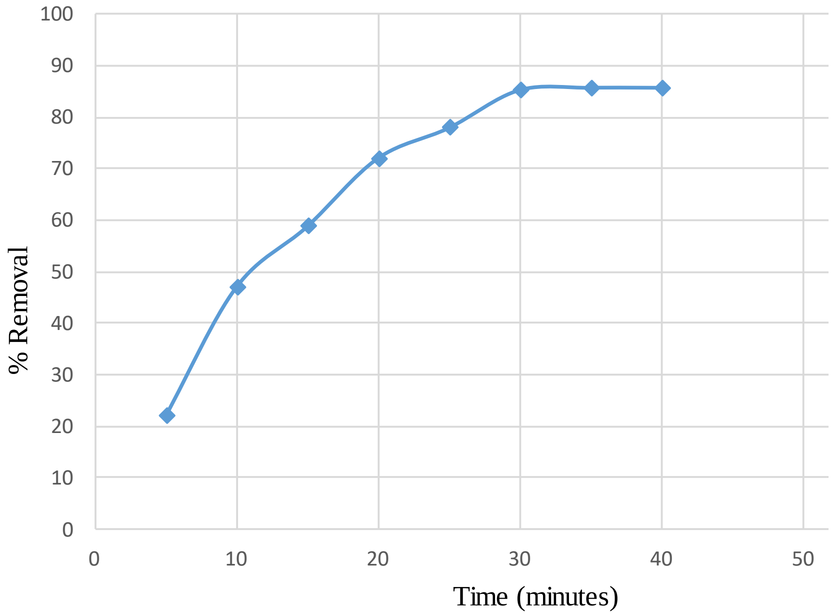

Figure 4. *Effect of contact time.*

3.4.2 Effect of dye concentration

In Figure 5, the dye uptake has been shown to decrease with increase in the dye concentration. This is as a result of excess dye molecules would have limited active contact with the blend’s surface. Hence, the free dye molecules would remain in the solution without being adsorbed. In this research work, it is observed that the blend adsorbent degraded 85.29 % of methylene blue at initial concentration of 20 mg/L.

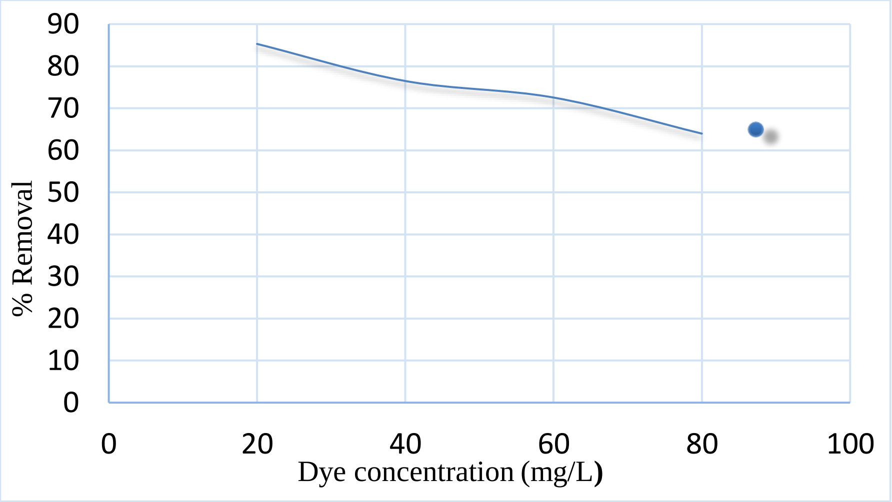

Figure 5. *Effect of dye concentration.*

3.4.3 Effect of amount of composite

The effect of composite dosage on the adsorption of methylene blue is shown in Figure 6. There is a general increase in the dye uptake with more amount of the composite sample until it reached a stage where it levelled-off and then started decreasing. High amount of composite would lead to a more active contact between the dye molecules and the surface of the composites. Thus, more dye uptake. In this experiment, 97.05% removal was observed at optimum adsorbent dosage of 1.5 g.

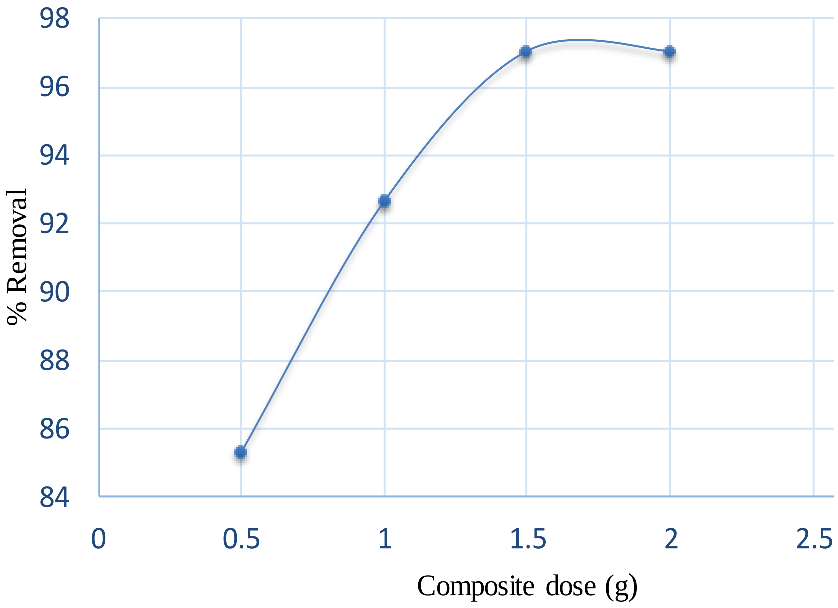

***Figure 6**. Effect of composite dose.*

3.4.4 Effect of pH on dye adsorption

The effect of pH on the percentage of the methylene blue dye removal is shown in Figure 7. There was a general increase in the dye uptake with increase in pH. The adsorption was observed to reach its optimum at a pH slightly less than 7. In this work, it can be concluded that at a more acidic or alkaline pH there is a general decrease in the dye uptake.

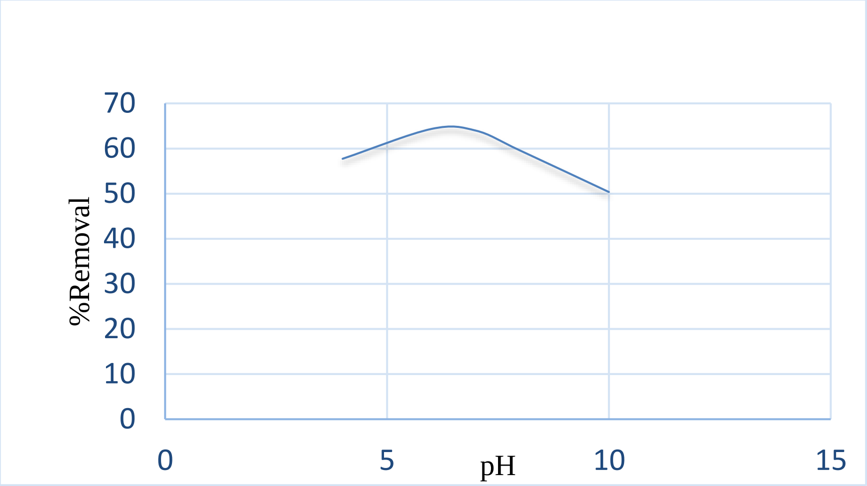

***Figure 7**. Effect of pH on dye uptake.*

4 CONCLUSION

In this study, methylene blue dye in aqueous solution was treated with PVA/M-Al foil blend as adsorbent. FTIR and EDXRF results showed that Aluminium foil have been successfully incorporated onto the polyvinyl alcohol. The results showed that PVA/M-Al foil blend proved to be a very effective adsorbent in the removal of methylene blue dye from waste water. The adsorption performance is strongly affected by parameters such as contact time, initial dye concentration, adsorbent dosage and pH. The maximum removal of methylene blue observed was 97.05% for 1.5 g of PVA/M-Al foil blend adsorbent at neutral solution. The optimum conditions of PVA/M-Al foil experiment are 30 minutes of contact time, 1.5 g adsorbent dose and PH of solution in between 6 and 7. It was also observed that, the percentage adsorption of methylene blue decreases with increase in the dye concentration and the amount of dye uptake increases with the increasing of adsorbent dose.

Conflict of Interest

There is no conflict of interest between the authors.

Authors contributions

Aliyu Danmusa Mohammed contributed with the Project proposal and title. Moreover, interpretations of results obtained in the manuscript were carried out by him. He also designed the article format in accordance with the journal guidelines.

On the other hand, Abubakar Tsagero contributed to the sample collections and preparation.

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Statement of research and publication ethics

The study is complied with research and publication ethics.

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