Jewel Journal of Scientific Research (JJSR) 5(1&2): 11–20, 2020
©Federal University of Kashere-Nigeria (Print ISSN: 2384 – 6267, Online ISSN 2756-651X)
jjsr.fukashere.edu.ng

The use of *Diospyros mespiliformis* seeds, *Ziziphus jujuba* seeds and *Balanites aegyptiacus* shell as Eco-Friendly and Low-Cost Biosorbents for Removal of Azo Reactive Dyes from Aqueous Solution

***Usman, A. H[1]., Abdullahi, M.[1] and Umar, A. S[1]**

[1]Department of Applied Chemistry, Federal University Dutsin-Ma, Katsina – Nigeria
* Corresponding Author: a.rasheedhallir@gmail.com; +2348036616025

Abstract
In the removal of Azo reactive dye (ARD), *Balanites aegyptiacus* shell (BAS), *Diospyros mespiliformis* seeds (DMS) and *Ziziphus jujuba* seeds (ZJS) were investigated as low-cost and environmentally friendly biosorbents. Parameters affecting the adsorption process were investigated, such as contact time, pH, adsorbent dosage, temperature and initial dye concentration. Experimental results showed that the percentage removal of all adsorbents increases with an increase in adsorbent dosage, initial dye concentration, temperature and time, the only difference being that the percentage removal of BAS adsorbent decreases with an increase in initial dye concentration. However, it was found that the optimum pH of BAS adsorbent was in a slightly acidic medium pH of 6.0, also that of DMS adsorbent was in acid medium pH of 2.5 and the best pH for adsorption process using ZJS adsorbent was in the basic medium pH of 10. Based on the data obtained, it is clear that BAS, DMS and ZJS could be used to remove Azo reactive dyes (ARD) from aqueous solution. Results obtained also indicated that the efficiency of the sorbents for the removal of ARD from aqueous solution was in the order of ZJS > DMS > BAS.

Keywords: Azo reactive dye; *Balanites aegyptiacus*; *Diospyros mespiliformis*; *Ziziphus jujube*; Biosorbent

Received: 20th Feb., 2020 *Accepted:* 25th May, 2020 *Published Online:* 25th June, 2020

Introduction

Over the past few years, water pollution related to dyes has become a significant threat to the world, introducing infectious diseases due to dyes discharge. Dye is used in many sectors, such as carpets, furniture, cosmetics, paper, food and textiles (Hajira *et al.*, 2008). Discharge of dyes from these factories into rivers causes severe problems, as dyes offer aquatic life toxicity and also harm the environment's esthetic quality (Aseel *et al*., 2007). Various dye removal methods have been suggested from time to time, including aerobic and anaerobic microbial degradation, coagulation, chemical oxidation, membrane separation, electrochemical treatment, filtration, reverse osmosis and adsorption (Panda *et al*., 2009).
Adsorption in terms of initial cost, ease of nature, use of procedure and insensitivity to toxic substances was found to be superior to other techniques (Ayesha and Ali, 2016). Due to their high adsorption ability, the use of activated carbons as adsorbents for dye is popular and very efficient for this reason. However, there is a constant search for alternative low-cost adsorbents in view of the high cost and associated regeneration issues. The quest for cheap and efficient substitute materials such as jute stick powder (Panda *et al*., 2009), hazelnut shells (Dogan *et al*., 2008), pecan nut shell (Patil,

and Shrivastava, 2010), sugarcane bagasse (Gong *et al*., 2005) and guava (Psidium guajava) leaf powder (Ponnusami *et al*., 2008) resulted in this challenge.

Batool *et al.* (2014) reported the efficient method for the removal of Cr(VI) and azo dyes. Dadvar *et al* (2017), reported the efficiency of graphene oxide-TiO_2 polymer membrane as a good adsorbent for removing azo dye from aqueous solution. Bimetallic nanoparticles made up of iron and nickel has been investigated to remove a contaminant from azo dye in aqueous solution (Shelby *et al*., 2019). Studies of adsorption of aqueous basic dye solutions using Sepiolite as adsorbent have been reported (Mesut *et al.*, 2009). Chemically modified sugarcane bagasse experiments have been identified as a possible low-cost biosorbent for removal of dye (Saad *et al*., 2010). The color removal of reactive procion dyes by clay adsorbent was stated by (Ari Rahman *et al*., 2013). Barun *et al* (2017), examined the impact of operating parameters on the removal by electrocoagulation process of brilliant green dye from aqueous solutions. Removal of Trypan blue dye using nano-Zn modified Luffa sponge was studied (Hayrunnisa *et al*., 2017). Despite the fact that most of the aforementioned adsorbents were not only very cheap but also easily available. However, their preparations involved some processes such as activations, functionalizations and modifications before they can be used. That make them a little bit costly as compared to the tested adsorbents which only requires simple grinding and sieving. The aim of this study was to determine the adsorption capacity of BAS, DMS and ZJS as low-cost and environmentally friendly adsorbents for removal of azo-reactive dyes in aqueous solution. The effect of different factors including initial dye concentration, contact time, initial pH, adsorbent dose and temperature on percentage were also investigated.

Materials and Methods

Preparation of Adsorbents

The method of Krishna *et al* (2014) was used in the preparation of adsorbents. The adsorbent samples were obtained from Safana local government area, Katsina state. They were then brought to the laboratory, washed thoroughly with tap water followed by distilled water. The washed samples were dried at room temperature and then ground using mortar and pestle and sieved using mesh (5 µm). The sieved samples were stored in a plastic container and labeled *Diospyros mespiliformis* Seeds as (DMS), *Balanites aegyptiacus* Shells as (BAS) and *Ziziphus jujuba* Seeds as (ZJS).

FTIR Analysis

Fourier Transform Infrared (FTIR) spectroscopy analysis of the adsorbents before and after was carried out using Fourier Transform Infrared spectroscopic machine (Agilent technology Cray 630) in a wave number range 400 – 4000 cm^{-1}.

Batch Adsorption Experiments

Adsorption experiment was conducted by batch method as reported by Mahvi *et* al (2012). The adsorption studies were conducted by mixing various amount of adsorbent in Erlenmeyer conical flask containing dye concentration of known concentration. Furthermore, the pH was adjusted to the desired value with 0.1 M HCl and NaOH solutions. Various parameters such as contact time ranges from (20 - 60 minutes), pH 2 to 10, adsorbent dosage (0.5 - 2.5 g/L), initial dye concentrations (10 - 50 mg/L) and temperatures (30 - 70 ^oC) were investigated in different experiments. The solution was agitated for 5 min at 4500 rpm and then the supernatant of the suspension was filtered using a Whatman filter paper. The final dye concentration was determined by UV-visible spectrophotometer (Hach DR 5000) at maximum wavelength (λmax) of 625 nm. Removal efficiency was calculated using the following equation:

$$\text{Percentage removal} = \frac{Co - Ce}{Co} X\ 100 \qquad 1$$

Where C_o (mg/l) initial dye concentration, C_e (mg/l) is the equilibrium concentration, t (min) is the time, V (l) is the volume of the dye solution used and w (g) is the mass of the adsorbent used

Results and Discussion

Figure 1, represent spectrum of DMS before adsorption. The broad band at 3260 cm^{-1} was assigned to O – H stretching and it was due to hydrogen bonding involving the hydroxyl groups on the adsorbent. The band at 2921 cm^{-1} was assigned to C – H stretching vibrations. Characteristic peak appeared at 1711 cm^{-1} was attributed to C = O bond stretching of the adsorbent. In the finger print, band at 1030 cm^{-1} was as a result of C - O vibration. However, figure 2, represent spectrum of DMS after adsorption. Compared with spectrum of DMS adsorbent before adsorption, a new peak appeared at 666 cm^{-1} which was corresponded to the stretching vibrations of the bond (C - X) formed between the adsorbent the dye molecule. The band for C – H was observed at 2925 cm^{-1} and the peak at 3152 cm-1 was a result of O - H band. In the finger print region, band at 1039 cm^{-1} was assigned to stretching vibration of C – O. Similar result was reported by (Barun *et al*., 2017).

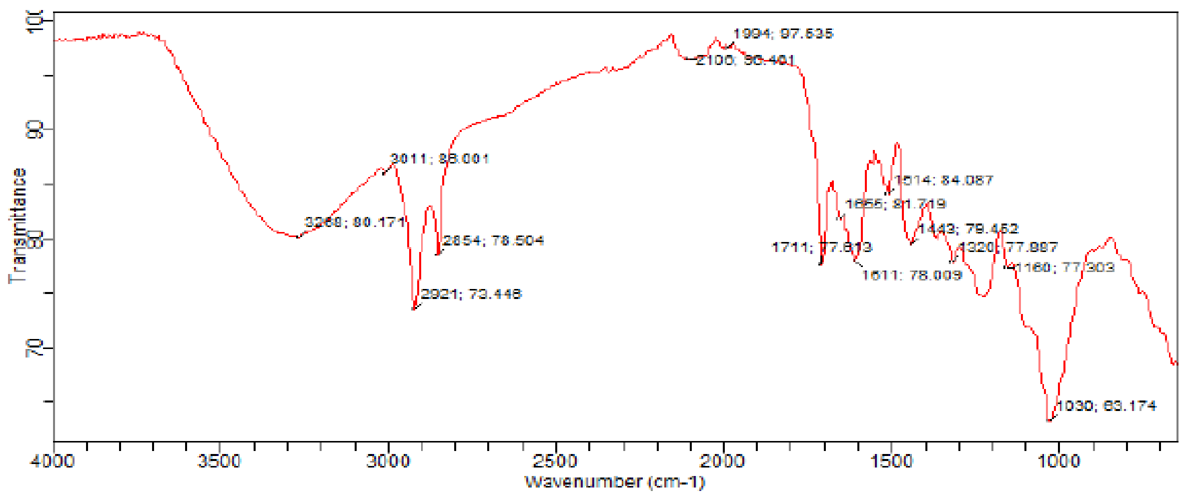

Figure 1: FTIR spectrum of *Diospyros mespiliformis* seeds (DMS) before adsorption

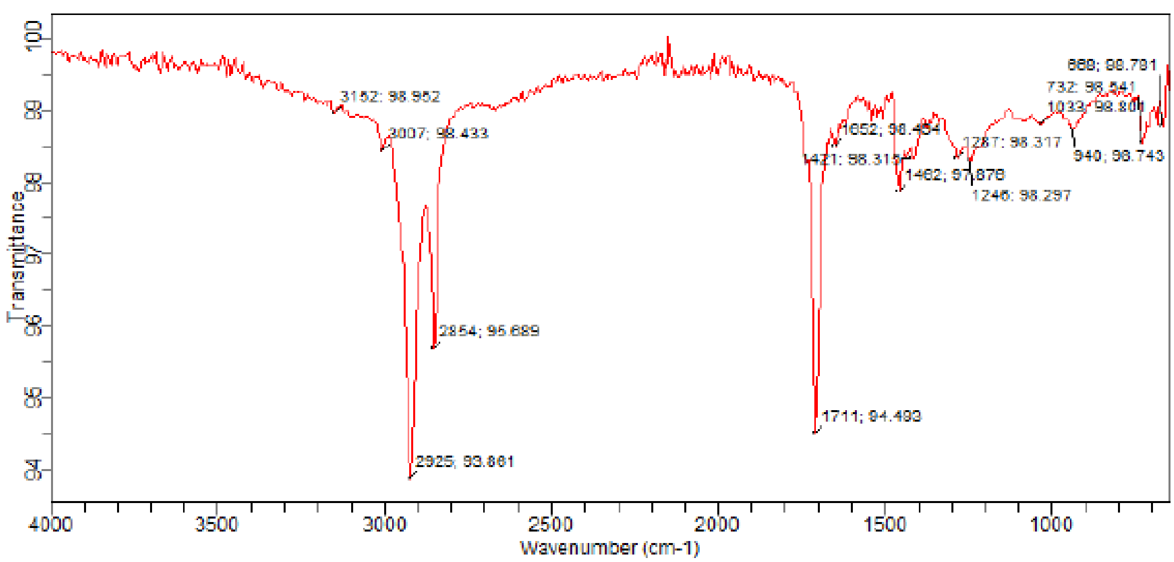

Figure 2: FTIR spectrum of *Diospyros mespiliformis* seeds (DMS) after adsorption

Figure 3, represents the spectrum of ZJS adsorbent before adsorption. The band for O – H appeared at 3294 cm^{-1} which was as a result of vibration of hydroxyl group in the adsorbent. The peak at 2919 cm^{-1} can be attributed to C - H vibration. Broad band at 1622 cm^{-1} was assigned to C = C stretching vibration. In the finger print region of the ZJS before adsorption, a sharp peak appeared at 1033 cm^{-1} which was attributed to C – O. However, spectrum of ZJS adsorbent after adsorption was shown in figure 4. In contrast with the spectrum of ZJS before adsorption, the peak at 1622 cm^{-1} (C = C) was change to 1745 cm^{-1} (C = O) as a consequence of the bond formed between the carbon atom of the adsorbent and oxygen atom of the dye molecule, thereby assigning the 1745 cm^{-1} band to C = O vibration. A new bond (C - X) formed between the dye and the adsorbent molecule was also assigned to the new band observed at 665 cm^{-1}. O - H and C - H band appeared at 3272 cm^{-1} and 2921 cm^{-1} respectively. Similar result was reported by (Somasekhara *et al*., 2017; Barun *et al*., 2017).

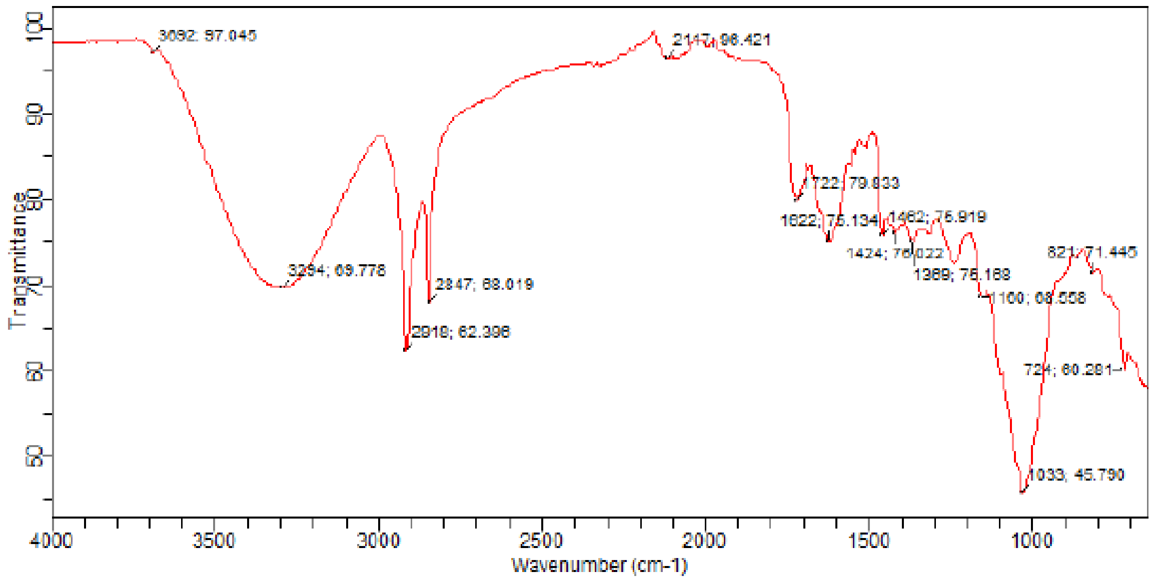

Figure 3: FTIR spectrum of *Ziziphus jujuba* seeds (ZJS) before adsorption

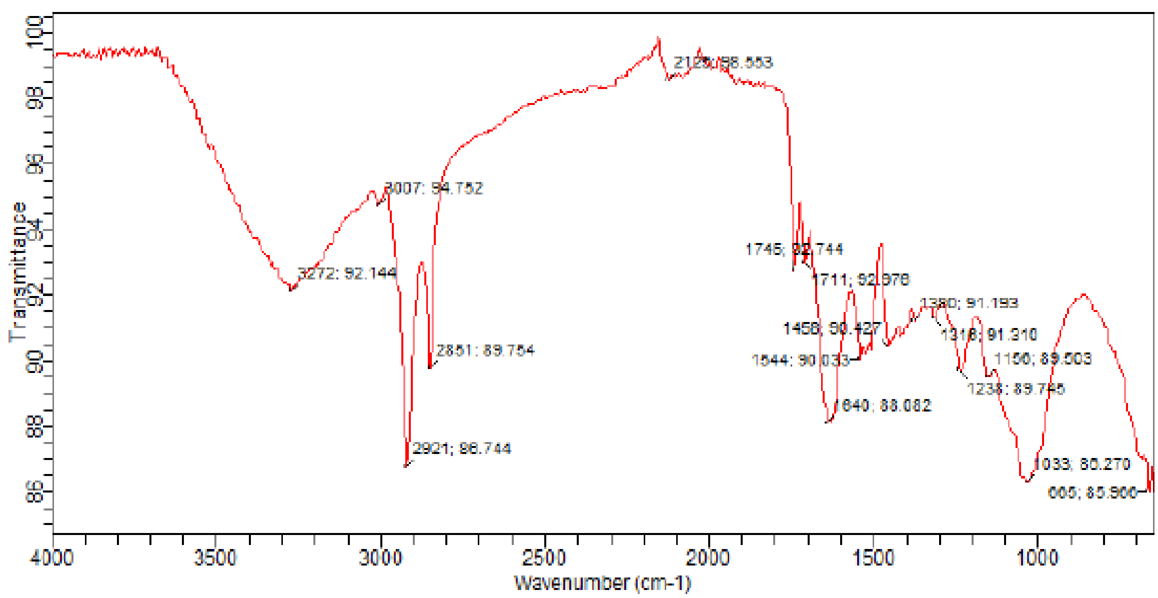

Figure 4: FTIR spectrum of *Ziziphus jujuba* seeds (ZJS) after adsorption

Figure 5, represent spectrum of BAS before adsorption. The band at 3275 cm^{-1} was a result of O - H stretching vibration, while the peak at 2916 cm^{-1} was attribute to C - H bond but the band observed at 1734 cm^{-1} was assigned to C = O from the adsorbent. However peak at 1629 cm^{-1} and 1033 cm^{-1} was as a result of C = O and C - O respectively. Figure 6, showing BAS spectrum after adsorption, in contrast with DMS spectrum before adsorption, new band found at 665 cm^{-1} was as a result of bond (C - X) formed between dye and adsorbent and a drastic improvement from 1734 cm^{-1} to 1707 cm^{-1} was also as a result of bonding between the dye and DMS adsorbent. The band for O – H observed at 3275 cm^{-1}, while that of C – H and C – O appeared at 2921 cm^{-1} and 1040 cm^{-1} respectively. Similar results were reported by (Somasekhara *et al*., 2017; Barun *et al*., 2017).

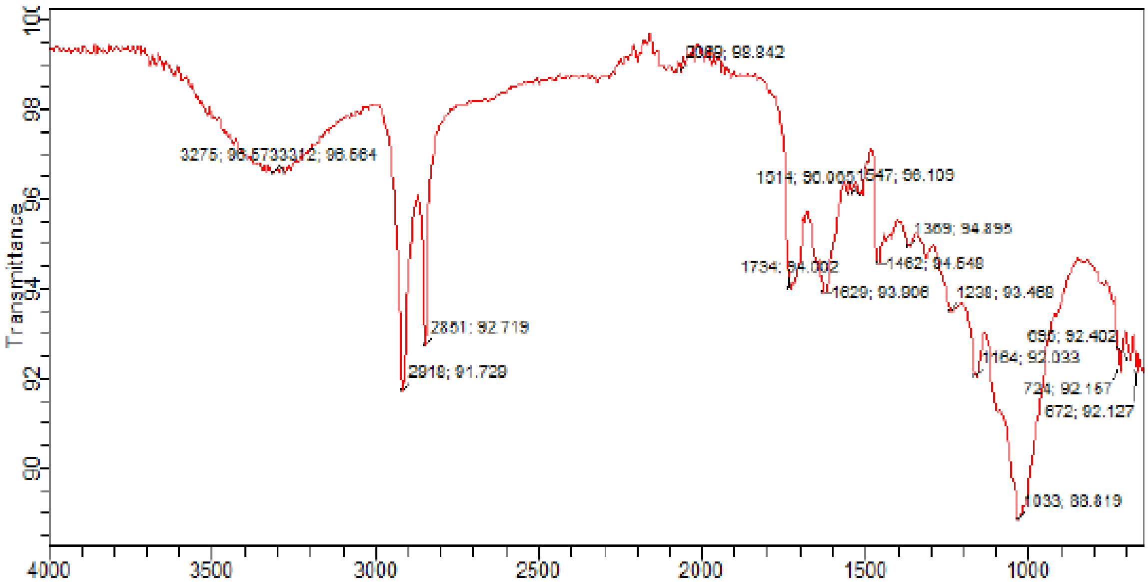

Figure 5: FTIR spectrum of *Balanites aegyptiacus* seeds (BAS) before adsorption

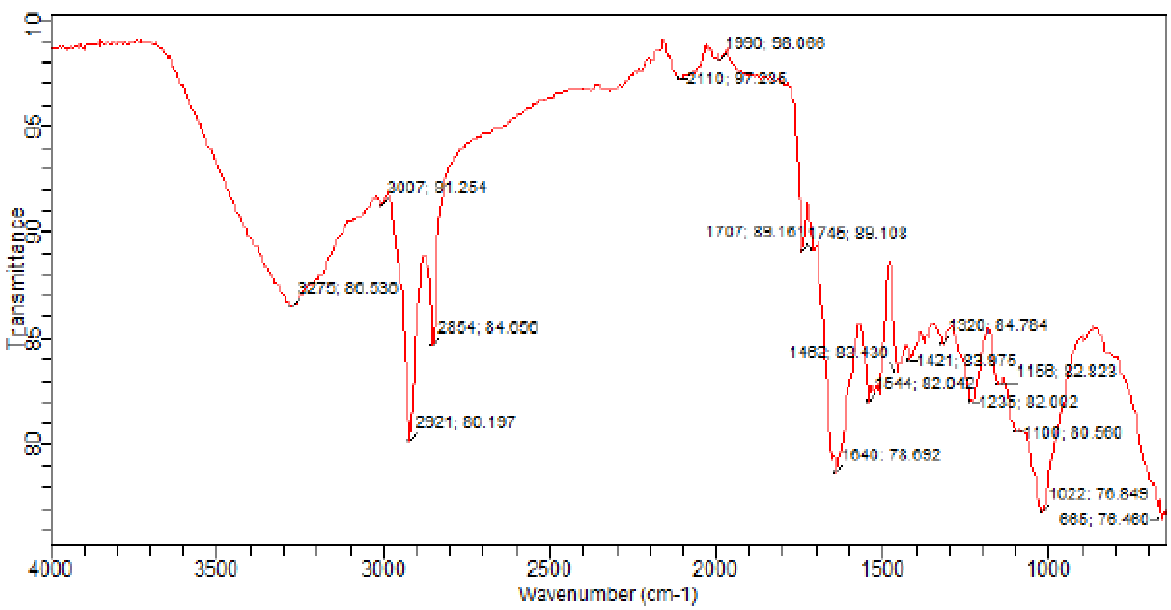

Figure 6: FTIR spectrum of *Balanites aegyptiacus* seeds (BAS) after adsorption

Effect of contact time

The contact time effect study provides useful information about the time taken to achieve equilibrium. The time taken to achieve equilibrium depends on the rate of mass transfer, which in turn depends on the conditions for contact between the solid and the liquid phase. Figure 7 represents percentage removal of ARB by BAS, DMS and ZJS at different time intervals. The final dye concentration did not differ significantly from the beginning of the adsorption process on BAS, DMS and ZJS adsorbent at approximately 60, 50 and 40 minutes respectively, which shows that equilibrium can be achieved at 60, 50 and 40 minutes of the consecutive adsorbents. This is mainly due to the saturation of the active site, which does not allow additional adsorption. Similar result was reported by (Aseel *et al*., 2017).

Effect of initial dye concentration

Figure 8 represent percentage removal of BAS, DMS and ZJS at different concentrations. However, with the increase in initial dye concentration (10-50 ppm), the percentage removal of BAS adsorbent decreases because the adsorbent has a limited number of active sites that become saturated after 10 ppm concentration, but the percentage removal of ARB by DMS and ZJS adsorbent increases with an increase in initial dye concentration this is because the adsorbent has more active site. However, with the increase in initial dye concentration from 10 to 50 ppm, the percentage removal of ZJS adsorbent increases sharply from 70.30 to 96.34 %, because the adsorbent has many active sites when compared to other adsorbents.

Similar result was reported by (Ayesha *et al*., 2016)

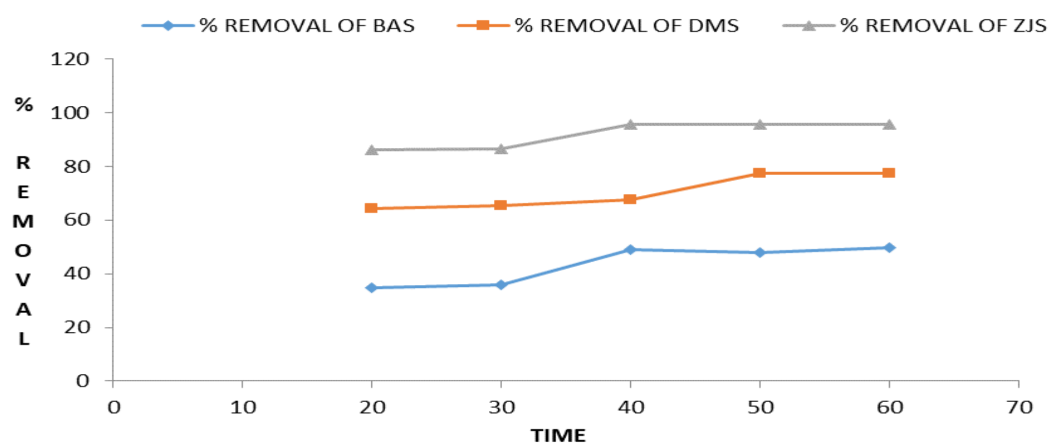

Figure 7: Effect of contact time on percentage removal of the adsorbents

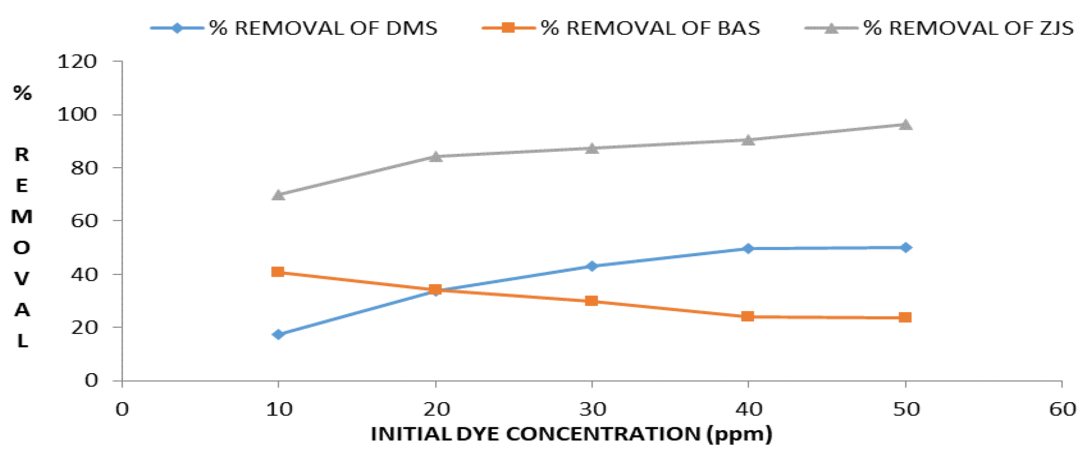

Figure 8: Effect of initial dye concentration on percentage removal of the adsorbents

The effect of pH

From figure 9 which represent percentage removal of BAS, DMS and ZJS at different pH values. BAS adsorbent was found to have optimal pH at 6.0 which had 60.66 % as a percentage removal, whereas DMS had optimum pH at 2.5 with a percentage removal of 69.21 % and ZJS adsorbent had optimum pH at 10 with a percentage removal of 50.79 %. The adsorption of ARD with BAS and DMS adsorbents was therefore favored in an acidic medium, while the adsorption of ZJS is favored in the basic medium. Similar result was reported by (Mahvi *et al*., 2012).

Effect of Adsorbent Dose (g)

Figure 10 described the effect of adsorbent dose of BAS, DMS, and ZJS on ARD removal. The removal of dyes increased with increased dosage of adsorbents. The result of this phenomenon was an increase in the surface area and the availability of more adsorbent sites. ZJS adsorbent with the highest percentage removal on the ARD shows that the adsorbent has more sites than BAS and DMS adsorbents that can interact with the dye. The BAS, DMS, and ZJS adsorbent maximum adsorption of the dye was 45.84 %, 61.74 %, and 97.38 %, respectively. However, the maximum adsorbent dosage was found to be 2 g for DMS and ZJS adsorbents, but it was found to be 2.5 g for BAS. Similar result was reported by (Hajira *et al*., 2008).

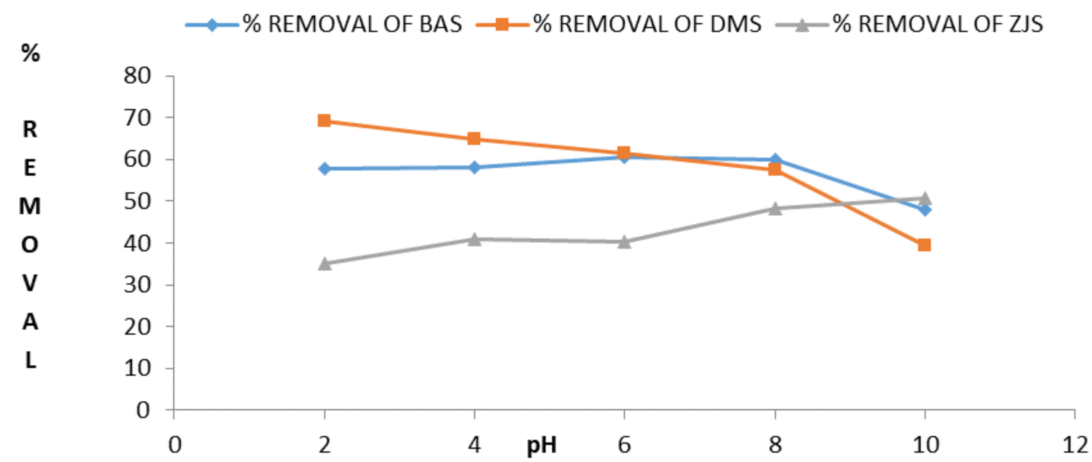

Figure 9: Effect of pH on percentage removal of the adsorbents

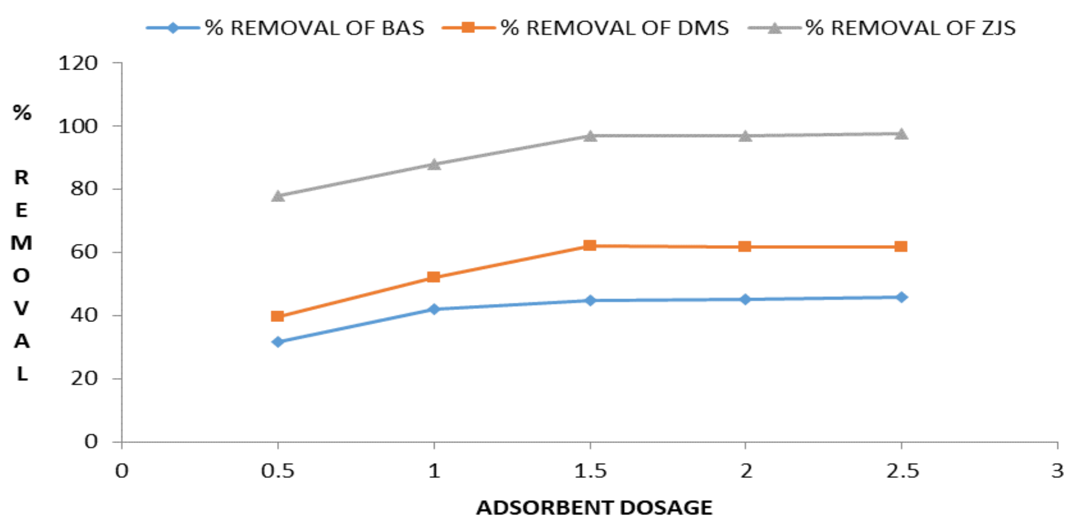

Figure 10: Effect of adsorbent dosage on percentage removal of the adsorbents

Effect of Change in Temperature of the System

Effect of temperature was shown in figure 11 in which results obtained indicate improved percentage reduction with increased temperature before the maximum temperature in which the absorption after the maximum temperature declines. This is because there would be a bond breakage between the dye and the adsorbents as the temperature rises after the maximum temperature. However, because of the less active site on the adsorbent, BAS adsorbent is favored at a higher temperature (60 °C). Whereas DMS has a higher percentage removal at a temperature of 40 °C and ZJS adsorbent has a maximum temperature of 50 °C, this is due to the presence of more active sites on DMS and ZJS adsorbents. Similar result has been published by (Krishna *et al*., 2014).

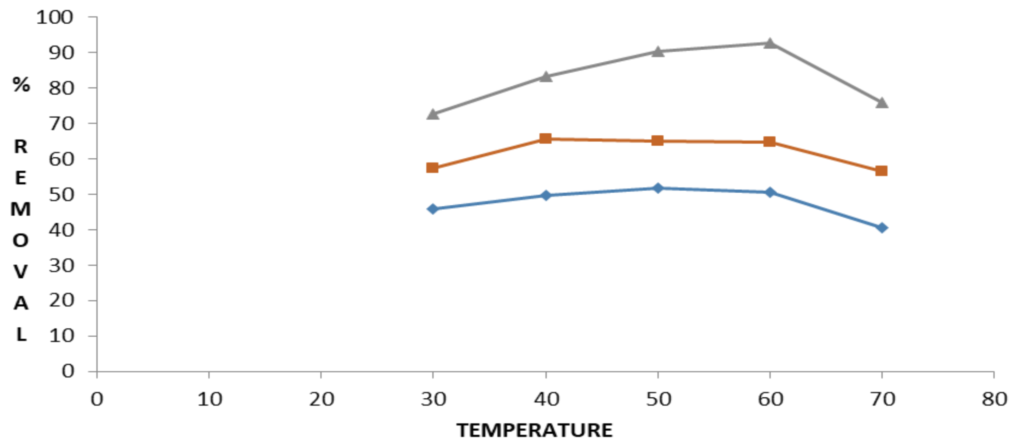

Figure 11: Effect of temperature on percentage removal of the adsorbents

Conclusion

Balanites aegyptiacus shell (BAS), *Diospyros mespiliformis* (DMS) and *Ziziphus jujuba* seeds (ZJS) have been found to be successful for use as low-cost and environmentally friendly adsorbents in removing azo-reactive dyes from aqueous solution. The maximum percentage removal efficiency of the dye molecule by BAS, DMS and ZJS were 33.12 %, 67.34 % and 92.37 % respectively. Results obtained indicated that BAS, DMS and ZJS could be used to remove Azo reactive dyes (ARD) from aqueous solution and the efficiency of the sorbents for the removal of ARD was in the order of ZJS > DMS > BAS.

References

Ari, R., Takeo, U., and Naoyuki, K. (2013). Color removal of reactive procion dyes by clay adsorbents. *Journal of Environmental Sciences*, 17: 270 – 278.

Aseel, M., Aljeboree, Abbas, N., Alshirifi, H., Ayad, F. Alkaim, A. (2017). Kinetics and equilibrium study for the adsorption of textile dyes on coconut shell activated carbon. *Journal of Arabian chemistry*, 10: 3381 – 3393.

Asgari, G., Ramavandi, B and Farjadfard, S (2013). Abatement of azo dye from wastewater using bimetal-chitosan. *Scientific World Journal*, 11: 476 - 486.

Ayesha, W., and Ali, M., A. (2016). Adsorption of textile dye onto modified immobilized activated alumina. *Journal of Arab Universities for Basic and Applied Sciences*, 20: 26 - 31.

Barun, K., N and Sunil, P. (2017). Effects of operational parameters on the removal of brilliant green dye from aqueous solutions by electrocoagulation. *Arabian Journal of Chemistry*. 10: 2961 – 2968.

Baseri, J. R., Palanisamy, P. N and Sivakumar, P (2012). Preparation and characterization of activated carbon from *Thevetia peruviana* for the removal of dyes from textile waste water. *Advances in Applied Science*, 3(1): 377 – 383.

Batool, S., Akib, A., Ahmad, M., Balkhair, K. S and Ashraf, M. A. (2014). Review Article Study of Modern Nano Enhanced Techniques for Removal of Dyes and Metals. *Journal of Nanomaterials*, 10: 865 – 885.

Chutima J. (2014). Removal of Reactive Dye by Adsorption over Chemical Pretreatment Coal Based Bottom Ash. *Journal of Advance Chemistry*, 9: 121 – 130

Dadvar, E., Kalantary, R. R., Panahi,H. A and Peyravi, M. (2017). Efficiency of polymeric membrane graphene oxide-TiO_2 for removal of azo dye. *Journal of Chemistry*, 11: 625 – 636.

Dogan,M., Abak, H and Alkan, M. (2008). Biosorption of methylene blue from aqueous solutions by hazelnut shells: equilibrium, parameters and isotherms. *Journal of Water, Air, and Soil Pollution*, 10(4): 141 – 15.

Gong, R. M., Ding, Y., Li, M., Yang, C. Liu, H. J and Sun, Y. Z (2005). Utilization of powdered peanut hull as biosorbent for removal of anionic dyes from aqueous solution. *Journal of Dyes and Pigments*, 64(3): 187 – 192.

Hajira, T., Muhammad, S and Qazi J. (2008). Colour removal of using modified carbon. *African Journal of Biotechnology*, 7(15): 2649 - 2655.

Hayrunnisa, N., Semra, C. and Azize, A. G (2017). Removing Trypan blue dye using nano-Zn modified *Luffa* sponge. *Journal of Molecular and Bimolecular*, 17(2): 2228 – 2238.

Krishna, L. S., Reddy, A. S., Zuhairi, W. Y., Taha, M. R and Reddy, A. V (2014). Indian *Jujuba* Seed Powder as an Eco-Friendly and a Low-Cost Biosorbent for Removal of Acid Blue 25 from Aqueous Solution. *Scientific World Journal*, 10: 184 - 195.

Mahvi, A. H., Shirmadi, M., Mesdaghinia, A., Nasseri, S and Nabizadeh, R (2012). Kinetics and Equilibrium Studies on Adsorption of Acid Red 18 (Azo-Dye) Using Multiwall Carbon Nanotubes (MWCNTs) from Aqueous Solution. *E-Journal of Chemistry*, 9(4): 2371 - 2383.

Mesut, T., Nihal, B., Cengiz, Y., H. (2009), Adsorption studies of aqueous basic dye solutions using sepiolite. *Journal of Desalination*, 24(9): 205 – 211.

Meroufel, B., Benali, O., Benyahia, M., Benmoussa, Y. and Zenasni, M., A. (2013).Adsorptive removal of anionic dye from aqueous solutions by Algerian kaolin: Characteristics, isotherm, kinetic and thermodynamic studies. *Journal of J. Mater. Environ. Sci.* 4(3): 482 - 491.

Nasuha, N., and Hameed, B. H. (2011). Adsorption of methylene blue from aqueous solution onto NaOH-modified rejected tea. *Chemical Engineering Journal*, 16(6): 783 – 786.

Panda, G. C., Das, S. K and Guha, A. K (2009). Jute stick powder as a potential biomass for the removal of congo red and rhodamine B from their aqueous solution. *Journal of Hazardous Materials*, 164(1): 374 – 379.

Patil, A. K and Shrivastava, V. S (2010). Alternanthera bettzichiana plant powder as low cost adsorbent for removal of Congo red from aqueous solution. *International Journal of ChemTech Research*, 2: 842 – 850.

Ponnusami, V., Vikram, S and Srivastava, S. N (2008). Guava (Psidium guajava) leaf powder novel adsorbent for removal of methylene blue from aqueous solutions. *Journal of Hazardous Materials*, 152(1): 276 – 286. .

Qu, J., Wu, R., He, H and Yu, Y. (2004). Removal of azo-dye Acid Red B (ARB) by adsorption and catalytic combustion using magnetic. *Journal of Applied Catalysis*, 48: 49 - 56.

Rajeswari, M., K., Revanth, T., Anirudh, A., and Prasad, B. (2017). Removal of Crystal Violet dye from aqueous solution using water hyacinth: Equilibrium, kinetics and thermodynamics study. *Journal of Resource-Efficient Technologies*, 10(3): 71 – 77

Saad, S., Isa, K., Mika, D and Bahari, R. (2010). Chemically modified sugarcane bagasse as a potentially low cost biosorbent for dye removal. *Journal of Desalination*, 264: 123 – 128.

Sharma, Y., C., Uma, and Upadhyay, S., N. (2011). An economically viable removal of methylene blue by adsorption on activated carbon prepared from rice husk. *The Canadian Journal of Chemical Engineering*, 89: 377 – 383.

Shelby, L., Foster, S. F., Estoque, K., Voecks, M., Rentz, N and Greenlee, L. F. (2019). Removal of synthetic azo dye using bimetallic nickel-iron nanoparticles. *Journal of NanoMaterials*, 9: 605 – 704.

Sivashankar, R., Sathya, A., B., Vasantharaj, K., Sivasubramanian, V. (2014). Magnetic composite an environmental super adsorbent for dye sequestration. *Journal of Environmental Nanotechnology, Monitoring and Management*, 10(2): 36 – 49.

Somasekhara, M., C., R.,and Nirmala, V. (2014). Bengal gram seed husk as an adsorbent for the removal of dyes from aqueous solutions – Column studies. *Arabian Journal of Chemistry*, 10: 765 – 772.

Somasekhara, M., C., R.,and Nirmala, V. (2017), Bengal gram seed husk as an adsorbent for the removal of dyes from aqueous solutions equilibrium studies. *Arabian Journal of Chemistry*, 10: 2406 – 2416.