Modified Pine Cone for Dye Pollutants Removal from Aqueous solution

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Abstract—Water pollution associated with discharge of dye effluents into the natural water resources is a major issue because of the adverse effects on human health and the ecosystem. During the past decade, the use of agricultural by-products as potential adsorbents in environmental remediation has received much attention due to their availability and exceptional properties. In this study, the ability of polyaniline (PANI) coated pine cone as a low-cost adsorbent on the removal of direct orange 26 (DO 26) dye from wastewater was investigated. The physicochemical properties of the adsorbent were studied using various characterization techniques such as Fourier transform infrared (FTIR), Scanning electron microscopy (SEM), X-ray diffraction (XRD) and Brunauer Emmett teller (BET). Batch equilibrium and kinetics adsorption experiments were performed to determine the efficiency of the adsorbents on dye removal and to establish the effect of various operational parameters on the adsorption process. Results showed that the removal of DO 26 dye occurs through the surface of the adsorbent this was confirmed by characterization. It was observed that percentage dye removal decrease with increasing solution pH. The results also indicate that adsorption efficiency increased with increase in temperature which predicts that the adsorption process is endothermic. Maximum percentage dye removal was found to be 99.98% at pH 4.17, adsorbent dosage 0.1g and initial dye concentration 50 mg/L. Kinetic studies revealed that equilibrium was reached within 90, 180 and 240 min of interaction for initial dye concentrations of 50 mg/L, 100 mg/L and 150 mg/L respectively. It can be concluded that PANI coated on pine cones can be used as an effective adsorbent for removal of dye from aqueous solutions.

Keywords— Adsorption, Agricultural waste, Dye removal, Equilibrium

I. INTRODUCTION

Due to rapidly increasing population growth, climate change, industrial activities and agricultural use the availability of fresh water has deteriorated drastically in the whole worldwide. Industrial waste discharges into natural water resources have been identified as a major source of water pollution. of toxic substances in water significantly affects the quality of water and highly contaminates underground water [40].

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Moreover, the released of dye-bearing effluents into natural water resources is doing unimaginable harm to the The presence In particular, there has been a growing interest from environmentalists on the presence of dyes in the water/wastewaters originating from industries such as textile, paper, plastic, tannery and paints [6]. environment, threatening the health of people and also increasing the cost of treatment [29]. This is because dyes are of synthetic origin and possess complex aromatic molecular structure, thus which making them more stable and difficult to biodegrade [25].
Dyes are soluble, coloured organic compounds with structures containing aryl ring which have delocalized electron systems [12]. Moreover, dyes have functional groups that are capable of forming covalent bonds between carbon atoms of improves wash- fastness, hence making them very difficult to biodegrade. As a result, they pass through the purification plant without further degradation and are released into the environment [33]. However, wastewater generated from those mentioned industries which contains dyes is being discharged into municipal streamlines and river constitutes the major sources of water pollution [1]. Consequently, the presence of color in water beyond the maximum limits recommended by regulatory bodies greatly affects the water quality [41], inhibits sunlight penetration into the stream and also reduces photosynthetic action [34]. In order to comply with environmental protection laws as well as minimize the aforementioned challenges, there is an urgent need to reduce dyes or completely remove them from wastewater using appropriate and efficient technology in an economical manner [10].

Furthermore, several treatment methods for dyes removal from wastewater have been developed such as coagulation/flocculation [23], reverse osmosis [18], membrane filtration , electrolysis, advanced oxidation, photocatalysis, ion exchange and adsorption [1, 2, 9, 27, 30]. However, some of these processes have been found to have many disadvantages such as high energy demand [11], formation of flocs together with dye stuff, large amount of sludge produced, and uneconomical. In fact, some are not effective at all for dye removal and they also have short half-life [33]. Among these methods, adsorption process has been identified as the most economical feasible and effective method for removal of dyes due to its wide range of applications, simplicity and low cost of operation [21]. In addition to the mentioned advantages, adsorption is also able to recover adsorbent for reuse and to prevent creation of secondary problems with dye-bearing sludge which is very difficult to dispose [14].

Since the performance of any adsorption process depends on the chemistry of the adsorbent and adsorbate, a variety of adsorption media have been developed and tested in the removal of dyes from aqueous solutions. These include commercially activated carbon (CAC), activated alumina, silica, clays and zeolites [16], to mention a few. However, most of these adsorbents have been linked with many limitations such as low capacity for dyes, slow reaction kinetics, high costs and difficulties in separation from wastewater [17, 18, 36]. Because cost is a very crucial pre-requisite of any adsorption media, lately many researchers have directed their interest in the usage of agricultural wastes such as almond husk, wheat bran, rice husk, pine cone wood and many more as the low cost adsorbents for dye pollutants removal from wastewater [16, 33, 36, 40]. As opposed to the high cost of activated carbon and other adsorbents, agricultural wastes are preferred for the adsorption applications because they are abundant in nature, readily available and environmentally friendly.

Up to date very little information exists in literature on the application of pine cone as a low cost adsorbent for direct orange 26 dye removal. Pine cones are agricultural by-product found in many parts of the world including South Africa. The scales of the mature cone are composed of epidermal and sclerenchyma cells which contain cellulose, hemicelluloses, lignin, rosin and tannins in their cell walls [37]. However, for better utilization of this inexpensive material, chemical modification using conducting polymer has been practiced by many researchers [3]. When chemically modified, the surface properties may be improved due to the anchoring of different functional groups hence improving their adsorption performances [46]. Recently, the use of conducting polymers as modifying agents have been a center of attention to many researchers due to their attractive properties that plays a key role in adsorption of a targeted pollutants [12]. Among the conducting polymers, polyaniline (PANI) has received a great deal of attention in recent years, due to its ease of synthesis, low cost, excellent environmental stability, unique physicochemical behavior towards the targeted contaminants [19].

Therefore, this work aimed at studying the adsorption behavior of modified pine cones for the removal of direct orange 26 (DO 26) dye from aqueous solution. The influence of process variables such as adsorbent dosage, initial pH solution, temperature and initial dye concentration will be explore under batch mode to understand adsorption mechanism modified pine cone in removal of dye pollutants. Kinetic studies were performed to understand adsorption rate and mechanism of the process.

II. MATERIALS AND METHODS

A. Materials

Raw pine cones were obtained from South Africa-Pretoria. Aniline monomer ($C_6H_5NH_2$), ammonium persulfate $[(NH_4)_2S_2O_8]$ for use as an oxidant for initiation of polymerization reaction, hydrochloric acid 32% (HCl) were purchased from Sigma-Aldrich, Germany. Direct orange 26 (DO 26) dye (chemical formula $C_{33}H_{22}N_6Na_2O_9S_2$, double azo class and molecular weight 756.67g/mol) was supplied by Merck chemicals (Pty) Ltd, South Africa and was used as received. All other reagents of analytical reagent (AR) grade used in this work were obtained from Sigma-Aldrich, Germany and were used without any further purification.

B. Preparation of synthetic dye wastewater

The dye stock solution was prepared by dissolving 1000 mg of DO 26 dye powder in 1000 mL of deionized water which makes up to a concentration of 1000 mg/L. All the experimental dye solutions were obtained by diluting the stock solution in accurate proportions as required.

C. Preparation of polyaniline coated pine cone

The synthesis of polyaniline (PANI) coated pine cones used in this work was performed via in-situ chemical oxidative polymerization technique [28]. 10 ml of concentrated hydrochloric acid 32% was added into a 250 ml glass beaker with 80 ml of deionized (DI) water and then it was stirred for 10 minutes using magnetic stirrer at 300 rpm. 2 ml of aniline monomer was injected into the mixture and also allowed to stir for 5 minutes in order to obtain a homogeneous mixture. The collected pine cones were washed, dried and milled using ball mill then 10g of pine cone powder was dispersed into a mixture under continuous stirring. Thereafter, ammonium persulfate (APS) solution was prepared by dissolving 3.064 g of APS into a 10 ml of deionized water then it was added drop wise to the above suspension to properly initiate the polymerization. The whole reaction mixture was further stirred in a magnetic stirrer for a period of 24 hrs to allow polymerization to take place completely. Finally, the suspension was filtered and washed well with acetone to remove the unreacted chemicals. The washed powder was dried in the oven at $60^{O}C$ overnight and sieved to achieve a specific particle size. The obtained final product was labeled as PANI-PC.

D. Characterization of PANI-PC

The physico-chemical properties of the modified pine cone adsorbent were studied by conducting the characterization analysis on PANI-PC before and after adsorption process. The evaluation of morphology of the adsorbent was tested using Scanning electron microscopy (SEM) instrument. Meanwhile Fourier transform infared (FTIR) and Brunauer Emmett teller (BET) instruments were used to study the functional groups and surface properties respectively.

E. Adsorption studies

Batch equilibrium experiment was carried out to study the effectiveness of polyaniline modified pine cone (PANI-PC) adsorbent on the removal of DO 26 dye and also to investigate the variation of process parameters such as adsorbent mass, initial pH solution, initial dye concentration and temperature towards the adsorption process. A fixed known amount of the adsorbent was placed in contact with dye solution samples of initial DO-26 concentration ranging between (50-400 mg/L), solution pH (3-10) and temperature (25 - 45^{0}C) in a 100 mL plastic bottle. The prepared samples were placed in a thermostatic water bath shaker operated at 160 rpm for 24 hrs. Afterwards, the samples were filtered through a 0.45µm syringe filter in order to analyse dye residual concentration in the filtrate. The amount of dye remaining was analysed using UV-spectrophotometer (Shimadzu UV-1800) at a wavelength of 494 nm. The equilibrium adsorption capacity and efficiency were calculated using equation 1 and 2 respectively:

$$q_e = \frac{c_o - c_e}{m} v \quad (1)$$

$$\%removal = \frac{c_o - c_e}{c_o} x100 \quad (2)$$

where, q_e is the adsorption capacity (mg/g), C_o and C_e are the initial and equilibrium concentration (mg/L) of dye, respectively. *V* is the volume (L) of solution and *M* is the weight (g) of adsorbent.

Kinetic adsorption study was conducted in a 2L plastic beaker containing 1000 mL of dye solution with 2.0g of PANI-PC adsorbent. The solution with different initial dye concentration (50 mg/L, 100 mg/L and 150 mg/l) was agitated using overhead stirrer at constant speed of 160 rpm under room temperature of 25±1^{0}C. At predetermined time intervals, 5 mL sample was withdrawn from a solution using a syringe, it was filtered and analyzed for remaining dye concentration. The amount of DO 26 dye adsorbed onto modified pine cones at time (t) was evaluated using below equation:

$$q_t = \frac{C_o - C_t}{m} V \quad (3)$$

where q_t (mg/g) is the time-dependent amount of dye adsorbed per unit mass of adsorbent at time *t*, C_t is the final concentration of dye at any time t (mg/L).

III. RESULTS AND DISCUSSION

A. Characterization of PANI-PC adsorbent

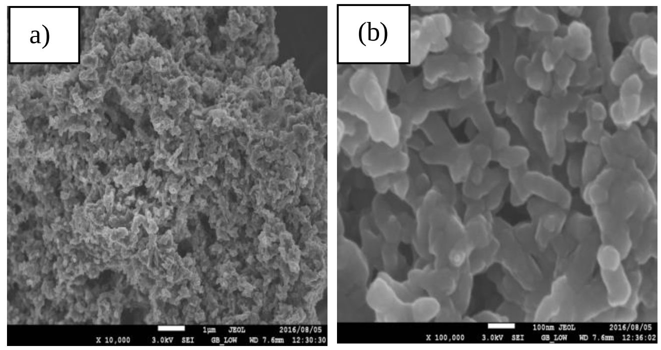

Fig 1: SEM images of PANI-PC (a) before adsorption and (b) after adsorption of DO 26 dye from synthetic water.

Scanning Electron Micrograph (SEM) is the mainly used method to analyze the surface morphology and physical properties of the adsorbent. Fig. 1a) and b) show SEM images of PANI modified pine cone before and after adsorption, respectively. It can be seen in image a) that the availability of pores and internal surface is more clearer than image b) which can be an evidence that adsorption did occur on the surface of adsorbent that is why in the image after adsorption there is a noticeable coverage of pores by the adsorbed DO 26 dye. In addition, EDS analysis (not presented) indicated adsorption of dye by showing high amount of sodium (Na) which is the main constituent of DO 26 DYE.

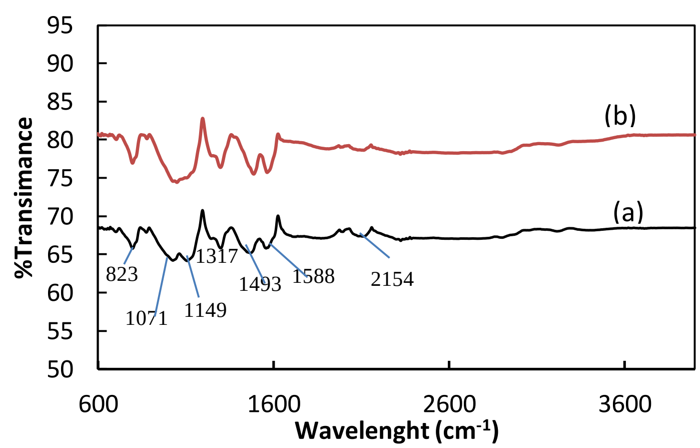

Fig 2: FTIR spectra of PANI-PC (a) before adsorption and (b) after adsorption.

The dye uptake depends upon porosity as well as chemical reactivity of functional groups that are present in the adsorbent. Therefore, a better understanding of functional groups which are involved in the adsorbent and also in dye molecule is necessary. Fig. 2 represents the FTIR spectra of PANI-PC before and after adsorption. The main peaks are observed at 2154 cm^{-1}, 1588cm^{-1}, 1493 cm^{-1}, 1317cm^{-1}, 1149 cm^{-1}, 1071 cm^{-1} and 823 cm^{-1}. These peaks are characteristics peak of both lignocellulose (raw pine cones) and PANI that was coated on the surface of pine cone. The bands at 1588 cm^{-1} and 1493 cm^{-1} representing carbonyl group stretching (amide) and N-H bonding accordingly. While the bands at 1317 cm^{-1} and 1149 cm^{-1} reflect the C-H bends and C-O stretching, respectively. The peaks between 1071 cm^{-1} and 823cm^{-1} may be a confirmation of –C-C and C-N stretching respectively [23]. It can be seen from spectra of PANI-PC loaded with dye molecule that there is no much change in the peaks except the bands at 1151 cm^{-1} and 1550 cm^{-1} which show high intensity than the peaks before adsorption; this might be due to the dye uptake that occurs on the surface of the adsorbent.

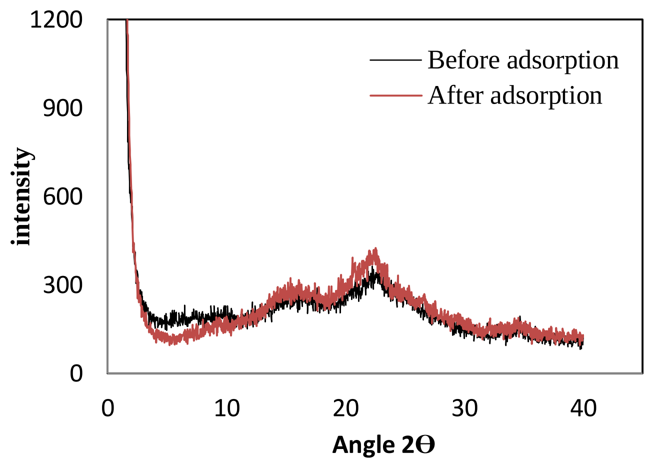

Fig 4: X-ray diffraction (XRD) analysis of PANI-PC before and after DO 26 adsorption.

In order to examine the crystalline structure of PANI-PC before and after adsorption of DO 26 dye, the X-ray diffraction was performed on the samples. The XRD plot is depicted in Fig. 4. It can be observed that diffraction peaks appearing at 2Θ values at 16.9° and 21.29° are attributed to the lignocellulosic structure of pine cones [9]. On the other hand, diffraction peak that normally appear at 25.20° which is the characteristic peak of amorphous PANI is absent, the reason for its disappearance is unknown. In addition, after adsorption there is only a slight change in the peak at 21.29°, which might be a confirmation of dye adsorption on the surface of adsorbent.

B. Equilibrium Studies

1) Effect of solution pH

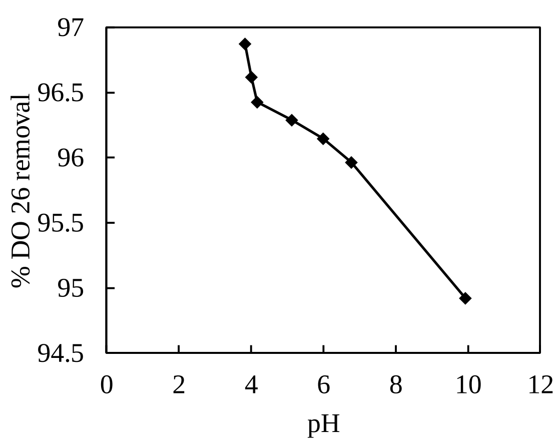

Fig 4: Effect of initial pH on DO 26 adsorption onto polyaniline pine cone. (Initial conc. 50 mg/L, Temp. 298K, adsorbent dose 0.1 g)

The adsorption of dye is highly dependent on the pH of solution as it determines whether dissociation and ionization of the dye molecule will take place through the surface of the adsorbent. Fig 4 displays the effect of pH on the removal of DO 26 onto PANI-PC adsorbent that was varied from pH 3- 10. The results reveal that dye percentage removal gradually decreases with increasing solution pH, this could be attributed by the fact that at lower pH the adsorbent surface is highly positively charged due to the protonated amino groups of PANI which allows electrostatic attraction to develop between positively charged adsorbent and negatively charged sulfonate groups of anionic dye DO 26 [3,9].The results also indicate that more than 97% dye removal was attained at pH = 3.83, therefore the optimal pH for this study was recorded as pH = 3.38.

2) Adsorbent Dosage

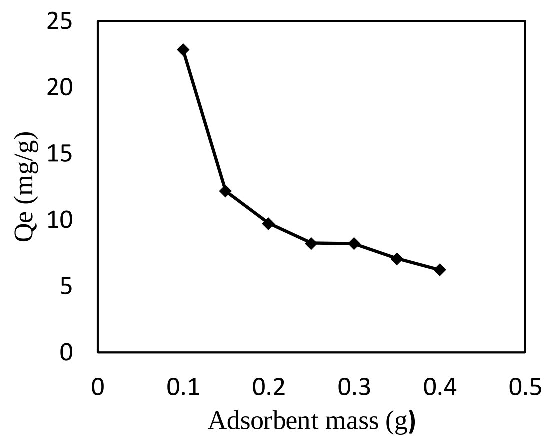

Fig 5: Effect of adsorbent dosage on the removal of DO 26 dye onto PANI-PC adsorbent. (Initial conc. 50 mg/L, Temp. 298K, pH = 3.83)

The influence of adsorbent mass on the remediation efficiency of the direct dye in aqueous solution was investigated under batch mode at 298 K, with sorbent dose between 0.1 - 0.4 g and an initial pH 3.83 as shown in Fig. 5. It is evident that an increase in the sorbent mass from 0.1g to 0.4 g resulted to a decrease in dye uptake from 22.9 mg/g to 6.21 mg/g. However, a reverse trend was observed in the removal efficiency which increases from 91% to 99%. This is due to the fact with large amount of adsorbent dosage there is high number of unsaturated adsorption sites left unoccupied with dye molecule during the adsorption process which causes adsorption capacity to decrease with increasing the dose of the adsorbent [31]. Meanwhile, at high sorbent dosage the number of available sorption site at the adsorbent surface will increase by increasing the adsorbent mass resulting in the increase in dye percentage removal from solution [33]. Similar behavior regarding adsorption of direct orange 26 on rice husk was observed by Safa and Bhatti, (2011b).

3) Effect of temperature

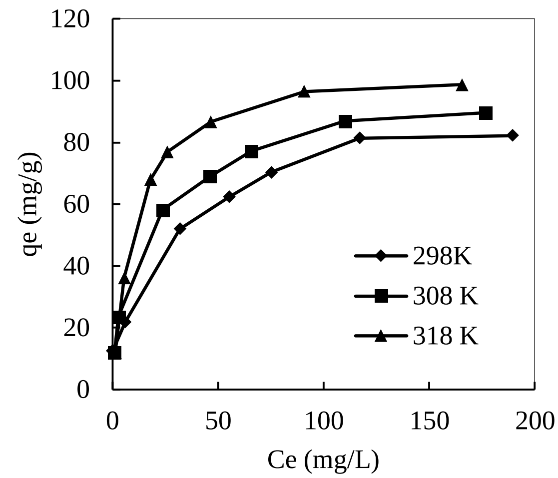

Fig. 6: Effect of temperature on DO26 removal onto PANI-PC adsorbent with solution volume = 50ml, adsorbent mass = 0.1g and initial pH solution = 3.83.

Temperature is an important parameter for any adsorption process as it indicates the nature of the adsorption whether it is an endothermic or exothermic process. The effect of temperature was carried out at different temperature (25, 35 and 45^0C) as it is illustrated in Fig 6. The results showed that the adsorption capacity of DO 26 dye increase with increasing with system temperature suggesting that the process was endothermic in nature. This increase in dye removal may be attributed to increase in rate of diffusion of the dye molecules across the external boundary layer and into the internal pores of the adsorbent particles [9]. Similar results were reported for various dye adsorptions by other biosorbents [18, 25, 29, 38, and 40].

C. Adsorption Kinetic Studies

1. Effect of contact time

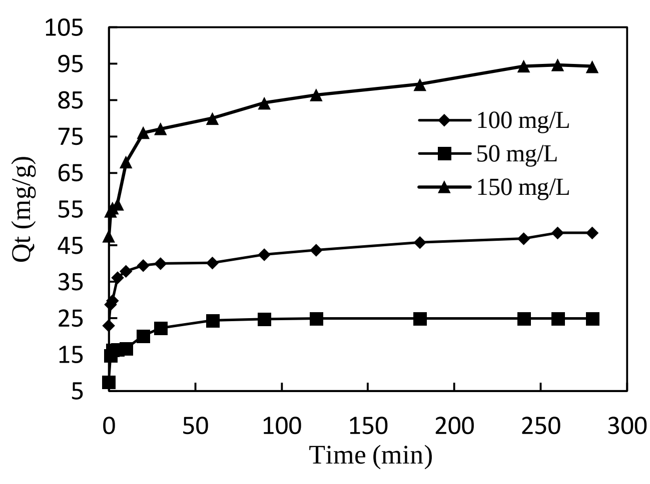

Fig 7: Effects of contact time and initial dye concentration on DO26 adsorption onto PANI-PC (dosage = 2.0g/L, agitation speed = 160 rpm, temp = 298 k and pH = 3.83)

The effect of contact time on the adsorption of DO 26 dye was explored under different initial DO 26 concentrations (50 to 150 mg/L) and results are presented in Fig 7. It was found that the amount of dye adsorbed increased with increasing initial concentration. Further, it was also revealed that equilibrium was attained within 90 min, 120 min and 180 min when concentration was from 50 mg/L, 100 mg/L and 150 mg/L, respectively. This can be explained by the fact that initial concentration provides the driving force to overcome the resistance to the mass transfer [35].

IV. CONCLUSION

The work revealed that utilization of polyaniline coated pine cones as adsorbent for remediation of anionic DO 26 dye from aqueous solution is viable. Results also revealed that the magnitude of adsorption was primarily dependent on the solution initial pH and the sorbent dosage. In particular, adsorption performance was favored at pH 3.83. This was justified by the fact that at low pH solution the positive charge at the solution-interface will increase allowing the surface of adsorbent to be positively charged which results in an increase in anionic DO 26 dye adsorption. Meanwhile, the maximum adsorption capacity was found to be 22.9 mg/g with 0.1 g, 50 mg/L at 25^0C. Based on the findings reported in this study, it can be concluded that PANI modified pine cone can be considered as a low-cost adsorbent which is environmentally benign for the effective removal of dyes from wastewater. Although in this work, PANI modified pine cone was tested for removal of dye using only synthetic dye solution. According to the study conducted by other researchers it is proven that modified pine cones can be used as an adsorbent for removal of contaminants from industrial effluents. Therefore, it is assumed that this bio-sorbent can potentially be used for real wastewater containing dyes pollutants. In order to confirm such assumption, similar study on removal of dye contaminants using a real wastewater shall be investigated.

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REFERENCES

[1] ADAK, A., BANDYOPADHYAY, M. & PAL, A. 2006. Fixed bed column study for the removal of crystal violet (C. I. Basic Violet 3) dye from aquatic environment by surfactant-modified alumina. Dyes and Pigments, 69:245-251.

[2] AL-JABARI, M. 2016. Kinetic models for adsorption on mineral particles comparison between Langmuir kinetics and mass transfer. Environmental Technology & Innovation, 6, 27-37.

[3] BALLAV, N., DEBNATH, S., PILLAY, K. & MAITY, A. 2015. Efficient removal of Reactive Black from aqueous solution using polyaniline coated ligno-cellulose composite as a potential adsorbent. Journal of Molecular Liquids, 209, 387-396.

[4] Cao, W., Dang, Z., Qiu Zhou, X., Yun Yi, X., Xiao Wu, P., Wu Zhu, N. *et al.* Removal of Sulfate from Aqueous Solution using Modified Rice Straw : Preparation, Characterization and Adsorption Performance. Carbohydrate Polymers BS (2011) 571-577

[5] CHAARI, I., MOUSSI, B. & JAMOUSSI, F. 2015. Interactions of the dye, C.I. direct orange 34 with natural clay. Journal of Alloys and Compounds, 647, 720-727.

[6] CHARUMATHI, D. & DAS, N. 2012. Packed bed column studies for the removal of synthetic dyes from textile wastewater using immobilised dead C. tropicalis. Desalination, 285:22–30.

[7] CHENG, Z., ZHANG, L., GUO, X., JIANG, X. & LI, T. 2015. Adsorption behavior of direct red 80 and congo red onto activated carbon/surfactant: Process optimization, kinetics and equilibrium. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 137, 1126-1143.

[8] DALVAND, A., NABIZADEH, R., REZA GANJALI, M., KHOOBI, M., NAZMARA, S. & HOSSEIN MAHVI, A. 2016. Modeling of Reactive Blue 19 azo dye removal from colored textile wastewater using L-arginine-functionalized Fe3O4 nanoparticles: Optimization, reusability, kinetic and equilibrium studies. Journal of Magnetism and Magnetic Materials, 404, 179-189.

[9] DAWOOD, S. & SEN, T. K. 2012. Removal of anionic dye Congo red from aqueous solution by raw pine and acid-treated pine cone powder as adsorbent: Equilibrium, thermodynamic, kinetics, mechanism and process design. Water Research, 46:1933-1 946.

[10] DEBNATH, S., BALLAV, N., MAITY, A. & PILLAY, K. 2015. Development of a polyaniline-lignocellulose composite for optimal adsorption of Congo red. International Journal of Biological Macromolecules, 75:199-209.

[11] EMENIKE, P.P., OMOLE, D.O., NBENE, B.U. & TENEBE, I.T. 2016. Potentiality of agricultural adsorbent for the sequestering of metal ions from wastewater. Global Journal of Environmental Science and Management, 2(4):411-442

[12] ETIM, U. J., UMOREN, S. A. & EDUOK, U.M. 2012. Coconut coir dust as a low cost adsorbent for the removal of cationic dye from aqueous solution. Journal of Saudi Chemical Society, 143:1945-2105.

[13] FALIL, F., ALLAM, F., GOURICH, B., VIAL, C. & AUDONNET, F. 2016. Adsorption of Astrazon Orange G onto natural Moroccan phosphate rock: A mechanistic study. Journal of Environmental Chemical Engineering, 4, 2556-2564.

[14] FERNANDEZ, M.E., NUNELL, G. V., BONELLI, P. R. & CUKIERMAN, A. L. 2010. Effectiveness of Cupressus sempervirens cones as biosorbent for the removal of basic dyes from aqueous solutions in batch and dynamic modes. Bioresource Technology, 101:9500-9507.

[15] FOO, K. Y. & HAMEED, B. H. 2012. Preparation, characterization and evaluation of adsorptive properties of orange peel based activated carbon via microwave induced K2CO3 activation. Bioresource Technology, 104, 679-686.

[16] FUNGARO, D. A., YAMAURA M. & CARVALHO, T. E. M. 2011. Adsorption of anionic dyes from aqueous solution on zeolite from fly ash-iron oxide magnetic nanocomposite. Journal of Atomic and Molecular Sciences, 2:305-316.

[17] GAUTAM, R. K., MUDHOO, A., LOFRANO, G. & CHATTOPADHYAYA, M. C. 2014. Biomass-derived biosorbents for metal ions sequestration: Adsorbent modification and activation methods and adsorbent regeneration. Journal of Environmental Chemical Engineering, 2:239–259.

[18] GUPTA, V. K. & SUHAS. 2009. Application of low-cost adsorbents for dye removal – A review. Journal of Environmental Management 90:2313–2342.

[19] GUSAIN, D., DUBEY, S., UPADHYAY, S. N., WENG, C. H. & SHARMA, Y. C. 2016. Studies on optimization of removal of orange G from aqueous solutions by a novel nano adsorbent, nano zirconia. Journal of Industrial and Engineering Chemistry, 33, 42-50.

[20] INYINBOR, A. A., ADEKOLA, F. A. & OLATUNJI, G. A. 2016. Kinetics, isotherms and thermodynamic modeling of liquid phase adsorption of Rhodamine B dye onto Raphia hookerie fruit epicarp. Water Resources and Industry, 15, 14-27.

[21] JANAKI, V., OH, B.-T., SHANTHI, K., LEE, K.-J., RAMASAMY, A. K. & KAMALA-KANNAN, S. 2012. Polyaniline/chitosan composite: An eco-friendly polymer for enhanced removal of dyes from aqueous solution. Synthetic Metals, 162, 974-980.

[22] LOFRANO, G., MERIÇ, S., ZENGIN, G. E. & ORHON, D. 2013. Chemical and biological treatment technologies for leather tannery chemicals and wastewaters: A review. Science of The Total Environment, 461–462, 265-281.

[23] MAHMOODI, N. M., HAYAT, B., ARAMI, M. & LAN, C. 2011. Adsorption of textile dyes on Pine Cone from colored wastewater: Kinetic, equilibrium and thermodynamic studies. Desalination, 268:117–125.

[24] MAHMOUD, M. E., NABIL, G. M., EL-MALLAH, N. M., BASSIOUNY, H. I., KUMAR, S. & ABDEL-FATTAH, T. M. 2016. Kinetics, isotherm, and thermodynamic studies of the adsorption of reactive red 195 A dye from water by modified Switchgrass Biochar adsorbent. Journal of Industrial and Engineering Chemistry, 37, 156-167.

[25] MOHAMMED, M. A., SHITU, A. & IBRAHIM, A. 2014. Removal of Methylene Blue Using Low Cost Adsorbent: A Review. Research Journal of Chemical Sciences, 4:91-102. J.A., Maree, J.P. and Adlem, C.J.L. 1991 Removal of sulfate from mine water. In: Proceedings of the ARD in Pyrite Environments, Lisbon, Portugal, 16-19 September 1990. 211-221.

[26] MOUSSAVI, G. & KHOSRAVI, R. 2011. The removal of cationic dyes from aqueous solutions by adsorption onto pistachio hull waste. Chemical Engineering Research and Design, 89, 2182-2189.

[27] MUNAGAPATI, V. S. & KIM, D.-S. 2016. Adsorption of anionic azo dye Congo Red from aqueous solution by Cationic Modified Orange Peel Powder. Journal of Molecular Liquids, 220, 540-548.

[28] PAHOVNIK, D., ŽAGAR, E., KOGEJ, K., VOHLÍDAL, J. & ŽIGON, M. 2013. Polyaniline nanostructures prepared in acidic aqueous solutions of ionic liquids acting as soft templates. European Polymer Journal, 49, 1381-1390.

[29] PAVAN, F. A., MAZZOCATO, A. C. & GUSHIKEM, Y. 2008. Removal of methylene blue dye from aqueous solutions by adsorption using yellow passion fruit peel as adsorbent. Bioresource Technology, 99:3162–3165.

[30] PIRKARAMI, A., OLYA, M.E. & YOUSEFI LIMAEE, N. 2013. Decolorization of azo dyes by photo electro adsorption process using polyaniline coated electrode. Progress in Organic Coatings, 76(4):682-688.

[31] RAGHUNATH, S., ANAND, K., GENGAN, R. M., NAYUNIGARI, M. K. & MAITY, A. 2016. Sorption isotherms, kinetic and optimization process of amino acid proline based polymer nanocomposite for the removal of selected textile dyes from industrial wastewater. Journal of Photochemistry and Photobiology B: Biology, 165, 189-201.

[32] RANGABHASHIYAM, S., ANU, N. & SELVARAJU, N. 2013. Sequestration of dye from textile industry wastewater using agricultural waste products as adsorbents. Journal of Environmental Chemical Engineering, 1, 629-641.

[33] RAO, K. S. P., RAO, M. V. & BANGARAIAH, P. 2013. Removal of methylene blue from aqueous solution using grewia orbiculata rottl: Equilibrium, Kinetic and Thermodynamic studies. International Journal of Engineering Research and Science & Technology, 2:2319-5991

[34] SAFA, Y. & BHATTI, H. N. 2011a. Biosorption of Direct Red-31 and Direct Orange-26 dyes by rice husk: Application of factorial design analysis. Chemical Engineering Research and Design, 89, 2566-2574.

[35] SAFA, Y. & BHATTI, H. N. 2011b. Kinetic and thermodynamic modeling for the removal of Direct Red-31 and Direct Orange-26 dyes from aqueous solutions by rice husk. Desalination, 272, 313-322.

[36] SALLEH, M. A. M., MAHMOUD, D. K., KARIM, W. A. W. A. & IDRIS, A. 2011. Cationic and anionic dye adsorption by agricultural solid wastes: A comprehensive review. Desalination, 280, 1-13.

[37] SEN, T. K. 2012. Agricultural by-product biomass for removal of pollutants from aqueous solution by adsorption. Journal of Environmental Research and Development, 6-3.

[38] SEN, T. K., AFROZE, S. & ANG, H.M. 2011. Equilibrium, Kinetics and Mechanism of Removal of Methylene Blue from Aqueous Solution by Adsorption onto Pine Cone Biomass of Pinus radiata. Water Air Soil Pollution, 218:499–515

[39] SINGH, H., CHAUHAN, G., JAIN, A. K. & SHARMA, S. K. 2017. Adsorptive potential of agricultural wastes for removal of dyes from aqueous solutions. Journal of Environmental Chemical Engineering, 5, 122-135.

[40] SINGH, U. & KAUSHAL, R. K. 2013. Treatment of wastewater with low cost adsorbent-A Review. International Journal of Technical & Non-Technical Research, 4:2319-2216.

[41] SIVRI, N., TUFEKCI, N. & TOROZ, I. 2007. Pollutants of Textile Industry Wastewater and Assessment of its Discharge Limits by Water Quality Standards. Turkish Journal of Fisheries and Aquatic Science, 7:97-103.

[42] SUBBAIAH, M. V. & KIM, D.-S. 2016. Adsorption of methyl orange from aqueous solution by aminated pumpkin seed powder: Kinetics, isotherms, and thermodynamic studies. Ecotoxicology and Environmental Safety, 128, 109-117.

[43] TAN, B. H., TENG, T. T. & OMAR, A. K. M. 2000. Removal of dyes and industrial dye wastes by magnesium chloride. Water Research, 34, 597-601.

[44] WAKSAKAL, O. & UCUN, H. 2010. Equilibrium, kinetic and thermodynamic studies of the biosorption of textile dye (Reactive Red 195) onto Pinus sylvestris L. Journal of Hazardous Materials, 181, 666-672.

[45] YAGUB, M. T., SEN, T. K., AFROZE, S. & ANG, H. M. 2014. Dye and its removal from aqueous solution by adsorption: A review. Advances in Colloid and Interface Science, 209, 172-184.

[46] YANEVA, Z. L. & GEORGIEVA, N. V. 2012. Insights into Congo red Adsorption on Agro-Industrial Materials -Spectral, Equilibrium, Kinetic, Thermodynamic, Dynamic and Desorption Studies: A Review. International Review of Chemical Engineering, 4:2035-1755.