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Removal of Congo Red From Dye Wastewater Using Adsorption

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Abstract:

The objective of this review discusses removal of Congo red from waste water effluents using various low cost adsorbents, eco-friendly and highly efficient. Dyes and pigments widely utilize in the textiles, paper, plastics, leather, and foodstuff, cosmetic industries as well as natural and artificial fibers to color products. Use of these dyes along with lots of water in textile industries has resulted in the production of polluted and coloured waters being discharged into the environment (nearby land or rivers) without any treatment because the conventional treatment methods are not effective. Congo red one of important dye that found in the waste water have higher solubility in the water about 1 g/30 mL. Therefore, Congo red containing effluents have to be efficiently treated before they are discharged into the water bodies or the environment. Over the past few decades, several processes have been used for the removal of dyes from wastewater such as biological (aerobic and anaerobic), chemical precipitation, coagulation/ flocculation, solvent extraction, membrane filtration, ion exchange, ozonation, electrochemical destruction and adsorption. Adsorption process has simplicity of design, more efficient, easy to operate, insensitivity to toxic substances and cost effective, hence, it has been suggested as a potential alternative to the existing physical / chemical /biological methods for the removal of congo red from industrial effluents or waste water. The variables comprises of equilibrium contact time, particle size, pH of the dye solution, initial concentration, amount of adsorbent, temperature. Hence the present study reviewed for the removal of Congo red from waste water effluents using various low cost adsorbents

Keywords — **Waste water, Congo red, pollution control, adsorption.**

Introduction:

There are three basic needs that a man possesses food, clothing, and shelter. The global textile and clothing industry is bound to be huge, as it fulfills the second basic requirement of man. It is worth $480 billion at present and is expected to reach $700 billion, shortly. This is because people are getting increasingly conscious of the way they dress. It has become a means to create an impression and represent their personality. Everybody wants to strike an impression with different and fashionable clothes. But the sad fact is that the human greed to look appealing and wear glamorous clothes has ended up causing harm to the environment. The textile industry is one of the most pollutants releasing industries of the world. Surveys show that nearly five percent of all landfill space is consumed by textile waste. Besides, 20 percent of all fresh water pollution is made by textile treatment and dyeing.

Dyeing industry is one of the oldest industries known to the mankind. Large amount of dyes are annually produced and used in textile, cosmetics, paper, leather, pharmaceutical, food and other industries. There are almost 10,000 various dyes are present and almost 2/3rd of dyes are used in textile industry[1]The discharge of these dye stuffs from industries into rivers and lakes leads to a reduction in dissolved oxygen concentration causing anoxic conditions, which subsequently affect aerobic organisms[2.3] In this present work, Congo Red (CR) was chosen as an anionic dye surrogate indicator due to its chemical composition and environmental concern. Effluent containing CR is produced from textiles, printing, dyeing, paper, and plastic industries.[4,5] Congo red (CR) is a benzidine-based anionic bisazo dye known to metabolize to benzidine, a known human carcinogen.[6] Congo red (CR) is toxic to animals and plants and thus its introduction to water stream is of potential health, environmental, and ecological concern[7] Therefore, CR containing effluents have to be efficiently treated before they are discharged into the water bodies or the environment. Over the past few decades, several processes have been used for the removal of dyes from wastewater such as biological (aerobic and anaerobic), chemical precipitation, coagulation/ flocculation, solvent extraction, membrane filtration, ion exchange, ozonation, electrochemical destruction and adsorption[8,9] Adsorption is carried out mostly by using activated carbon because of having high adsorptive capacities. But the production of activated carbon is expensive and its regeneration is very difficult[10] Recent research has been directed towards the looking alternatives to investigate a low cost method, which is both economical and effective which can be used on an industrial scale. Among the treatment technologies biosorption is getting prominence because it is economically favourable, effective and technically feasible[11]. Recent research has been concentrated on the low cost adsorbents such as tenduwaste[12], Agricultural Waste [13], bauhinia purpurea leaves [14], biomass of Zea mays [15] Aloe vera leaves [16] Lignocellulosic Agro-Industrial Materials [17], Neem Leaves [18] marine algae Valoria bryopsis [19], ChitosanMontmorilonite[20] sycamore bark activated carbon [21], Water hyacinth roots [22], rice hull ash [23], Azadirachta indica leaf [24], Jujuba seeds [25], red mud [26], polypyrrole–polyaniline nanofibres [27], anion exchange membrane [28], and ball-milled sugarcane bagasse [29] saw dust[30] etc.In this present review repoted the removal of congo red from waste water using different low cost adsorbents and the percentage removal of Congo red.

Materials and Methods:

Preparation of adsorbate Solutions:

Analytical grade CR dye ($C_{32}H_{22}N_6O_6S_2Na_2$; molecular weight 696.68; λ max = 500nm) was obtained from the laboratory. A stock solution of CR dye of concentration 1000mg/L was prepared by dissolving 1g of powder CR dye in 1L of distilled water. Experimental dye solutions of desired concentration were obtained by appropriate dilution of the stock solution.

Batch Adsorption Experiments:

Batch adsorption of CR dye onto the adsorbent was conducted in a 250ml airtight Erlenmeyer flask containing 100ml of known concentration of the CR dye solution and an accurately weighed amount of the adsorbent. The mixtures in the flasks were agitated on a mechanical shaker operating at a constant speed of 180 rpm. The effect of contact time adsorbent dosage, initial CR dye concentration, pH and temperature were evaluated. The flask containing the samples were withdrawn from the shaker at predetermined time intervals, filtered and the final concentrations of CR dye in the supernatant solutions were analyzed using the UV-visible spectrophotometer .The pH of the solution was adjusted using 1M HCl or NaOH. The amount of equilibrium uptake of CR dye was determined using

Percentage of dye removal and dye biosorption capacity:

Percentage of dye removal and dye uptake are calculated as follows

$$\%\ \text{Biosorption} = \frac{(C_i - C_f)}{C_i} \times 100 \qquad (1)$$

$$q = (C_i - C_f)\,(v/m) \qquad (2)$$

Where, C_i and C_f are the initial and final concentrations of dyes in aqueous solutions respectively (mg/L), q is the dye uptake (mg of dye/ g of biosorbent), V is the volume of solution taken (L), and m is the mass of biosorbent taken (g).

Prior to 1914 only a few theoretical interpretations of biosorption isotherms were in use. But thereafter, a number of isotherm equations were proposed by different investigators. Some of those in frequent use are:

- Langmuir isotherm
- Freundlich isotherm
- Temkin isotherm

1. Langmuir isotherm

The Langmuir biosorption isotherm[31] was based on the following assumptions:

- Fixed number of biosorption sites: at equilibrium, at any temperature, a fraction of the biosorbent surface sites (θ) is occupied by adsorbed molecules and the rest (1-θ) is free.
- All sorption processes are homogeneous.
- There is only one sorbate
- One sorbate molecule reacts with only one active site.
- No interaction between the sorbate species.
- A monolayer surface phase is formed.

The equation proposed by Langmuir was universally applicable to chemisorption with some restrictions involving physical biosorption. This equation is applicable to the physical or chemical biosorption on solid surface with one type of biosorption active center. As long as its restrictions and limitations are clearly recognized, the Langmuir equation can be used for describing equilibrium conditions for sorption behavior in different sorbate-sorbent systems or for varied conditions within any given system. The Langmuir equation is given by:

$$q = \frac{q_{\max} K_{a\,eq}}{1 + K_{a\,eq}} \qquad (3)$$

Where Q_{max} indicates the monolayer biosorption capacity of biosorbent (mg/g) and the Langmuir constant *b* (L/mg) is related to the energy of biosorption. For fitting the experimental data, the Langmuir model was linearized as

$$\frac{1}{q} = \frac{1}{q_{\max}} + \frac{1}{K_a q_{\max} C_{eq}} \qquad (4)$$

2. Freundlich isotherm

Freundlich biosorption isotherm was proposed by Boedecker in 1895 as an empirical equation. Later Freundlich[32] made some useful modifications as a result of which, it assumed great importance. The Freundlich biosorption equation can be written as:

$$q = KC_{eq}^{\frac{1}{n}} \qquad (5)$$

Taking the ln of both sides,

$$\ln q = \ln K + \frac{1}{n}\ln C_{eq} \qquad (6)$$

Where ‘q’ is equilibrium biosorption capacity (mg/g), ‘C_e’ is the equilibrium concentration of the adsorbate in solution, ‘K’, and ‘n’ are constants related to the biosorption process such as biosorption capacity and intensity respectively.

3. Temkin isotherm

Temkin and Pyzhev suggested that due to the indirect adsorbate/biosorbent interaction, the heat of biosorption of all the molecules in the layer would decrease linearly with coverage[33]. The linear form of Temkin isotherm can be written as:

$$q = \frac{RT}{b}\ln\left(A_T C_{eq}\right) \qquad (7)$$

Where A_T (L/mg) and b_T are Temkin isotherm constants, ‘T’ is absolute temperature in Kelvin and ‘R’ is the universal gas constant (J/mol.K). C_{eq} is the equilibrium concentration of the adsorbate.

4. Biosorption kinetic models

The study of biosorption kinetics in wastewater is significant as it provides valuable insight into the reaction pathways and into the mechanism of the reaction. Further, it is important to predict the time at which the adsorbate is removed from aqueous solution in order to design an appropriate sorption treatment plant. Any biosorption process is normally controlled by three diffusive transport processes for the adsorbate:

- From bulk solution to the film surrounding the biosorbent.
- From the film to the biosorbent surface.
- From the surface to the internal sites followed by binding of the dyes onto the active sites.

But in kinetic modeling, all these three steps are grouped together and it is assumed that the difference between the average solid phase concentration and equilibrium concentration is the driving force for biosorption. Further, it is established from the experimental observations that at optimum agitation speed, the external boundaries have hardly any effect. So application of the kinetic model depends only on the initial and final concentrations of the solution at different time intervals. It is incorrect to apply simple kinetic model such as first and second order rate equations to a sorption process with solid surface, which is rarely homogenous. Secondly, the effects of transport and chemical reaction are often experimentally inseparable.

Several kinetic models have been proposed to clarify the mechanism of a solute sorption from aqueous solution onto a biosorbent:

- Lagergren first order kinetic model
- Pseudo second order kinetic model

4.1. Lagergen first order kinetic model

The Pseudo first order or Lagergen kinetic rate equation for the sorption of liquid solid system was derived based on solid biosorption capacity. It is one of the most widely used sorption rate equations for sorption of a solute from a liquid solution[34]. According to the authors, the overall biosorption rate is directly proportional to the driving force, i.e., the difference between initial and equilibrium concentrations of the adsorbate (q_e-q). Therefore, the pseudo first order kinetic equation can be expressed as:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{8}$$

Where q_e and q_t are the sorption capacities at equilibrium and at time *t*, respectively (mg/g) and k_1 is the rate constant of pseudo first-order sorption (min^{-1}). After integration and applying boundary conditions, q_t =0 at t = 0 to q_t = q_t at *t* = t; the integrated form of Eq. (8) becomes:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \tag{9}$$

'k_1'can be calculated from the slope of the linear plot between log (q_e-q_t) vs't' for different adsorbate concentrations.

4.2. The pseudo-second-order equation

If the rate of sorption is a second-order mechanism, the pseudo-second-order chemisorption kinetic rate equation is expressed as[35]:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \tag{10}$$

Where q_e and q_t are the sorption capacity at equilibrium and at time *t*, respectively (mg/g) and *k* is the rate constant of pseudo-second-order sorption (g/(mg min)). For the boundary conditions q_t =0 at t = 0 to q_t = q_t at *t* = *t*; the integrated form of Eq. (10) becomes:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \tag{11}$$

where *t* is the contact time (min), q_e (mg/g) and q_1 (mg/g) are the amount of the solute adsorbed at equilibrium and at any time, *t*. Eq. (1) does not have the problem of assigning as effective q_e. If pseudo-second-order kinetics is applicable, the plot of t/q_t against *t* of Eq. (11) should give a linear relationship, from which q_e and *k can* be determined from the slope and intercept of the plot and there is no need to know any parameter beforehand.

5. Thermodynamic parameters

In environmental engineering practice, both energy and entropy factors must be considered in order to determine what processes will occur spontaneously. Gibb's free energy change, $\Delta G°$, is the fundamental criterion of spontaneity. Reactions occur spontaneously at a given temperature if $\Delta G°$ is a negative value. The thermodynamic parameters, Gibbs free energy change ($\Delta G°$), enthalpy change ($\Delta H°$), and entropy change ($\Delta S°$), for the biosorption processes are calculated using the following equations[36,37]:

$\Delta G° = - RT \ln K_d$ (12)

and

$\ln K_d = \Delta S^0/R - \Delta H^0/RT$ (13)

Substitution of Eqn. 13 in Eqn 12. gives the Van't Hoff equation as follows:

$$\ln K_d = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (14)$$

where R is universal gas constant (8.314 J/mol K) and T is the absolute temperature in K. A plot ln K_d versus temperature $1/T$, was found to be linear. The values of $\Delta H°$ and $\Delta S°$ were determined from the slope and intercept of the vant Hoff's plot.

Response Surface Methodology*:*

Optimization of different process parameters depending on the Congo red dye removal is highly required for the effective design and accurate control of bio sorption technique. So, response surface methodology is time saving and precise alternative to conventional optimization methods. The main objective is to optimize the response surface that is shaped under the influence of process parameters.

The effect of different process parameters such as solution pH (X_1), initial dye concentration (X_2), bio sorbent dosage (X_3) and temperature (X_4) on congored dye removal from aqueous solutions was studied by using full factorial rotatable central composite design (CCD)[38] . Total thirty experiments, which include 16 cube point runs, 8 axial point runs and 2 centre point were required and all of them were done in duplicate. All the experiments were conducted at contact time (t) and a constant speed of agitation 180 rpm.

All independent variables were coded to five levels as X_i according to Eqn.15[39]

$$X_i = \frac{(X_i - X_{oi})}{\Delta X_i}, \; i = 1,2,3,\ldots\ldots\ldots k \quad (15)$$

Where X_i is the dimensionless value of an independent variable, x_i is the real value of an independent variable, x_{0i} is the real value of the independent variable at the centre point, and Δx_i is the step change. A second degree polynomial equation (Eqn. 16) was developed to estimate the percentage of bio sorption of dyes at different operating conditions of the bio sorption process by using STATISTICA 6.0 (Stat Soft Inc.).

$$Y=b_0+b_1X_1+b_2X_2+b_3X_3+b_4X_4+b_{11}X_1^2+b_{22}X_2^2+b_{33}X_3^2+b_{44}X_4^2+b_{12}X_1X_2+b_{13}X_1X_3+b_{14}X_1X_4+b_{23}X2X_3+b_{24}X_2X_4+ b_{34}X_3X_4 \quad (16)$$

Where , Y is the predicted response, X_1, X_2, X_3 and X_4 are independent variables: b_0 is an offset term; b_1,b_2,b_3 and b_4 are linear effects; b_{11}, b_{22}, b_{33} and b_{44} are squared effects and b_{12}, b_{13}, b_{14}, b_{23}, b_{24} and b_{34} are interaction terms.

RESULTS AND DISCUSSION:

Table 1 percentage removal of Congo red dye using various low cost adsorbents.

Adsorbent	**% Bio sorption**	**Time(min)**	**particle size(µm)**	**pH**	**initial concentration of dye(mg/l)**	**bio sorbent dosage (gm)**	**Temperature(k)**
tenduwaste	73	60	**-**	6.2	50-100	0.5	301
bauhinia purpurea leaves	84	40	81-162.3	6	20-100	0.1	303
Aloevera leaves	91	100	300-500	2-12	100-500	0.5	298
neem leaves	99.70	240	75-300	2-12	100-300	0.1	298
marine algae Valoria bryopsis	97.77	180	-	1-5	5-25	0.5	303
sycamore bark activated carbon	98.2	120	-		150-350	0.3	293
Water hyacinth roots	46.15	180	-	5-10	25-100	0.1-0.5	298
saw dust	90	120	150	9	50-100	0.1	308
Agricultural Waste	93	60	300	2	50-100	1.0	303

Adsorbent	**RPM**	**researcher**	**references**
tenduwaste	**250**	G. K. Nagda, and V. S. Ghole	12
biomass of Zea mays	**200**	H.M.Asfour and O.A.Fadeli	15
Aloe vera leaves	**150**	Yusef Omidi Khaniabadi et al	16
Neem leaves	**300**	Muhammad B. Ibrahim et al	18
marine algae Valoria bryopsis	**120**	R. Jayaraj et al	19
ChitosanMontmorilonite	**120**	Riskiono Slamet & Erdawati	20
sycamore bark activated carbon	**60**	Li Cong et al	21
Water hyacinth roots	**200**	N. Rajamohan	22

Table 2: removal of Congo red dye using various RPM

Effect of contact time:

The effect of agitation time on the biosorption of congored dye from aqueous solution using *various* biosorbents were studied at different initial dye concentrations, various constant temperatures , and constant agitation speed of 180 rpm and solution different pH for the dye . The percentage of biosorption and dye uptake of congored onto *various* biosorbent steeply increased with an increase in agitation time and they gradually increased with an increase in agitation time and there after reached plateau after attaining equilibrium time.

Effect of particle size of bio sorbent:

The % biosorption and congored dye uptake decreased with an increase in biosorbent particle size. This is because of the decrease in specific surface area of the biosorbent with an increase in the particle size of the biosorbent.

Effect of solution pH:

The changes in % biosorption and congored dye uptake with varying of pH could be explained on the basis of influence of solution pH on the activity of functional groups present on the biosorbent surface.

Effect of initial concentration of dye:

The percentage of biosorption decreased and congo red dye uptake increased with an increase in initial concentration of dyes at all the temperatures.

Effect of biosorbent dosage:

The % biosorption increased with an increase in biosorbent dosage. This is because of the increase of available active sites on the biosorbent surface.

Effect of Temperature:

The % biosorption and Congo red dye uptake increased with an increase in temperature of the solution. This suggests the endothermic nature of the process.

CONCLUSIONS:

In this review the maximum removal efficiency using neem leaves was predicted to be 99.70% at a temperature of 298 K, solution pH of2-12, and initial dye concentration of 100-300 mg/L and biosorbent dosage of 0.1 mg/g. The experimental data of biosorption of the Congo red dye onto the *various* biosorbents fitted well with the Freundlich isotherm model. The isotherm reveals that the bio sorption of the Congo red onto *various* bi sorbents were favourable.

References

[1] A.Riccardo, F.Carletto, F.Chimiri, F.Bosco, F.Ferrero; Bio Resources, 3(4), 1146-1155 (2008.
[2] Chander M., Arora D. S. Dyes pigm. 72 (2007) 192.
[3] Vigiyaraghavan K. , Yun Y. Biotechnol. Adv. 26 (2008) 266.
[4] Purkait M. K., Maiti A., DasGupta S. J. Hazard. Mater. 145 (2007) 287

[5] Pavan F.A., Dias S.L.P., Lima E.C., Benvenutti E.V. Dyes Pigm. 76 (2008) 64
[6] R. Ahmad, and R. Kumar, Adsorption studies of hazardous malachite green onto treated ginger waste, Appl. Surf. Sci., 91(4), 2010, 1032-1038
[7] N. Nasuha, H.Z. Zurainan, H.I. Maarof, N.A. Zubir, and N. Amri, Effect of cationic and anionic dye adsorption from aqueous solution by using chemically modified papaya seed, International Conference on Environment Science and Engineering, 8, 2011, 50-58.

[8] R. Malik, D.S. Rametke, and S.R. Wate, Adsorption of malachite green on groundnut shell waste based powdered activated carbon, J. Was. Manag. 27, 2006, 1 – 8.

[9] G. Crini, (2006) Non-conventional low-cost adsorbents for dye removal: A review, J. Bioreso. Technol. 97, 2006, 1062-1070 .
[10] V .S.Shrivastava; International Journal of ChemTech Research CODEN (USA), 4(3), 1038-1043 (2012). [11] W.Xing, H.H.Ngo, S.H.Kim, W.S.Guo, P.Hagare; Bioresource Technology, 99, 8674-8678 (2008).
[12] G. K. Nagda, and V. S. Ghole , Biosorption of Congored by hydrogen peroxide treated tendu waste, Iran. J. Environ. Health. Sci. Eng., 2009, Vol. 6, No. 3, pp. 195-200.
[13] Enenebeaku K. Conrad1 et al, Adsorption of Congo Red Dye from Aqueous Solution Using Agricultural Waste, IOSR Journal of Applied Chemistry (IOSR-JAC) e-ISSN: 2278-5736.Volume 9, Issue 9 Ver. I (Sep. 2016), PP 39-51.
[14] P.Kalpana1 et al, Removal of congo red from aqueous solutions using plant biomass: equilibrium & kinetic studies, CTAIJ 11(2) 2016 [043-050].
[15] H.M.Asfour and O.A.Fadeli, Removal of Congo red Dye from Aqueous Solution by Using Saw Dust as an Adsorbent, Int. Journal of Engineering Research and Applications ISSN : 2248-9622, Vol. 4, Issue 4(Version 1), April 2014, pp.47-51 .
[16] Yusef Omidi Khaniabadi et al, Removal of Congo red dye from aqueous solutions by a low-cost adsorbent: activated carbon prepared from Aloe vera leaves shell, Environmental Health Engineering and Management Journal 2017, 4(1), 29–35.
[17] Zvezdelina L et al, Insights into Congo Red Adsorption on Agro-Industrial Materials - Spectral, Equilibrium, Kinetic, Thermodynamic, Dynamic and Desorption Studies. A Review, International Review of Chemical Engineering (I.RE.CH.E.), Vol. 4, N. 2 ISSN 2035-1755 March 2012.
[18] Muhammad B. Ibrahim et al ,Assessment of Adsorption Properties of Neem Leaves Wastes for the Removal of Congo Red and Methyl Orange, 3rd International Conference on Biological, Chemical & Environmental Sciences (BCES-2015) Sept. 21-22, 2015 Kuala Lumpur (Malaysia).
[19] R. Jayaraj et al , Removal of Congo red Dye from Aqueous solution using Acid Activated EcoFriendly Low Cost Carbon prepared from marine algae Valoria bryopsis, J. Chem. Pharm. Res., 2011, 3(3):389-396.
[20] Riskiono Slamet & Erdawati ,Adsorption of congored using chitosan montmorilonite in batch and column method, International Journal of Chemical & Petrochemical Technology (IJCPT) ISSN 2277-4807 Vol. 3, Issue 2, Jun 2013, 13-24.
[21] Li Cong et al, Study on the Adsorption Characteristics of Congo Red by Sycamore Bark Activated Carbon ,Environment. Technology. Resources, (2017), Volume I, 64-69.
[22] N. Rajamohan, Equilibrium studies on sorption of an anionic dye onto acid activated water hyacinth roots African Journal of Environmental Science and Technology Vol. 3 (11), pp. 399-404, November, 2009 .
[23] Shankar S, Rai A, Ahmad A, Sastry M. Rapid synthesis of Au, Ag, and bimetallic Au core–Ag shell nanoparticles using Neem (Azadirachta indica) leaf broth. J Colloid Interface Sci 2004; 275(2): 496–502. doi: 10.1016/j.jcis.2004.03.003.
[24] Reddy MC, Sivaramakrishna L, Reddy AV. The use of an agricultural waste material, Jujuba seeds for the removal of anionic dye (Congo red) from aqueous medium. J Hazard Mater 2012; 203-204: 118-27. doi: 10.1016/j. jhazmat.2011.11.083.
[25] Tor A, Cengeloglu Y. Removal of Congo red from aqueous solution by adsorption onto acid activated red mud. J Hazard Mater 2006; 138(2): 409-15. doi: 10.1016/j. jhazmat.2006.04.063.

[26] Bhaumik M, Maity A, Srinivasu V, Onyango M. Removal of hexavalent chromium from aqueous solution using polypyrrole-polyaniline nanofibers. Chem Eng J 2012; 181182: 323–33. doi: 10.1016/j.cej.2011.11.088.
[27] Khan MA, Akhtar S, Zafar S, Shaheen A, Khan MA, Luque R, et al. Removal of Congo red from aqueous solution by anion exchange membrane (EBTAC): adsorption kinetics and themodynamics. Materials 2015; 8(7): 4147-61. doi: 10.3390/ma8074147.
[28] Zhang Z, Moghaddam L, O'Hara IM, Doherty WOS. Congo Red Adsorption by Ball-Milled Sugarcane Bagasse, Chem Eng J 2011; 178: 122-8. doi: 10.1016/j.cej.2011.10.024.
[29] Ibrahim, M. B. and W. L. O. Jimoh (2008). Adsorption studies for the Removal of Cr(VI) ion from aqueous Solution, Bayero Journal of Pure and Applied Sciences. 1(1):99 – 103.
[30] D. A. Nimkar, and S. K. Chavan, Removal of Congo red Dye from Aqueous Solution by Using Saw Dust as an Adsorbent, Int. Journal of Engineering Research and Applications ISSN : 2248-9622, Vol. 4, Issue 4(Version 1), April 2014, pp.47-51.
[31]I. Langmuir, The adsorption gasses on plane surface of glass, mica and platinum, J. Am. Chem. soc. 40 (1916)1361-1368.
[32]H.M.F. Freundlich, over the adsorption in solution, J. Phys. Chem. 57 (1906) 385-470.
[33]C. aharoni, M. Ungarish, Kinetics of activated chemisorption Part 2. The oriental models, J. Chem. Soc. Faraday Trans. 73 (1977) 456-464.
[34]S. Lagergren, S. Kungliga Svenska Ventenskapsakademiens, Handlingar, Band 24 (4) (1898) 1.
[35]Y.S. Ho, E. McKay, "The kinetics of sorption of basic dyes from aqueous solution by *Sphagnum moss peat*, Can. J. Chem. Eng. 76 (1998) 822–827.
[36]A. E Martell and R. M. Smith, Critical Stability Constants (Inorganic Chemistry), vol. IV, Plenum, New York, (1977).
[37]J. M. Murray and J. R. Dillard, *Geochim. Cosmochim. Acta* 43 (1979) 781.

[38]G. E. P. Box, W. G. Hunter and J.S. Hunter, Statistics for experimenters, New York: Wiley Series in Probability and Mathematical Statistics, John Wiley & sons Inc., (1978).
[39]G. E. P. BOX and K.B. Wilson, On the experimental attainment of optimum conditions, Journal of the Royal Statistical Society, B13 (1951) 1-45.