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ADSORPTION STUDIES OF CADMIUM (II) ON SAWDUST TREATED WITH SULPHURIC ACID

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Abstract: *Equlibrium sorption of acid treated sawdust was studied. The physico-chemical properties of the treated sawdust were determined. The equilibrium sorption data were fitted into Langmuir, Freundlich, and Temkin isotherms. Of the three adsorption isotherm, the R^2 values of Freundlich and Langmuir isotherm models were the highest. The maximum monolayer coverage (Qo) from Langmuir isotherm model was determined to be 51.02mg/g, the separation factor indicating a favourable sorption experiment is 0.10. Also from Freundlich Isotherm model, the sorption intensity (n) which indicates favourable sorption and the correlation value are 1.35 and 0.74 respectively. The heat of sorption process was estimated from Temkin Isotherm model to be 0.198J/mol which vividly proved that the adsorption experiment followed a physical process.*

Keywords: *Heavy metals, Isotherms sawdust and Sorption.*

I. Introduction

Heavy metals are widely released or distributed into the environment by both natural and anthropogenic sources such as industrial discharge, automobile exhaust and solid mineral mining. Unlike organic pollutants, these metals have tendency to accumulate in living beings and later become toxic and carcinogenic. Several industrial activities are important sources of these metals which are mainly distributed by air and water (Manavi *et al*., 2020). Bio-accumulation and bio-magnification increase the concentration of heavy metals in organisms or targeted organ over time until they become hazardous to health. For example, cadmium is bio-persistent and, once absorbed by an organism, it remains resident for many years (over decades for humans) although it is eventually excreted. In human, long term exposure is associated with renal dysfunction, lung disease and cancer and bone defects (osteomalacia, osteoporosis) and also in animals (Lenntech *et al*., 1998).

Various treatment techniques employed for the removal of heavy metals from polluted water bodies include chemical precipitation, ion exchange, chemical oxidation, reduction, reverse osmosis, ultra-filtration, electrodialysis and adsorption (Fu *et al.,* 2011). Among all these methods for the removal of heavy metals, adsorption is the most efficient as the other techniques have inherent limitations such as the generation of a large amount of sludge, low efficiency, sensitive operating conditions and costly disposal (Dada *et al.,* 2012). The adsorption method is a relatively new process and is emerging as a potentially preferred alternative for the removal of heavy metals because of its high – quality treated effluent, reversibility, provision of flexibility in design adsorbent regeneration (Fu *et al.,* 2011), simplicity, non- toxicity, cost- effectiveness, efficiency and local availability on removing toxic heavy metals from aqueous medium (Koron, 2010).

Sawdust (or wood shaving), a by-product or waste product of woodworking operations such as sawing, sanding, milling, planning, and routing which mainly compose of small chippings of wood. The main elemental components of sawdust are carbon (60.8%), hydrogen (5.2%), oxygen (33.8%) and nitrogen (0.9%) which is primarily composed of cellulose, lignin, hemicelluloses and minor amounts (5-10) of extraneous materials (Baran *et al*., 2007). It has variety of practical uses, such as in particle board production, mulch (an alternative to clay cat litter, or as a fuel), insulating material, in artistic displays, and as a scatter in railroad (and other models), cutler's resin, charcoal briquettes (Green *et al.,* 2006) etc. Airborne sawdust and sawdust accumulations present a number of health and safety hazards (Wan Azlina *et al*., 2014). Wood dust becomes a potential health problem when, for example, the wood particles, from processes such as sanding, become airborne and are inhaled. Wood dust is a known human

carcinogen. Some organizations in the United States such as the Occupational Safety and Health Administration (OSHA), the National Institutes for Occupational Safety and Health (NIOSH) etc. recognize wood dust as carcinogenic in relation to the nasal cavities and paranasal sinuses (Baran *et al.*, 2007).

Adsorption is the adhesion of atoms, ions, or molecules from a gas, liquid or dissolved solid to a surface (Brown and Land Revitalization Technology Support Centre, 2008). This process creates a film of the adsorbate on the surface of the adsorbent. A relation between the amount of adsorbate adsorbed on a given surface at constant temperature and the equilibrium concentration of the substrate in contact with the adsorbent is known as Adsorption Isotherm; Example of notable isotherms include Langmuir, Freundlich, Temkins, etc., where each describes adsorbate-adsorbent relation from different perspective.

In the Langmuir model, the adsorbent surface is considered to possess a number of active interaction sites for adsorption. Langmuir derived a relation between adsorbed material and its equilibrium concentration. The main assumptions of this isotherm are thus: there are fixed adsorption sites on the surface of the adsorbent at a given temperature and pressure, some fraction of these sites are occupied by adsorbate molecules (let this fraction be Ǿ); each site on the surface of the adsorbent can hold one adsorbate molecule; the heat of adsorption is the same for each site and is independent of Ǿ and; there is no interaction between molecules on different sites". Considering the processes of adsorption and desorption of the molecules on the surface, the Langmuir adsorption isotherm may be obtained as follows:

$$q_e = \frac{Q_o K_L C_e}{1+K_L C_e} \quad (1)$$

$$\frac{1}{\mathrm{qe}} = \frac{1}{\mathrm{Qo}} + \frac{1}{\mathrm{Qo\ KL\ Ce}} \quad (2)$$

Where:

q_e = the equilibrium concentration of adsorbate (mg/L)

C_e = the amount of metal adsorbed per gram of adsorbent at equilibrium (mg/g)

Q_o = maximum monolayer coverage capacity (mg/g)

K_L = Langmuir isotherm constant (L/mg)

The values of q_{max} and K_L were computed from the slope and the intercept of the Langmuir plot of 1/ q_e versus 1/ C_e.. The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter R_L, which is a dimensionless constant referred to as separation factor or equilibrium parameter (Nethaji *et al*., 2013*).*

$$R_L = \frac{1}{1+(KL\ + Co)} \quad (3)$$

Where: C_o = initial concentration K_L = the constant related to the energy of adsorption (Langmuir constant). R_L value indicates the adsorption nature to be either unfavorable, if $R_L > 1$, linear if $R_L = 1$, favorable if $0 < R_L < 1$ and irreversible if $R_L = 0$.

The Freundlich adsorption isotherm is based on the equilibrium sorption on heterogeneous surfaces. This isotherm is derived from the assumption that adsorption sites are distributed exponentially with respect to heat of adsorption (*Mall et al.,* 2006).The adsorption isotherm is expressed by the following equation:

$$Q_e = K_f C_e^{1/nf} \quad (4)$$

Which is linearized as:

$$\log Q_e = \log K_f + \frac{1}{nf} \log C_e \quad (5)$$

Where Q_e is the amount of adsorbate adsorbed at equilibrium (mg/g) and C_e is the concentration of adsorbate in the aqueous phase at equilibrium (ppm). K_f(L/g) and $1/n_f$ are the Freundlich constants related to adsorption capacity and sorption intensity respectively. The constant K_f is an approximate indicator of adsorption capacity, while 1/n is a function of the strength of adsorption in the adsorption process (*Voudrias et al.,* 2002). If n = 1 then the partition between the two phases are independent of the concentration. If value of 1/n is below one it indicates a normal adsorption. On the other hand, 1/n being above one indicates cooperative adsorption *(Mohan et al.,* 1997*).* The function has an asymptotic maximum as pressure increases without bound. As the temperature increases, the constants *k* and *n* change to reflect the empirical observation that the quantity adsorbed rises more slowly and higher pressures are required to saturate the surface. However, K_f and *n* are parameters characteristic of the sorbent-sorbate system, which must be determined by data fitting and whereas linear regression is generally used to determine the parameters of kinetic and isotherm models (*Guadalupe et al.,* 2008*).* Specifically, the linear least-squares method and the linearly transformed equations have been widely applied to correlate sorption data where 1/n is a heterogeneity parameter, the smaller 1/n, the greater the expected heterogeneity. This expression reduces to a linear adsorption isotherm when 1/n = 1. If n lies between one and ten, this indicates a favorable sorption process *(Goldberg*, 2005*).*

The Temkin adsorption isotherm assumes that the heat of adsorption decreases linearly with the sorption coverage due to adsorbent-adsorbate interactions (*Jusoh et al.,* 2011).
The Temkin isotherm equation is given as:

$$Q_e = \frac{RT}{b} \text{In}(A_T C_e) \quad (6)$$

Which is presented in a linearized form as:

$$Q_e = \frac{RT}{bT} \text{ In } A_T + \frac{RT}{b} \text{ In } C_e \quad (7)$$

$$B = \frac{RT}{bT} \quad (8)$$

$$Q_e = B \text{ In } A_T + B \text{In } C_e \quad (9)$$

where A_T (L/g) is the Temkin isotherm constant, b_T (J/mol) is the constant related to heat sorption, R is the ideal gas constant(8.134J/mol k), T is the absolute temperature (K) and B = Constant related to heat of sorption (J/mol).

II. Experimental Methods

2.1 Collection and Preparation of Adsorbate and Adsorbent

All chemicals and reagents used are of analytical grade. Sawdust was obtained from a local sawmill in Ede, Osun State and was pre-treated according to the method reported by *Milind et. al; 2009.* The sawdust was screened, sundried, grinded, and sieved with the mesh in the range of 25µm in order to increase its surface area. The modification was done by the chemical treatment of 100g of the sawdust with 1M of H_2SO_4 heated on hot plate with a magnetic sterile at 100^0C until it formed a paste. It was then washed with deionized water until the mixture attains a pH of 6. It was later dried in the oven at about 80°C to remove moisture and named treated sawdust.

The preparation of cadmium adsorbate was carried out by preparing stock solution containing 22.32 g/L of cadmium. 20 g of $CdCl_2.H_2O$ was weighed and dissolved in 500 ml of deionized water.1 g/L of the cadmium adsorbate was then prepared by measuring 11.2 cm^3 of the stock solution and dissolving it in 250cm^3 of deionized water. Working concentrations in the range of 20m g/L - 200m g/L were prepared by serial dilution.

The sawdust was characterized by determining the following: specific surface area, moisture content, loss of mass on ignition, pH, and bulk density using standard procedures.

2.2 Specific Surface Area

Saers' method was used for the determination of surface area. A sample containing 0.5 g of the sawdust was acidified with 0.1M HCl to pH 3 - 3.5, 10.0 g of NaCl, the volume was made up to 50 cm^3 with deionized water. The titration was carried out with standard 0.1M NaOH in a thermostatic bath at 25^0C to pH 4.0 and then to pH 9.0. The volume V required to raise the pH from 4.0 to 9.0 was noted and the surface area was computed from the following equation:

$$S(m^2/g) = 32V - 25 \text{ (Dada } \textit{et al.,} \text{ 2012).} \quad (10)$$

2.2.1 Determination of Moisture Content

This was done by weighing 5 g of sawdust into a crucible. This was placed in the oven and heated for 5hours at constant temperature of 105^0C. The sample was then removed and put rapidly into a desiccator in order to prevent more uptakes from atmosphere. The sample was reweighed. This procedure was repeated several times until a constant weight was obtained. The differences in the mass constitute the amount of moisture content of the adsorbent.

$$\% \text{ Moisture content} = \frac{W2-W3}{W2-W1} \text{ x } 100 \quad (11)$$

W_1 = Weight of crucible
W_2 = Initial weight of crucible with sample
W_3 = Final weight of crucible with sample (Panida *et al.,* 2014)

2.2.2 Determination of Loss of Mass

The determination of loss of mass on ignition as done by weighing 10g of adsorbent sawdust and put inside furnace at constant temperature of 600°C for 2hours. After roasting, the sample was removed and put in a desiccator for cooling. The residual product is then weighed and the difference in mass represented the mass of organic material present in the sample. This operation was repeated four times (Dada *et al*., 2012).

2.5 pH Determination

The determination of pH of the samples was done by weighing 1g each of sawdust, boiled in a beaker containing 100 cm^3 of distilled water for 5minutes, the solution was diluted to 200 cm^3 with distilled water and cooled at room temperature, the pH of each was measured using a pH meter and the readings were recorded (Nethaji *et al*., 2013).

2.6 Determination of Bulk Density

The bulk density of each of the samples sawdust was determined using Archimedes' principle by weighing a 10 cm^3 measuring cylinder before and after filling with the samples. The weight of the sample packed in the measuring cylinder was determined from the difference in weight of the filled and empty measuring cylinder. The volume of water in the container was determined by taking the difference in weight of the empty and water filled measuring cylinder. The bulk density was determined using the equation below.

$$\text{Bulk Density} = \frac{W2-W1}{V} \quad (12)$$

W_1 = Weight of empty measuring cylinder
W_2 = Weight of cylinder filled with sample
V= Volume of cylinder (Toshiguki *et al*., 2003).

2.7 Sorption Experiment

The equilibrium sorption of the cadmium unto sawdust was carried out by contacting 1g of the substrate with 100 cm^3 of different concentrations from 20 mg/L – 200 mg/L in 250 cm^3 Pyrex conical flask intermittently for 90 minutes on the mechanical shaker. The mixture was filtered and the residue concentration of the filtrate was analyzed using Atomic Absorption Spectrophotometer. The amount of absorbed (mg/g) was calculated using the formulae reported by Vanderborght and Van Griekenm (Vadi *et. al*., 2013):

$$Q_o = \frac{V(Ci - Ce)}{W} \quad (12)$$

Where Q_o = the amount of solute adsorbed from the solution.

V= volume of the adsorbate, C_i= the concentration before adsorption, C_f= the concentration after adsorption and W= the weight in gram of the adsorbent. The data was fitted into the following isotherm: Langmuir, Freundlich, and Temkin. The removal efficiency was determined by computing the percentage sorption using the formulae;

$$\% \text{ Sorption} = \frac{C_i - C_e}{C_i} \times 100 \text{(Igwe } et\ al\text{., 2006)} \quad (14)$$

III. RESULT

Table 1.0 Some Physico-Chemical Parameters of the Saw Dust

PROPERTIES	SAWDUST
pH	3.63
% Moisture Content	11
% Loss of mass on ignition	0.54
Bulk density (g/cm^3)	0.20
Surface Area(m^2/g)	5.72

3.1 Discussions

3.1.1 Langmuir Adsorption Isotherm

In the Langmuir model, from the data calculated in table 3.0, the R_L is greater than 0 but less than 1 indicating that Langmuir isotherm is favorable. From this research work, the maximum monolayer coverage capacity (Q_o) from Langmuir Isotherm model was determined to be 51.02 mg/g, K_L (Langmuir isotherm constant) is 0.1832 L/mg, R_L (the separation factor) is 0.10 indicating that the equilibrium sorption was favorable and the R^2 value is 0.97 proving that the sorption data fitted well to Langmuir Isotherm model.

3.1.2 Freundlich Adsorption Isotherm

In the Freundlich adsorption isotherm, from the data in Table 3, that value of 1/n = 0.74 while n=1.35 indicating that the sorption of Cd^{2+} unto sawdust is favorable and the R^2 value is 0.994.

3.1.3 Temkin Adsorption Isotherm

In the Temkin adsorption isotherm, from the Temkin plot shown in Fig. 3.0, the following values were estimated: A_T = 43737.20 L/g, B=0.198J/mol which is an indication of the heat of sorption indicating a physical adsorption process and the R^2*=0.88*.

Table 2.0 Parameters for Plotting Langmuir, Freundlich and Temkin Adsorption Isotherms of Cd (II) Ion unto Sawdust.

Sample	C_e	Q_e	C_o	1/ C_e	1/ Q_e	Log C_e	Log Q_e	Ln C_e
A	6.095	0.695	20	0.164	1.439	- 0.158	0.785	1.808
B	9.211	1.540	40	0.109	0.649	0.187	0.964	2.220
C	13.921	2.305	60	0.072	0.434	0.363	1.144	2.633
D	17.911	3.105	80	0.056	0.322	0.492	1.253	2.885
E	21.514	3.924	100	0.047	0.255	0.594	1.333	3.069
F	23.98	4.801	120	0.042	0.208	0.687	1.380	3.177
G	27.81	5.61	140	0.036	0.178	0.749	1.444	3.325
H	30.30	6.485	160	0.033	0.033	0.812	1.481	3.411
I	32.58	7.371	180	0.031	0.136	0.868	1.513	3.484
J	35.75	8.213	200	0.028	0.122	0.915	1.553	3.577
K	37.98	9.101	220	0.026	0.110	0.959	1.580	3.637

Table 3: Langmuir, Freundlich and Temkin Isotherm constants for the adsorption of Cd(II) ion unto sawdust

Metal ions	**Langmuir isotherm**				**Freundlich isotherm**				**Temkin isotherm**			
Cd^{2+}	Qo (mg/g)	K_L (L/mg)	R_L	R^2	$\frac{1}{n}$	n	k_f (mg/g)	R^2	A_T(L/mg)	b_T	B	R^2
	51.02	0.183	0.10	0.97	0.74	1.35	7.54	0.994	43737.20	11506.1	0.198	0.88

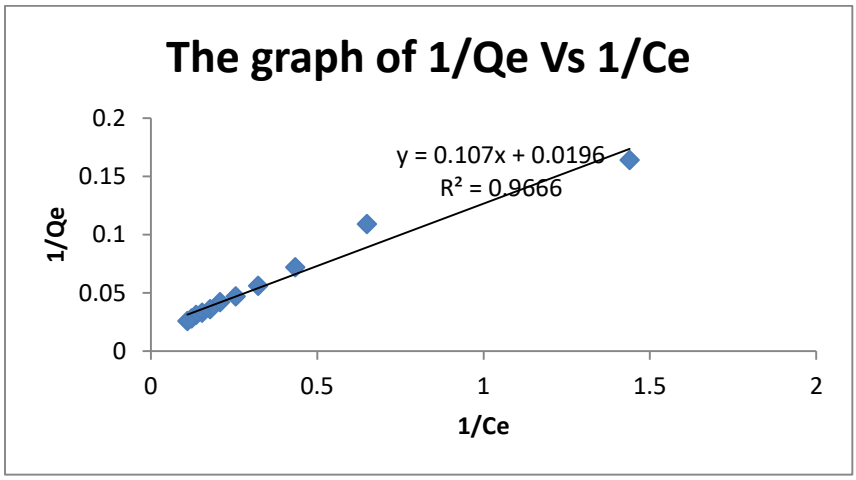

Figure 1.0: The graph of log 1/Qe Vs log 1/Ce showing Langmuir isotherm

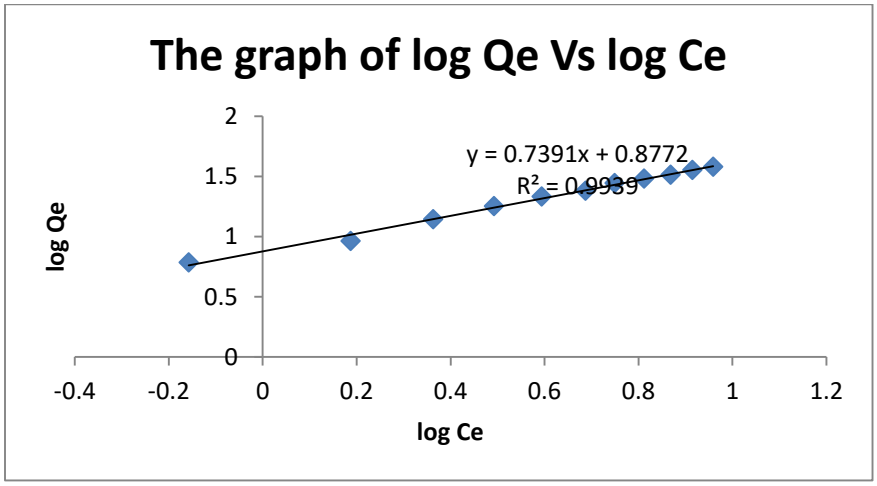

Figure 2.0: The graph of log Qe Vs log Ce showing Freundlich isotherm

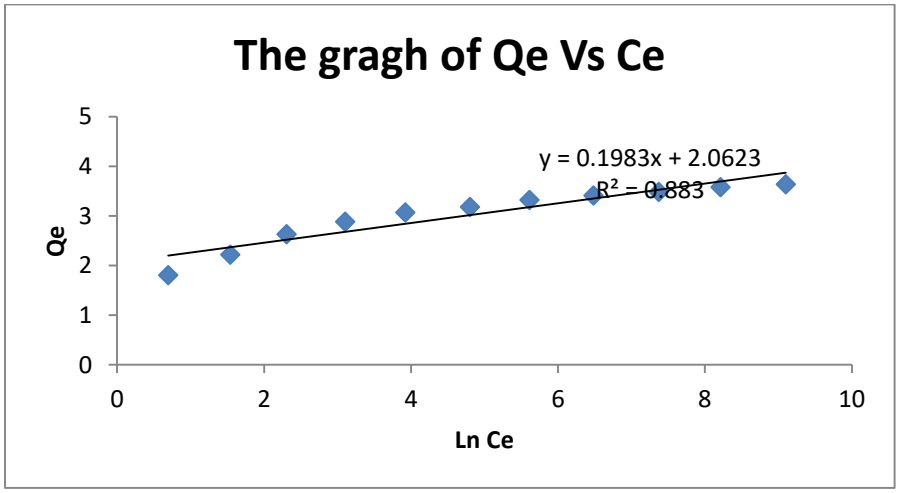

Figure 3.0: The graph of Qe Vs ln Ce showing Temkin's isotherm

IV. Conclusion

In this paper, investigation of the equilibrium sorption was carried out at 25ºC and pH between 3.60 and 3.70. Other physico-chemical parameters were determined and four adsorption isotherm models were studied. The sorption data fitted into Langmuir, Freundlich and Temkin isotherms out of which Freundlich and Langmuir Adsorption models were found to be have the highest regression value and hence the best fit. It could be concluded that treated sawdust with sulphuric acid is a potential and active biosorbent for removal of Cadmium ions from its aqueous solution and industrial waste water remediation.

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References

Baren, S., and Teul, I. (2007): *Wood Dust: An Occupational Hazard Which Increases The Risk Of Respiratory Disease. Journal Of Physiology And Pharmacology 58, Suppl. 5., 43- 50*

Dada, A.O., Olalekan, A.P., Olatunya, A.M. and Dada O. (2012): *Langmuir, Freundlich, Temkin and Dubinin–Radushkevich Isotherms Studies of Equilibrium Sorption of Zn^{2+} Unto Phosphoric Acid Modified Rice Husk IOSR Journal of Applied Chemistry (IOSR-JAC) ISSN: 2278-5736. Volume 3, Issue 1(Nov. – Dec. 2012), PP 38-45* www.iosrjournals.org www.iosrjournals.org

Fu F. and Wang Q. (2011): *Removal of Heavy Metals Ions From Wastewaters: A Review Journal of Environmental Management *92(3), 407-418.**

Guadalupe R., Reynel-Avila H. E., Bonilla-Petriciolet A., Cano-Rodríguez I., C. Velasco-Santos C., and Martínez-Hernández A. L.,(2008): "Recycling poultry feathers for Pb removal from wastewater": kinetic and equilibrium studies‖. *Proceedings of World Academy Of Science, Engineering And Technology 2008 Volume* **30**

Goldberg S. (2005): "Equations and Models Describing Adsorption Processes in Soils". *Soil Science Society of America*, 677 S. Segoe Road, Madison, WI 53711, USA. *Chemical Processes in Soils. SSSA* Book Series, (2005) no. 8.

Green, Harvey (2006) *Wood: Craft, Culture, History Penguin Books, New York, Page 403, Isbn978-1-1012-0185-5*

Igwe J.C. and Abia A.A; (2006): "*A Bioseparation Process For Removing Heavy Metals From Waste Water Using Biosorbents''.African Journal Of Biotechnology .***5** *(12), 1167- 1179.*

Itodo, A.U. and Itodo, H.U.(2010): *Sorption Energies Estimation Using Dubinin-Radushkevich and Temkin Adsorption Isotherms, Life Sciencejournal, Vol.7, 2010, Pp. 31-39.*

Jusoh, A. Hartini, W.J.H. N. Ali, N. and Endut, A. (2001): *Study On The Removal Of Pesticide In Agricultural Run Off By Granular Activated Carbon, Bioresource Technology, Vol.102. 2011, Pp. 5312-5318.*

Koron, H. (2010).*"Cadmium And Cadmium Alloys".Kirk-Othmer Encyclopedia Of Chemical Technology.John Wiley & Sons. Pp. 1-36*

Lenntech B.V., (1998): "*Metals In Aquatic Freshwater". (W.W.W.Lenntech.Com). Copyright 1998-2021*

Mall D.I., Srivastava V.C., Agarwal N.K. (2006): *Removal Of Orange-G And Methyl Violet Dyes By Adsorption Onto Bagasse Fly Ash Kinetic Study And Equilibrium Isotherm Analysis, Dyesand Pigments, Vol.69, 2006, Pp. 210-223.*

Manavi Yadav, Ridhika Gupta, Gunjan Arora, Priya Yadav, Anju Srivastava And Rakesh Kumar Sharma (2020): "*Current Status Of Heavy Metal Contaminants And Their Removal/Recovery Techniques". Copyright ©2020 American Chemical Society.* Dio:10.1021/Bk-2020-1352.Ch003

Milind R.O.., Julie D., and Snehal J*;(2009). __Comparative adsorption studies on Activated Rice Husk and Rice Husk Ash by using Methylene Blue as dye,'' International Congress on Environmental Research at Bits Pilani GOA, 1 – 11*

Mohan S, and Karthikeyan J. (1997): "*Removal of Lignin and Tannin Color from Aqueous Solution by Adsorption on to Activated Carbon Solution by Adsorption on to Activated Charcoal'', Environ. Pollut. 97, (1997) Pp.183-187*

Nethaji S., Sivasamy A. and Mandal A. B. (2011): *"Adsorption isotherms, kinetics and mechanism for the adsorption of cationic and anionic dyes onto carbonaceous particles prepared from Juglans regia shell biomass". Int. J. Environ. Sci. Technol. (2013) 10:231–242 DOI 10.1007/s13762-012-0112-0*

Panida S., Pisit C. and Xianshe F. (2014): *"Equilibrium Isotherm Models for Adsorption of Zinc (II) ion from Aqueous Solution on Pulp Waste". WSEAS TRANSACTIONS on ENVIRONMENT and DEVELOPMENT Volume 10, 2014 E-ISSN: 2224-3496*

Toshiguki S.and Yukata K;(2003): "*Pyrolysis Of Plant, Animal And Human Wastes‖; Physical And Chemical Characterization Of The Pyrolytic Product' Bioresource Technology, **90**(3), 2003, 241-247*

Vadi M.,Mansoorabad A. O.,Mohammadi M. and Rostami N.,(2013): *Investigation of Langmuir, Freundlich and Temkin Adsorption Isotherm of Tramadol by Multi-Wall Carbon Nanotube Asian Journal Of Chemistry · August 2013 Doi: 10.14233/Ajchem.2013.14786*

Voudrias E., F. Fytianos F. and E. Bozani E. (2002): "Sorption Description isotherms of Dyes from aqueous solutions and Waste Waters with Different Sorbent materials", *Global Nest, The Int.J*. 2002 **4**(1),75-83

Wan Azlina W. K. G., Gabriel S., and Azil B. A.,(2014): *"Physico-Chemical Characterizations of Sawdust-Derived Biochar As Potential Solid Fuels" The Malaysian Journal of Analytical Sciences, Vol. 18 No 3 (2014): 724 - 729*