Agricultural Based Low Cost Absorbents

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Abstract:-Adsorption is one of the preferred techniques in recent years to remove the color and inorganics from waste water. Activated carbon derived from the agricultural byproduct, acts as an effective adsorbent for the removal of dyes from waste water. The removal of dyes and metal ions at different, contact time, adsorbent dosage, pH, initial dye concentration, column diameter, bed height, flow rate and temperature by different agriculture based adsorbent has been studied. The result shows that among the compared adsorbents, moringa oleifera derived adsorbent is effective for waste treatment. The adsorption data were well fitted by Freundlich isotherm model. Kinetic data were best described by pseudo-second order model.

Keywords: Adsorption, agriculture waste, dye, metal ions.

I. INTRODUCTION

Dollution has been a wide problem in all over a world. In most of the industries used dyes as a coloring agent such as textile (Y.C. Wong et al., 2013), paint (King et al., 2008), leather (Sugashini S. et al., 2012), cosmetic (Suantak kamsonlian et al., 2011), paper, printing, cloth (George Z. Kyzas) and food industries. The wastewaters discharged from dying industries which contains high biological oxygen demand (BOD), high chemical oxygen demand (COD) are highly colored and large amounts of dissolved solids. Similarly wastewater contains metal ions do affect living and non-living things. These types of wastes affect the originality of land as well as water bodies (Y.C.Wonget al.2013). Wastewater which contains dyes and metal ions may lead to severe damage of lungs, kidneys, bones (Rajeswari M et al., 2013) eyes, skin problems etc. (Rozaini C.A.et al 2010). A variety of treatments were examined in various periods. Among them Activated carbon adsorption is well suited for removing dyes and metal ions in recent years. Activated carbon method is the effective method for removing organic compounds as well as metal ions having excellent adsorption capacity. Of late, low cost agricultural adsorbents are widely available for their removal (Sachin M.Kanawade et al 2010). In bio sorption process, using these low cost materials, metal ions were recovered from wastewater and also efficiently removed dyes from wastewater (Peter papoh ndibewu et al. 2011).

II. MATERIALS AND METHODOLOGY

2.1 Adsorbent preparation

The agricultural wastes or other natural wastes are collected and washed many times with double distilled

water. Purified materials dried in a hot air oven at reasonable temperature for one or two days (normally 24h). The dried materials put in mixer and sieved +60 to -85 meshes. The materials were stored in dry places (V.Vadivelan et. al., 2005).Similarly the wastes such as Moringa oleiefera (Kumar rohit raj et al. 2012; M. Rajeshwari et al.2012), biomass derived from tea waste (Suantak kamsonlian et al.2011), micro algal resin (R. Ramsenthil et al.2010), rice husk ash (Uma R.Lakshmi et al.2008; V.Vadivelan et al.2005: Mohammed mokthar mohammed 2003: upemdrakumar et al.2005; VenkatS.Mare et al.2006; Long lin et al.2013), Green pea peals (Ramesh dod et al.2012), Mangrove barks (Rozaini C.A et al.2010), Sugar cane bagasse ash (Sachin M.Kanawede et al.2011), Coconut fibre (Y.C. Wong et al.2013).

Coconut shell powder (V.yesuratram et al.2012), Palm tree waste (Zohra Belala et al.2009), Vegetable waste such as potato and carrot peals (Rohamagill et al.2013), Araucaria cookie bark (P.Kalpana et al.2013), Rose waste (M.Jamshaid Iqbal et al.2012), Beach saw dust (F.A Batzias et al.2004), Rice straw (Farhana Mazher et ai.2012).

Following treatments are adopted if needed

1. Chemical treatment:

Sulphuric acid, Hydrogen peroxide

2. Thermal treatment:

Using under a flow of Hydrogen or Nitrogen gas. Above the two treatments improves an adsorption efficient of activated carbon with no change of its textural properties (George Z. Kyzas et al. 2013).

2.2 Batch experiment

Batch experiment mainly depends upon the adsorbent dosage (w), adsorbent particle size (d_p) , Initial dye concentration (c_o), varying contact time (t), adjusting pH and temperature (T). 30 mL of dye solution is added to known weight of adsorbent dosage in a 250 mL conical flask and the mixture is agitated in shaker at required rpm. Sediment samples are withdrawn at regular intervals.

% adsorption = $[(C_o - C_t) \times 100] / C_o$

Where, C_o - Initial concentration of dye mg/L.

Ct - Final concentration of dye mg/L.

W- Weight of adsorbent.

Dye uptake, $q_t = [(C_o - C_t) \times v] / w$

From above formula % of adsorption of dyes is calculated (V.Yesuratram et al. 2011). Adsorption kinetics, adsorption isotherms, langumuir and freundlich isotherms gives the best-fit model to describe the sorption process of these agricultural wastes (Mike A. Acheampong et al., 2013).

2.3 Fixed bed column setup and experiments

Perspex cylinder (required length and diameter) constructed as column. Adsorbent material loaded with certain depth is called total effective depth, glass beds packed at top and gravel at bottom. Metal ions presenting waste water flow allow through the bed with known pH as well as initial concentration, out let is collected in tank. The result reported with 3% standard deviation error (Mike A. Acheampong et al., 2013).

III. RESULTS AND DISCUSSION

3.1 Removal of dyes and metal ions by different adsorbents:

The percentage removal of dyes and metals ions by different adsorbents under specified conditions is furnished in the following tables 1 and 2.

3.2 Effect of pH

The effect of pH on dye removal was studied over a pH range of 2–11. It was found that the color was stable at the natural pH 2.9. However, color reduction changes due to gradually increased pH concentration, with the maximum color removal at pH 11.Color removal due to pH change alone may be due to the structural changes being effected in the dye-molecules (Venkat S et al., 2005) In these studies pH changed in every trial, optimum efficiency noted and all removal efficiency with correspondent pH are noted. Initially, solution pH was observed in the range of 6.6 - 6.8. The metal solutions were precipitated in the pH range of above pH 11. At pH 3 the sorption was about 45% by chemically treated rice husk adsorbent. Adsorbent concentration increased to about 78%, 85% and 89% with increasing pH 2 units. (Upendra Kumar et al., 2005).

DYES	ADSORBENT	TEMPERATURE	рН	% OF REMOVAL	REFERENCE
Methylene blue	Green pea peals	30°C	7-10	98.21	Ramesh dod et al, 2012
Acid orange II	Sugar cane bagasse ash	45°C	6-7	999	Sachin M Kanawade et al, 2011
Methylene blue& Malachite green	Coconut fiber	35°C	1	98.3 & 99	Y.C.Wong et al,2013
Methylene blue	Coconut shell powder	30°C	10	96	V.Yesuratram et al, 2012
Malachite green	Araucaria cookie bark	33.97°C	2.95	96.1	P.Kalpana et al, 2013
Methylene blue &congo red	Moringaoleifera seed powder	34°C	6.5 & 2.5	90.27 & 98.52	Kumar rohit raj et al, 2012
Methylene blue	Saw dust	100°C	1.5-5	98	F.A.Batzias et al, 2004

 Table 1: Percentage (%) Removal of dyes by adsorbents

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METAL ION	ADSORBENT	TEMPERATURE	рН	% OF REMOVAL	REFERENCE
Nickel & Copper ion	Mangrove barks	27±2°C	2-10 & 5	90 & 85	Rozaini C.A et al, 2010
Fe (III) & Cr (III) Hydroxide	Industrial solid waste	32-60°C	10	65	C.Namasivayan et al, 2007
Copper	Data stone & palm tree waste	25±2°C	5	60-80	Zohrabelala et al,2009
Nickel (II)	Vegetable waste	35°C	4	79.32	Rohamagill et al, 2013
Cr (III) & Cr (VI)	Rose waste	30°C	2 & 5	86.35 & 81.35	M.JamshaidIqbal et al, 2012
Copper (II)	Coconut shell	28°C	4	91.5	Mike A.Acheamping et al, 2013

Table 2: Percentage removal of Metal ions by adsorbents

3.3 Effect of temperature

Temperature is important factor in removing of dyes and metal ions. In such removal, efficiency is considerable in high temperatures. Methylene blue dye removed (98%) using saw dust at 100 °C (F.A. Batzias et al 2004), The effect of temperature within the range of 25 to 45°C has been studied. The removal of acid orange-II dye increased from 95.12 to 99.95% increasing the temperature from 25 to 45 °C (Sachin M. Kanawade et al., 2011) optimum efficiency noted and all removal efficiency with correspondent temperature are noted.

3.4 Effect of contact time

The effect of contact time on rate of bio sorption has been studied for different concentration (ppm) present in sample solution at different time periods after maintaining reasonable temperature. An increase in rate of bio sorption was observed with increase in time period (example 5 minutes to few hours). Initially adsorbent having large number of vacant active sites which leads to a high reaction rate. During reaction time there is a reduction in the number of available sites because of their saturation. Here they are consumed in the process of adsorption resulting in the reduction in adsorption. (Rohama Gill et al., 2013)

3.5 Adsorption kinetics

Two Simplified kinetic equations are the pseudo first-order and pseudo second-order kinetic model, initially proposed by Lagergren (1989) and Ho and McKay (2000) respectively. The pseudo - first order kinetic model of Lagergren's equation assumes that the bio sorption rate is proportional to the number of unoccupied sites at the bio sorption surface (Ozdemiret el., 2003). The kinetic model based on solid capacity can be formed using Equation 1:

$q = q_e (1 - e^{-K_1 t})$ Equation ... (1)

Where, q_e is the dye uptake rate at equilibrium (mg.g-¹), K_1 is the pseudo first-order rate constant (min-1) and t is the contact time (min). The pseudo-second order kinetic model of Ho's equation based on the sorption capacity of the solid phase assumes the driving force for the adsorption rate comes from the square of the difference between q and q_e (Ho, 2006). Equation 2 can thus be obtained:

 $q = q_e^2 K_2 t / (1 + q_e K_2 t)$ Equation ... (2)

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Where, K_2 is the pseudo second-order rate constant modified (g.mg⁻¹min⁻¹)

3.6 Adsorption isotherms

The adsorption characteristics of microorganism were described by both the Langmuir and Freundlich adsorption isotherms. Langmuir equation is based on the assumption of monolayer sorption on to a surface of a finite number of identical sites (equal energy of adsorption). This has the linear form shown in Equation (3) (Volesky and Holan, 1995)

 $(1/q_e) = (1/K_aQ_{max}) (1/C_e) + (1/Q_{max})$ Equation... (3)

Where, q_e = amount of monolayer coverage of solute adsorbed per unit weight of adsorbent (mg g⁻¹ of algae) at equilibrium, Q_{max} = Maximum monolayer coverage for sorbate uptake under the given conditions (mg g⁻¹), K_a =Coefficient related to the affinity between the sorbent and sorbate (L mg⁻¹). Similarly, the Freundlich equation is based on monolayer sorption. However, the energy of adsorption was assumed to be heterogeneous, hence heterogeneous surface of adsorption. It has the linear form shown in Equ. (4) (Volesky and Holan,1995) ln $q_e = \ln K_F + (1/n) \ln c_e$ Equation...(4)

CONCLUSION

Activated carbon is one of the best adsorbent to remove dyes as well as metal ions. Moringa oleifera showed the removal of 60.21% for As (III), 85.60% for As (V), 76.59% for Cd (II), 68.85% for Cr (III) and 60.52% for Ni (II). This study clearly explained Moringa oleiferais suitable for removing metal ions at higher rate (Peter Papoh Ndibewu et al., 2011). The rice husk derived carbon, removed 90 % Methylene blue. Removal efficiency is mainly dependent on pH, temperature, contact time, adsorbent dosage, and porosity of adsorbent.

REFERENCES

- [1] V.Yesuratnam, Deepameghavathu, R. Padma sree "*Removal of methyleneblue from aqueous solution using coconut shell powder*". January 2012.
- [2] Y.C. Wong,M.S.R.Senan and N.A. Atiqah "Removal of Methylene blue andMalachite Green Dye using different form of Coconut Fiber as Absorbent". Journal of basic & Applied Sciences, 2013,9,172-177.
- [3] C. NamasivayamS.Sumithra "Adsorptive removal of phenols byFe(III/Cr(III) hydroxide, an industrial solid waste". Clean TechnEnviron Policy (2007) 9:215-223.Published online:22 February 2007.
- [4] Sachin M.Kanwade and R.W.Gailkwad "Removal of Dyes from Dye Effluent by using Sugarcane Bagasse ASH as an Adsorbent". International Journal of Chemical Engineering and Applications, Vol.2, No.3, June 2011.
- [5] Peter Papoh Ndibewu, Robert L.Mnisi, Sharon N.Mokgalaka and Rob 1.McCrindle "Heavy Metal Removal in Aqueous Systems Using Moringaoleifera" A review. Journal of Materials

Science and Engineering B 1(2011)843-853. Formerly part of Journal of Materials Science and Engineering, ISSN 1934-8959.

- [6] Rozaini C.A., Jain k., Oo c. W.Tan K.W., Tan L.S, Azraa A. and Tong K.S. "Optimization of Nickel and Copper Ions Removal by Modified Mangrove Barks". International Journal of Chemical Engineering and Applications, Vol.1 June 2010 ISSN: 2010-0221.
- [7] George Z. Kyzas, Jie Fu and Kostas A. "MatisThe change from past to Future for Adsorbent Materials in Treatment of Dyeing Wastewaters". Materials 2013,6, 5131-5158;doi:10.3390/ma6115131.
- [8] Ramesh Dod, Goutam Banerjee, and S.Saini: Adsorbent of Methylene Blue Using Green PEA Peels (Pisumsativum) "A Cost-effective Option for Dye-based Wastewater treatment". Biotechnology and Bioprocess Engineering 17:862-874(2012) DOI 10.1007/s12257-011-0614-5
- Zohra Belala, Mejdi Jeguirium, Meriem Belhachemi, Fatima Addoun, GwenaelleTrouve "Biosorption of copper from aqueous solutions by date stones and palm-trees waste". Environ Chemlet(2011) 9:65-69. DOI 10.1007/s10311-009-0247
- [10] Farhana masher. Abdul ghaffar, Ammara arooj and mudassara Iqbal "Studies of biosorption of heavy metals in soil by using rice straw". Asian Journal of Chemistry; Vol.24, No.6(2012), 2425-2432.
- S.Sugashini, K.M. Meera Sheriffa Begum "Optimization using central composite design (CCD) for the biosorption of Cr(VI) ions by cross linked chitosan carbonized rice husk (CCACR)". Clean techn Environ Policy (2013) 15:293-302 DOI 10.1007/s10098-012-0512-3.
- [12] Suantak Kamsonlian, S.Suresh, C.B,Majumder, S.Chand "Bio sorption of As(V) from contaminated water onto tea waste biomass: sorption parameters optimization, equilibrium and thermodynamic studies". I-manger's Journal on Future Engineering & Technology, Vol.71 No.1 August-October 2011.
- [13] M.Rajeswari, Pushpa Agarwal, S.Pavithra, Priya, G.R. Sandhya, and G.M.Pavithra "Continuous Biosorption of Cadmium by MoringaOlefera in a packed column". Biotechnology and bioprocess Engineering 18:321-325(2013) DOI 10.1007/s12257-012-0424-4.
- [14] Ackmez Mudho, Viond K. Garg, Shaobin Wang "Removal of heavy metals by biosorption". Environ Chem Lett (2012) 10:109-117 DOI 10.1007/s 10311-011-0342-2.
- [15] Rohama Gill, Anum Mahamood, Rabia Nazir, "Biosorption potential and kinetic studies of vegetable waste mixture for the removal of Nickel(II)". J. Mater Cycles waste Manag (2013) 15-115-121. DOI10.1007/s10163-012-0079-4.
- [16] P.Kalpana, and P.King "Biosorption of malachite green dye onto araucaria cookil bark: optimization using response surface methodology". Asain Journal of Chemistry; Vol.26, No. 1(2014), 75-81.
- [17] Kumar Rohit Raj, Abhishek Kardam, Jyoti Kumar Arora, ShaliniSrivastava, M.M. Srivastava "Adsorption behavior of dyes from aqueous solution using agricultural Waste; modelling approach". Clean Techn Environ Policy(2013) 15:73-80. DOI 10.1007/s10098-012-0480-7.
- [18] M. Jamshaid Iqbal, Farhan cecil, Khalil ahmad, Munawar Iqbal, M.Mushtaq, M.N. Naveem and T.H. Bokhari "Kinetic study of Cr(III) and Cr(VI) biosorption using rosa damascene phytomass: A rose waste biomass. AsainJounal of Chemistry" Vol.25, No.4(2013), 2099-2103.
- [19] V.Vadivelan, K.Vasanth Kumar "Equilibrium, kinetics, mechanism, and process design for the sorption of methylene blue onto rice husk". Journal of Colloid and Interface Science 286(2005)90-100.
- [20] 20. Venkat S.Mane, Indra Deo Mall, Vimal Chandra Srivastava "Kinetic and equilibrium isotherm studies for the adsorptive removal of Brilliant Green DYE from aqueous solution by rice husk". Journal of Environmental Management 84(2007) 390-400.

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- [21] Uma R. Lakshmi, Vimal Chandra Srivastava, IndraDeo Mall, Dilip H. Latye "Rice husk ash as an effective adsorbent: Evalution of adsorptive characteristics for Indigo Carmine dye". Journal of Environmental Management 90(2009) 710e720.
- [22] Upendra Kumar, ManasBandyopathyay: "Sorption of cadmium from aqueous solution using pretreated rice husk". Bioresource Technology 97(2006)104-109.
- [23] Long Lin, Shang-RuZhai, Zuo-Yi Xiao, Yusong, Qing-Da An, Xiao-Wei Song: "Dye adsorption of mesoporous activated carbons produced from NaOH-pretreated rice husks". Bio resource technology 136 (2013)437-443.
- [24] Yun Chen, Shang-Ru Zhai, Na Liu, Yu Song, Qing-DA An, Xiao-Wei song: "Dye removal of activated carbons prepared from NaOH-pretreated rice husks by low-temperature solutionprocessed carbonization and H3PO4 activation". Bio resource Technology 144(2013)401-409.
- [25] Mohamed Mokhtar Mohamed "Acid dye removal: Comparison of surfactant-modified mesoporous FSM-16 with activated

carbon derived from rice husk". Journal of Colloid and Interface Science 272(2004)28-34.

- [26] Mike A. Acheampong, Kannan Pakshirajan, Ajit P. Annachhatre, Piet N.L. Lens "Removal of Cu (II) by biosorption onto coconut shell in fixed-bed column systems". Journal of Industrial and Engineering Chemistry 19(2013)841-848.
- [27] S.Sugashini, K.M.Meera sheriff Begum "Optimization using central composite design (CCD) for the biosorption of Cr (VI) ions by cross Linked chitosan carbonized rice husk (CCACR)". Clean Techn Environ Policy (2013)15:293-302.
- [28] Natarajan Saravanan, Tiruvenkadam kannadasan, Chiya Ahmed, BashaanaVeerasamy Manivasagam, (2013).
- [29] Ozdemir.G, Ozturk.T, Ceyhan.N, Isler.R, and Cosar.T "Heavy metal biosorption by biomass of Ochrobactrumanthropiproducingexoplysaccharide in activated sludge". Bioresourc. Technol, 90:71-74(2003)
- [30] Ho,Y.S., and Mckay.G.,2000 "The kinetics of sorption of divalent metal ions onto sphagnum moss peat". Water Res, 34:735-742.