Research Article

Removal of dyes and metals using natural adsorbents

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ABSTRACT

The present study deals with the comparison of removal of dyes and metals using natural adsorbents such as rice husk, jack fruit leaf powder, coconut shell etc. The study deals with various research papers in which variety of biosorbents are used for the removal of dyes and metals. The entire working principle uses fixed bed column system for isolating and removing the impurities such as dyes and metals from the water sources. Dyes such as acid dyes, reactive azo dyes, food dyes, crystal violet dyes etc. and heavy metals such as lead, copper, cadmium etc. can also be effectively removed by adopting fixed bed column system through different adsorbing materials. The comparison between the various adsorbents is given in table. The adsorbing materials used here are Activated carbon, Rice husk, jack fruit leaf powder, coconut shell etc.

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INTRODUCTION

Recent EU environmental policy, including measures affecting all member states, requires that zero synthetic chemical compounds should be released into the marine environment (Min-Yu-Teng et al 2006). Due to their chemical structure, dyes, present in the waste water streams of many industrial sectors, such as dyeing, textile, tannery and the paint industry, are resistant to exposure to light, water and many chemicals is and therefore difficult to decolourise once released into the aquatic environment. Activated carbon is the most efficient adsorbent used widely, but its high cost limits its applicability (F. A. Batzias et al, 2004). Research is currently focusing on the use of low-cost commercially available organic materials as viable substitutes for activated carbon; in fact, sawdust, a relatively abundant and inexpensive material, is being extensively investigated as an adsorbent for removing contaminants from water. Other adsorbent materials that have been studied included wood and agricultural residues, untreated or treated in various ways(Mike A. Acheampong et al 2012).

Many modern technologies such as photo degradation (Sun and Xu, 1997), Coagulation(El-Geundi, 2001), flocculation (Al-Qodah, 2000), chemical oxidation, electro-chemical oxidation (Mustafa Turn et al, 2005), Biological process (Runping Han et al 2006) are all available for the removal of dye from the waste water. (Asok Adak et al, 2005)

Adsorption, which has been extensively used in industrial process for a variety of separation and purification purposes, is rapidly becoming a prominent method of treating aqueous effluents. The colour removal from textile waste water is considered as an important application of the adsorption process using low-cost adsorbents such as shale oil ash (Al-Qodah, 2000), chitosan (Juang et al, 1997), sunflower stalk (Sun and Xu, 1997), natural clay (El-Geundi, 2001) against expensive adsorbents such as activated carbon

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EXPERMENTAL SECTION

The method adopted for standard configuration of fixed bed column studies were done by (McKay and Bino, 1990). A standard rate of flow has been maintained throughout the analysis with a known dye concentration passes through the packed bed of granular activated carbon (GAC), Main adsorbent ingredients used were GAC F 400, Adsorbate, such as acid dye Tectilon orange 3G are used (G. M. Walker et al 1997). The major crises arises in the fixed bed column's working operation is not deaerated before to the adsorption test, as a result air masses were formed to the column formation of the air masses leads to critics of falling level of pressure, earlier deformation and mass level deformations between the solutions and the carbon (G. M. Walker et al 1997)

2.1. Clays and solutions
The main ingredients are Montmorilloite SAz^{-1} (Al_2O_3 .$4SiO_2$ .nH_2O) as a source clay mineral element .the composition of the elements includes SiO_2 60.4% Al_2O_3 17.4% Fe_2O_3 1.42% MgO 6.42% Na_2O 0.068% CaO 2.282% (Su-Hsia Lin et al 2004). The clay minerals have found to be effective size of 0.03mm, cation shifting tendency of 120 meg/100g. The cation exchanging tendency of clay minerals were done by using strata of copper (II) ion (0.02 M cu (II) triethletramine) (Min-Yu-Teng et al 2006)

2.2. Adsorbent
Activated carbons extracted from the coconut husks were used. These constitute a minimal iodine number of 850mg of 12g of carbon each. The content of ash was very low (lower than 10%) and a relevant density of 500 ± 50 kgm^{-3}. The layer of the activated carbon is multilayered packed phase**,** irrelevant and irregular with a huge BET area ($772m^2g^{-1}$). The porous width of the surface 22.1Å (Anderson Marcos Dias Canteli et al 2013)

2.3. Biomass Preparation
Natural quantitative mass of rice husk were sampled and collected. It is rinsed with distilled water and made it to dry for a period of 8 hours at a temperature of 60°c. Then the biomass was sieved to an effective diameter of (0.5 mm) was used in column studies (Runping Han et al 2006).

2.4. Experimental procedures
The fixed bed tests were carried out in a water-jacketed glass column with an inside diameter of 1.1 cm and a length of 12.8 cm. A typical procedure was as follows. To one end of the column a small glass fibre inserted, aqueous slurry of the clays was then aspirated into the column to obtain the clay bed. A second portion of glass fibre was plugged to another embed the loaded clay in order to prevent the loss of the clay. (Asok Adak et al,2005) The aqueous solution with a known dye concentration was fed to the top of the column at a desired flow rate driven by a micro-metering pump (Cole-Parmer, Master flex 7518-10, USA) until the breakthrough curve was completed. The temperature was controlled at 25 ∘C. The samples in the outlet were taken at the present time intervals and the concentrations of dye were analysed with an UV– visual spectrophotometer (F.A.Batzias et al, 2004)

2.5. Mathematical description
The break through-curve analysis was used here to study about the column performance based on the shape and time of the curve where it traces over the column bed studies was known. The curve decides the factor of explaining the progress loading behaviour of MB intake from a solution in fixed bed= C_t/C_o. The factor depends on the function of time, quantity of the solvent, width and height (Runping Han et al 2008).

2.6. Adams-Bohart models
In 1920 Adams and Bohart was found the relationship between C/C_i and t in a continuous system, which is applied to gas-solid system. Residual capacity of the solid and the concentration of the sorbed substance proportional to the sorption rate is a main assumption in this model. The Initial part of the breakeven curve can be obtained as above relationship using with following formulae:

$$\frac{C}{C_i} = \frac{e^{k_{AB}C_i t}}{e^{(k_{AB}N_o z/v)} - 1 + e^{k_{AB}C_i t}} \qquad \text{(M.Calero et al 2009)}$$

Where, C_i is the inlet metal concentration in solution in mg/L, k_{AB} is the kinetics constant in L/mg min, N_o is the maximum volumetric sorption capacity in mg/L, v is the linear flow rate in cm/min and z is the bed depth in the column in cm.

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2.7. Thomas model
The Thomas model was mostly used in column performance modelling. Its expression assumes Langmuir kinetics of adsorption-desorption and no axial dispersion so that the driving force for adsorption obeys second-order reversible reaction kinetics. The formulae for the Thomas model for adsorption column is given as (Emmanuel I. Unuabonah et al 2012)

$$\frac{c_t}{c_o} = \frac{1}{1 + \exp[\left(\frac{k_{Th} q_e x}{Q}\right) - k_{Th} c_o t]}$$

Where k_{Th} is the Thomas rate constant [mL/(h µmol)], q_e is the equilibrium uptake capacity (µmol/g), x the mass of sorbent packed in the column (g) and Q is the volumetric flow rate (m h^{-1}); c and c_o are the concentration (µmol L^{-1}) of PCP in the effluent and in the influent at any time (h), respectively.(Mouloud Lezehari et al 2012)

2.8. Yoon-Nelson model
The model states the relation between the probability of adsorption of adsorbate molecules and adsorbate absorption they were directly proportional to one another. The model is not a complex one in nature and not requires information related to type of adsorbent or else the properties of column bed (Emmanuel I. Unuabonah et al 2012). The Yoon-Nelson model not only was less difficult than other models, but also necessitates no detailed data concerning the characteristics of adsorbate, the physical properties of the adsorption bed and the type of adsorbent, The Yoon-Nelson formulae for a single component system was. (Runping Han et al 2008)

$$\frac{C_t}{C_o - C_t} = exp(K_{YN} t - \tau K_{YN})$$

The approach involves a plot of ln [C_t/C_o-C_t] Vs sampling time (t) according to the equation. The parameters of K_{YN} and τ can be obtained using the nonlinear regressive method (Mike A. Acheampong et al 2012)

2.9. Dynamic adsorption models
The dynamic adsorption models nominated, Bed-depth-service-time (BDST), Thomas and Yoon–Nelson was employed to represent the experimental breakthrough curves. The BDST model elucidates a relation between the time and the packed-bed depth of the column where K is the adsorption constant rate, N0 is the adsorption capacity, h is the bed depth of fixed-bed (cm), and u is the linear flow rate.(Mustafa turan et al,2005)

RESULT AND DISCUSSION

3.1. Effect of bed height
The adsorption column used in this study was designed to contain sampling points at 5 cm interval, to facilitate the study of the effect of bed height on the life-span of the column. This flow profile has been observed previously by other researchers for the adsorption of Cu (II), Ni (II) and Cd (II) onto banana pith and moss (S.Y. Quek et al 2006)**.**The property of adsorbent present inside the column bed plays a major role in the separation of metals bed height of 10cm, 20cm and 30cm to produce an yield of isolation of metals 3.5, 7.0, 10.5 g adsorbent material were used. The break through curve is plotted for material of varied quantity at a flow rate of 10 ml/min and 100 mg/L initial nickel compactness for waste tea biomass (Emine Malkoc et al 2006)

3.2. Effect of dye concentration
The break analysis curve increases by increases in inflow quantity of adsorbate concentration whose volume was minimized before the carbon regeneration. Increase in the dye concentration of inlet at constant rate reduces the output. This is due to more adsorbate a component isolating the activated carbon rapidly thus reduces the break even time (G.M. Walker et al 1997)

3.3. Application of Thomas and Yoon-Nelson model
The adsorption phenomenon was examined by adopting Thomas and Yoon Nelson models at different flow rates. The Thomas equation relates the break even time and the isolation time of the adsorption in column. It shows a reasonable experimented R_2 values varied from 0.96 to 0.98 for VBC-NMG and 0.94 to 0.97 for GMP-PVC (Esra Bilgin Simsek et al 2014).The kinetic constant, KT, tends to increase as the flow rate increases, while qe, cal becomes smaller, as obtained by other researchers. Moreover, the maximum column capacities calculated from the

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Thomas model (qe, cal, and mg/g) are very close to the experimental column capacities (qe, exp, and mg/g).(Baudu et al, 2012)

3.4. Regeneration of column

M.L.G. Vieira et al 2013, these method is very essential in industrial aspects as it's effectively minimal the cost of the operation. NaOH solution was carried out for the azo dyes used in the method. The output obtained was same for FD&C red40, FD&C yellow5, FD&C yellow6 for a NaOH solution of 1.0 mol L^{-1} at a flow rate of 5 ml min^{-1}. The study conducted after 20 mins noted that all the dyes were removed. The efficiency obtained in removed of dyes were 99.3%, 97.5%, 95%, 92.1% and 90.3% for the five corresponding adsorption elution cycles

3.5. Adsorption kinetics

The modeling of the adsorption kinetics may be described by two common models, namely, the pseudo-first-order Lagergen rate model and a pseudo-second-order model. Lagergen's kinetics equation had been most widely used for the adsorption of an adsorbate from an aqueous solution.(Yu-Na et al 2011). Adsorption was a time-dependent process and the rate of pollutant removed from aqueous solution is essential in order to design suitable sorption treatment plants. Moreover, the study of adsorption kinetics of in waste water treatment provides helpful insights into the mechanism of sorption reaction (Esra Bilgin Simsek et al 2014)

Table 1: Removal of Metals using with different adsorbents

Heavy metal	Adsorbent	pH values	Temperature	% of Removal	Reference
Boron	Selective polymeric resins	3-8	95	98	EsraBilginSimsek et al, 2014
Cadmium	Noval polymer clay	5.5	85	87.4	Emmanuuel I. Unuabonah et al, 2010
Cadmium	Protonated sargassummuticum	3.5 & 4.5	60-100	89.5	P.Lodeiro et al,2006
Cobalt (II)	Natural hemp fibers	1-5	75	86.5	LaviniaTofan et al, 2013
Cobalt (II)	Sunflower biomass	3-5	95	88	EnsarOguz et al, 2013
Copper	Chitosan immobilized on bentonite	4.5-8	40-110	92	Cybelle Morales Futalan et al, 2010
Cromium	Olive stone	4-5.5	60	91.5	M.Calero et al, 2009
Lead	Zeolite and Sepiolite	8-11	40-80	94	Mustafa Turn et al, 2005
Nickel (II)	Waste tea	4	25	89%	EmineMalkoc et al,2005

Table 2: Removal of Dyes using with different adsorbents

Dyes	Adsorbent	pH values	Temperature	% of Removal	Reference
Food azo dye	Glass beads coated with chitosan	3.5, 4.5 and 6	50°c	40.9-74.7%	M.L.G.Vieira et al 2013
Methyl Orange	Montmorillonite	4	60°c	76%	Min-YuTeng et al 2005
Methyl blue	Phoenix tree leaf powder	4-10	50-110	60.7%	Runping Han et al 2007
Toluenediamine	Activated carbon	4-10	30-50°c	72.43%	Yu-Na Hu et al 2011
Benzaldehyde	Granular activated carbon (Coconut husk)	8.4	20.15°c	88%	Anderson Marcos et al, 2014
Acid dye	Pristine & acid activated clay	3.5-9	65°c	78.42%	Su-Hsia Lin et al, 2004
Reactive azo dye	Argano-zeolite	3-10	85-125°c	81.24%	y.e.Benkli et al, 2007
Tectilon blue	Granular activated carbon	7.4	140°c	85.2%	G.M.Walker et al, 1996
Crystal violet dye	Surfactant modified alumina	3.5, 8 &11.5	44-85°c	74.6%	Asok Adak et al 2008
Acid dye	Activated carbon	3.5-9	74°c	86.8%	G.M.Walkeret al, 1998
Methylene blue& red22	Beech saw dust	3-5	23°c & 100°c	68-74%	F.A.Batzias et al 2004
Methylene blue	Rice husk	7.5 & 9	70-140°c	84.6%	Runping Han et al, 2006
Methylene blue	Jack fruit leaf powder	3.9-10	50-120°c	87.4%	Md. TamezUddin et al, 2008
Pentachloro phenol	Alginate-encapsulated pillared clay	5.3	35°c	70.25%	MouloudLezehari et al, 2012

3.6. Effects of electrolyte

Calculated values for some operating characteristics of the npolymer–clay composite adsorbent premodified with 0.1MNaNO3 and 0.1M Ca(NO3)2 for the adsorption of Cd2+. The results showed that at the same initial Cd2+ concentration, polymer–clay composite adsorbent treated more volume of the metal ion solution at breakthrough than with polymer–clay composite adsorbents pre-modified with electrolytes. (Emmanuel I. Unuabonah et al 2010)

3.7. Effect of flow rate

The effect of flow rates from 5 to 20mL min−1 on breakthrough curves can be observed as expected, an increase in flow rate produces a diminution in breakthrough and exhaustion times, and as a consequence, the curves become steeper with a shorter mass transfer zone (P. Lodeiro, et al 2006) an increase in flow rate from 0.20 mL/min to 0.60 mL/min increases the volume of effluent treated from 165.40mL to 247.00mL but decreases the Cu(II) removal efficiency as well as the uptake capacity of Cu(II). At lowest flow rate of 0.20 mL/min, the highest Cu (II) removal of 80.20% and highest bed adsorption capacity at breakthrough and exhaustion is obtained at 15.80 mg/g and 26.52 mg/g, respectively (Cybelle Morales Futalan et al 2010)

CONCLUSION

In this work, continuous biosorption operation in a fixed-bed column had been performed for heavy metals and dyes biosorption by varying adsorbent. This paper shows that the varying adsorbent could be used as an effective biosorbent for aqueous solutions containing this metals and dyes. The continuous laboratory scale studies suggested the following conclusions. First, the influence of various operational parameters on solute uptake by biosorbent in the contactor had been presented. The flow rate was decreases with the increases of the break through and saturation time. When the bed depth was increased, the same affect of decrease the flow rate. On the other hand, the breakthrough and saturation time decreases as the inlet concentration increases, for the same flow rate and bed depth. The capacity of removal obtained at optimum conditions was close to 0.800mg of metal/g biosorbent. Adams–Bohart, Thomas, Yoon–Nelson and Dynamic adsorption models were applied to experimental data obtained from dynamic studies performed on fixed column to predict the breakthrough curves and to determine the column kinetic parameters. The initial region of breakthrough curve was defined by the Adams–Bohart model. The analysis of the pH evolution during the operation of the column showed a pH increase at the beginning of the test due to the H+ ions were being sorbet in the matrix of the biosorbent. When the sites in the bed were saturated, no more protons were sorbet and the pH tends to the initial value.

REFERENCES

[1] A.M. El-Kamash, *Journal of Hazardous Materials* 151 (**2008**) 432–445.
[2] Anderson Marcos Dias Canteli, Luciana Igarashi-Mafra, Danielle Carpine, Agnes de Paula Scheer, Marcos R. Mafra, Fixed-bed column adsorption of the coffee aroma compound benzaldehyde from aqueous solution onto granular activated carbon from coconut husk (**2014**)
[3] Asok Adak, Manas Bandyopadhyay, Anjali Pal, *Dyes and Pigments* 69 (**2006**) 245-251.
[4] Cybelle Morales Futalan, Chi-Chuan Kan, Maria Lourdes Dalida, Chelo Pascua, Meng-Wei Wan, *Carbohydrate Polymers* 83 (**2011**) 697–704.
[5] Emine Malkoc, Yasar Nuhoglu *Journal of Hazardous Materials* B135 (**2006**) 328–336.
[6] Emmanuel I. Unuabonah, Bamidele I. Olu-Owolabi, Esther I. Fasuyi, Kayode O. Adebowale, *Journal of Hazardous Materials* 179 (**2010**) 415–423.
[7] Emmanuel I. Unuabonah, Mohammad I. El-Khaiary, Bamidele I. Olu-Owolabi, Kayode O. Adebowale, *chemical engineering research and design* 90 (**2012**) 1105–1115.
[8] Ensar Oguz, Muhammed Ersoy, *Ecotoxicology and Environmental Safety* 99(**2014**)54–60.
[9] Esra Bilgin Simsek,, Ulker Beker, Bahire Filiz Senkal, *Desalination* 349 (**2014**) 39–50.
[10] F.A. Batzias, D.K. Sidiras, *Journal of Hazardous Materials*,114(**2004**), 167–174.
[11] G.M. Walker, L.R. Weatherley, *War. Res.* Vol. 31, No. 8, pp. 2093~101, 1997.
[12] G.M. Walker, L.R. Weatherley, *Environmental Pollution* 99 (**1998**) 133-136.
[13] Lavinia Tofan, Carmen Teodosiua, Carmen Paduraru, Rodica Wenkert, *Applied Surface Science,* 285P (**2013**) 33– 39.
[14] M. Calero, F. Hernáinz, G. Blázquez, G. Tenorio, M.A. Martín-Lara, *Journal of Hazardous Materials* 171 (**2009**) 886–893.
[15] M.L.G. Vieira, V.M. Esquerdo, L.R. Nobre, G.L. Dotto, L.A.A. Pinto, *Journal of Industrial and Engineering Chemistry,* 20 (**2014**) 3387–3393 (2013).
[16] Md. Tamez Uddin, Md. Rukanuzzaman, Md. Maksudur Rahman Khan, Md. Akhtarul Islam, *Journal of Environmental Management*, 90 (**2009**)3443–3450.
[17] Mike A. Acheampong, Kannan Pakshirajan, Ajit P. Annachhatre, Piet N.L. Lens, *Journal of Industrial and Engineering Chemistry* 19 (**2013**) 841–848.
[18] Min-Yu Teng, Su-Hsia Lin, *Desalination* 201 (**2006**) 71–81.

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[19] Mouloud Lezehari, Michel Baudu, Omar Bouras, Jean-Philippe Basly, *Journal of Colloid and Interface Science* 379 (2012) 101–106 (**2012**)

[20] Mustafa Turan, Ugur Mart, Baris Yuksel, Mehmet S. Celik, *Chemosphere* 60 (**2005**) 1487–1492.

[21] P. Lodeiro, R. Herrero, M.E. Sastre de Vicente T, *Journal of Hazardous Materials* B137 (**2006**) 244–253.

[22] Runping Han, Yu Wang, Xin Zhao, Yuanfeng Wang, Fuling Xie, Junmei Cheng, Mingsheng, Tang *Journal of Hazardous Materials* 141 (2007) 713–718 (**2008**).

[23] Runping Han, Yuanfeng Wang, Weihong Yu, WeihuaZou, Jie Shi, Hongmin Liu, *Journal of Hazardous Materials*141(**2007**)713–718.

[24] S.Y. Quek, B. Al-Duri, *Chemical Engineering and Processing* 46 (**2007**) 477–485.

[25] Salwa A. Ahmed, *Carbohydrate Polymers* 83 (**2011**) 1470–1478.

[26] Su-Hsia Lin Ruey-Shin Juang Yuen-HuaWang, *Journal of Hazardous Materials* 113 (**2004**) 195–200.

[27] XuegangLuo, Feng Liu, Zaifang Deng, Xiaoyan Lin, *Carbohydrate Polymers* 86 (**2011**) 753– 759.

[28] Y.E. Benkli, M.F. Can, M. Turan, M.S. Celik, *Water Research* 39 (**2005**) 487–493.

[29] Yu-Na Hu, Hao-Yi Wang, Gui-Ping Cao, Chen Meng, Wei-Kang Yuan, *Desalination* 279 (**2011**) 54–60

[30] Z. Zulfadhly, M.D. Mashitah, S. Bhatia, *Environmental Pollution* 112 (**2001**) 463-470.