

Removal of pollutants from freshwater using foam biocomposites in a fixed bed packed column: Adsorption and kinetic study

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Abstract—In this study, biocomposite materials have been synthesized and used in freshwater treatment. Total solids (TS) such as silt, clay, organic matter, organic compounds and dissolved inorganics were measured in terms of turbidity. Ground natural fibers with particles size < 300 μm including coconut coir, palm leaves, rice and wheat straw were sieved and mixed with foamed polyurethane. The removal efficiency of total solids using foamed polyurethane biocomposites was compared with commercial activated carbon. Significant removal of total solids was observed using PU-biocomposite. Removal efficiency has been obtained up to 80 % using PU- ground rice straw, PU-palm leaves, PU-wheat straw and PU-coconut coir biocomposites showed 67%, 64% and 68% total solids removal respectively. Experiments were conducted in a vertical Plexiglas cylindrical packed column filled with hollow spherical PU-biocomposites with 5mm diameter. Langmuir and Freundlich adsorption isotherm equilibrium models were applied and evaluated. Surface morphology of biocomposites was investigated using scanning electron microscope.

Keywords— Bio-composites; fresh water; bioadsorbent; foam

I. INTRODUCTION

Pollutants are transported and transformed in water, atmospheric air and sites (soil). Water, air and soil are named as environmental impellers and connected to each other by to the global water cycle. Water treatment can be classified in to main three groups (i) Mechanical (ii) Biological and (iii) physical /chemical processes as illustrated in figure 1.

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Process selection depends on the type of pollutants have to be removed. Settleable (undissolved) solids can be removed by mechanical process. Dissolved solids can be removed by biological or physical/chemical processes. Biological process can be carried out if the pollutants are biodegradable. Physical/chemical process can be applied to remove the non-biodegradable matters where are found in industrial wastewater and ground water. Adsorption process is one of the most effective techniques can be applied to remove non-biodegradable matters. Adsorption process can be taken place by physisorption or chemisorption process. Adsorbate is attached to the adsorbent physically by Van der Waals forces. The chemisorption can be achieved by chemical bond with the molecules of the adsorbent. Adsorption processes based on physisorption can usually be reversed. Mass transfer of the adsorbate includes mainly four stages (i) convection, (ii) film diffusion (iii) grain diffusion and then (iv) Attachment by physical or chemical bonding. Kinetics of adsorption can be controlled mainly by film diffusion and grain diffusion [1-4]. Adsorbent has an outer and inner surface. The inner surface represents the overall surface of all pores. Pore size and structure play a crucial role in the adsorption capacity. PU-biocomposites have different applications [5-7]. Recently, considerable efforts have been made for agricultural waste recycle [8-9]. In this study, a closed system was used. Foam polyurethane biocomposites (PU-Biocomposites) were used as adsorbent. The pollutants (adsorbate) concentrations decrease in water with respect to time. While the loading PU-biocomposites increases [10-15]. Mass of pollutants (adsorbate) “ m_1 ” removed from water at a given level at time “ t ” as given in equation 1:

$$m_1 = V_w \times [c_0 - c(t)] \quad (\text{Eq. 1})$$

Where V_w : volume of water sample (L); c_0 : Initial concentration of the adsorbate (mg/l); and $c(t)$: adsorbate concentration (mg/l) with respect to time (t).

The common adsorption isotherm methods are Freundlich, Langmuir and Redlich-Peterson as tabulated in table 1 [16-20]. In this study, data fitting was carried out with respect to Freundlich, and Langmuir-2.

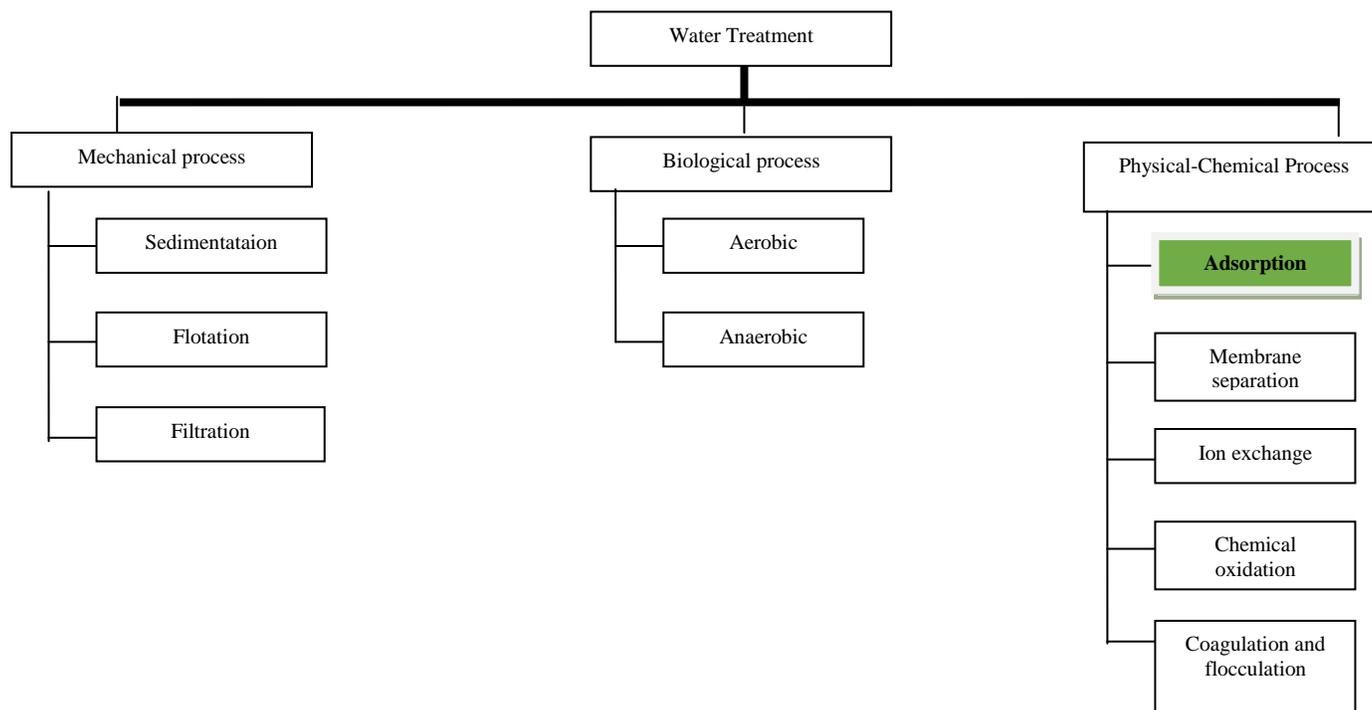


Fig. 1 Schematic diagram of water treatment processes

TABLE I ISOTHERM MODELS

Isotherm	
Freundlich	$q_e = K_F C_e^{1/n}$
Langmuir 1,2,3 and 4	$q_e = \frac{q_m K_a C_e}{1 + K_a C_e}$
Redlich-Peterson	$q_e = \frac{A C_e}{1 + B C_e^g}$

Mass of pollutants (adsorbate) “ m_2 ” adsorbed by PU-biocomposites at a given level and time “ t ” can be given by equation 2.

$$m_2 = m_{PU-Biocomposite} [q(t) - q_0] \quad (\text{Eq. 2})$$

Where; $m_{PU-Biocomposites}$: mass of adsorbent (g); q_0 : initial loading (mg/g) at time=0; $q(t)$: loading (mg/g) at time (t). Since m_1 is equal to m_2 , the resulting equation (3) is:

$$V_w \times [c_0 - c(t)] = m_{PU-Biocomposite} [q(t) - q_0] \quad (\text{Eq. 3})$$

Langmuir and Freundlich adsorption isotherm models are widely used for data fitting. Results can interpret the relationship between sorbed and aqueous concentration at equilibrium. Langmuir model hypothesize that the monolayer adsorption of adsorbed ions occurred on an even

$$q_e = \frac{K_L C_e}{1 + a_L C_e} \quad (\text{Eq.4})$$

surface with no interactions among the adsorbed ions [21-26]. The Langmuir model can be presented by equation 4:

where q_e (mg/g) is the amount of ions adsorbed onto the unit mass of the adsorbent. K_L is the Langmuir equilibrium constant; C_e is the concentration of ion in solution, and a_L is the Langmuir constant [27-30]. The constant K_L which indicates the reactivity of binding sites and a_L are the characteristics of the Langmuir equation and can be determined from a linearized form of Langmuir model. Langmuir isotherm can be linearized

Freundlich equation is an empirical equation based on adsorption on a heterogeneous surface. The equation is commonly given by equation 5:

$$q_e = a C_e^b \quad (\text{Eq.5})$$

where a and b are the Freundlich constants. They indicate the adsorption capacity and the adsorption intensity, respectively. To simplify the derivation of (a) and (b) in equation 5. It can be linearized as:

$$\text{Log} q_e = b \text{log} C_e + \text{log} a \quad (\text{Eq.6})$$

Therefore, the constant a and exponent b can be determined by plotting $\text{log} q_e$ versus $\text{log} C_e$. The Langmuir and Freundlich models were applied to describe the values derived from the adsorption of TS by each bioadsorbent through concentration range (1-10 g/l).

II. EXPERIMENTAL

2.1 MATERIAL AND METHODS

2.1.1 RAW MATERIALS

Commercial castor oil (polyol) was purchased, Egypt market. The polyol functionality, hydroxyl value (KOH/g) and

molecular weight are 2.64, 161 and 930 respectively. Water content was removed by heating the polyol at 90 °C for 4 h under vacuum (-1 bar). Polymeric diphenyl methane di-isocyanate (PMDI) was received from DOW Company. PMDI (NCO 33% wt/wt) was used without further purification. Activated carbon was obtained from Samoral Company, Egypt. Coconut coir; palm leaves, rice and wheat straw were collected from the agricultural fields. Fibers were ground using ball-mill at 300 r.p.m. for 6 h.

2.1.2 POLYURETHANE SYNTHESIS

Polyurethane foam was synthesized using polymeric diphenyl methane di-isocyanate (PMDI) and castor oil in the presence of distilled water (4.2 % wt/wt). Dispersing agent (Anfomu 5000) was added to control the cell size. PMDI was added gradually to the castor oil at room temperature. Exothermic reaction was generated due to isocyanates – hydroxyl reaction. Water cooling system was applied to keep the temperature of the exothermic system around 30 °C. Mixing time is 20 minutes with 1000 r.p.m. speed.

2.1.3 PREPARATION OF NATURAL FIBERS

Natural fibers were collected, ground and then sieved to obtain an average grain size less than 300 µm as shown in figure 2. Pores generation have been obtained by increasing the fiber surface roughness in the presence of dilute sodium hydroxide 5 (w/w) %. Ground natural fibers were dried at 100 °C for 24 hours.

2.1.4 SYNTHESIS OF BIO-COMPOSITES

Ground natural fibers were sieved to maintain particle size less than 300µm. Ground natural fibers were mixed with the polyol (castor oil) before starting the addition polymerization. Intensive mixing rate 2000 r.p.m. was applied for creating good bioparticles dispersion in the PU matrix. The bio-composite in liquid state is injected into the mould after 20 minutes under pressure.

2.1.5 MOULD

Aluminum mould with a Teflon layer coating was used to prepare the PU- ground natural fiber bio-composites. Figure 3 shows the mould components. The adsorbents are produced in hollow sphere shapes. Outside and inside diameter are 30 mm and 25 mm respectively.

2.1.6 SYNTHESIS OF POLYURETHANE USING RESIN TRANSFER MOLDING (RTM)

Polyurethane foam-bio-composite production unit consists of four main parts: (i) Two storage tanks filled up polyol and PMDI, these tanks connected with two drums one of them for polyol and other for isocyanate, pressurized by pumps to deliver the material from the drums to the tanks. (ii) Mixing unit to mix the polyol and isocyanate into the cup and pump the mixture into the mold. (iii) Secondly ram for polyurethane injection after mixing process. (iv) Rotating mold holder to hold the mould. There is control panel to control pressure, flowrate of polyol and isocyanate to optimize the mixing ratio and temperature. Control panel includes timer to adjust methylene chloride as cleaning solvent. Chiller was used to cool the mould and the mixing head. The mold made of

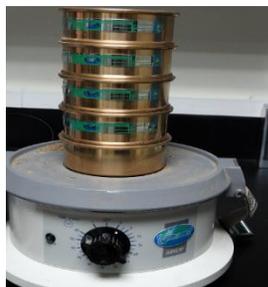


Fig. 2 Sieving unit



Fig. 3 Mold consists of four hollow spheres

aluminum, It consists of two sides each side contain 4 semi-circle each one of them with diameter 4 cm, also there are 2 steel stick with diameter 2 cm, which make hole in the polyurethane ball.

2.1.7 ADSORPTION UNIT

The adsorption process was conducted using one step adsorption unit (CE 583, GUNT, Germany). The adsorber is incorporated into the pipe system at both ends by flange connections. The flanges are sealed with screws. Adsorber column was filled during operation with foam PU-Bio-composites fixed bed. There is a sintered metal base plate in the bottom flange of each adsorber. The base plate ensures that the composites remain in the adsorbers. Adsorber is used to conduct and evaluate the experiments. Therefore this adsorber is fitted with eight sampling valves (V5...V12). These sampling valves are used to determine the trend of the adsorbate concentration in the fixed bed of adsorber (concentration profile). The distance between each of the sampling valves is 5cm. Adsorber is fitted with a bleed valve at the upper end (V13, V18) as shown in figure 4.

Removal efficiency (E) of the adsorbent on (TS solids) turbidity, is given by equation 7:

$$E (\%) = [(C_0 - C_1) / C_0] \times 100 \quad (\text{Eq.7})$$

Where C_1 and C_0 are equilibrium TS and initial concentration in fresh water (mg/l), respectively. The TS sorption was studied by varying the concentrations of adsorbents from 1 to 10 g/l, at pH = 7.3 and room temperature. Contact time was adjusted to 30 min.

2.1.8 MICROSCOPY MEASUREMENTS

The morphology of PU-ground fiber composites were investigated using scanning electron microscopy. Bioparticles conductivity was improved by spraying monolayers of gold. Fractured surfaces of the bio-composites were examined under a scanning electron microscope (SEM), JEOL model JXA 840A (ADS+OM-Japan).

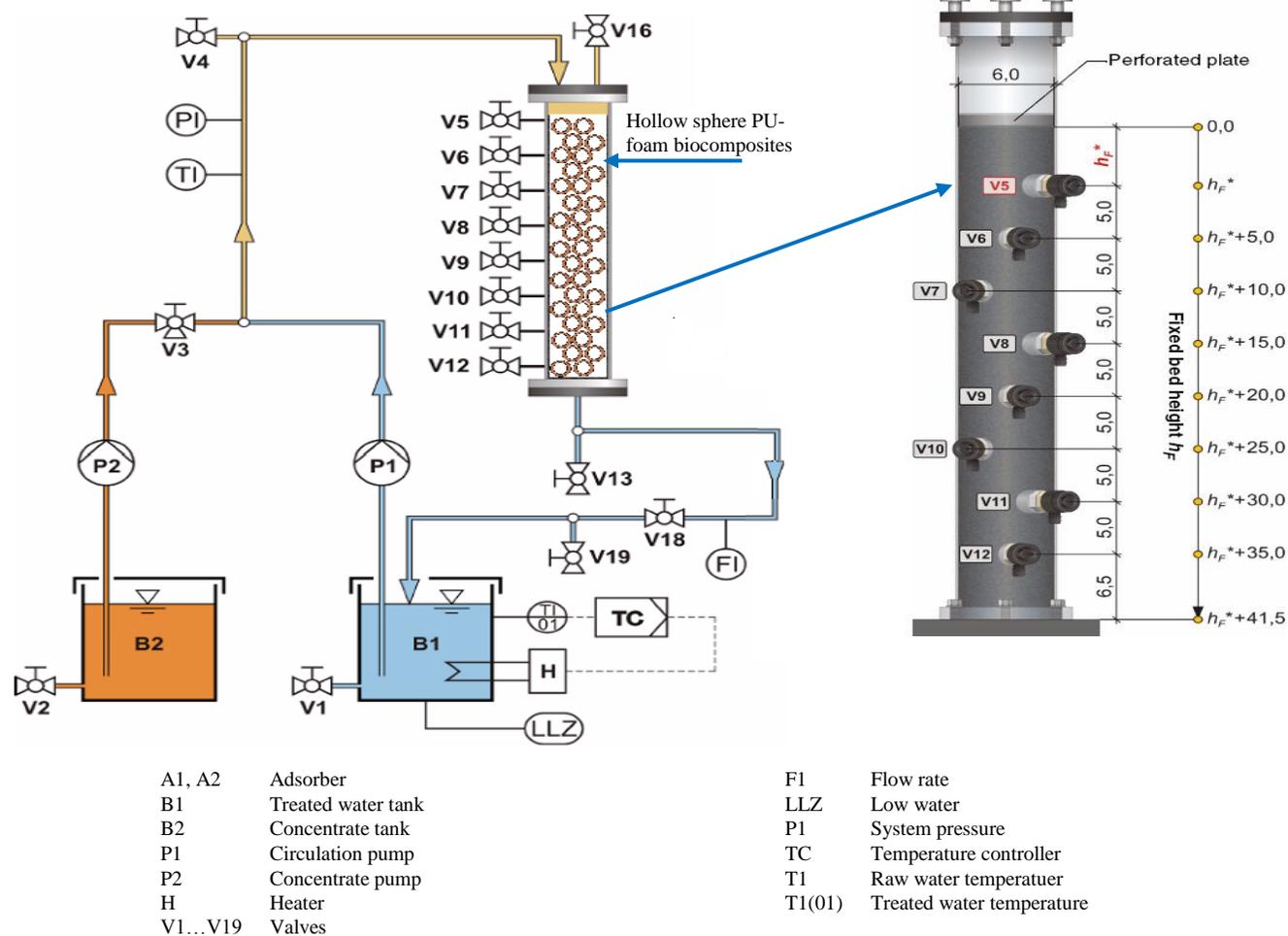


Fig. 4 Adsorption unit

III. RESULTS AND DISCUSSION

3. 3.1 Efficiency Of Ts Removal

The dependence of TS sorption on PU- biocomposites was studied by varying the amount of adsorbents from 3 to 13 g/l. Figure 5 shows the TS removal efficiency for four types of bio-composites adsorbents and the activated carbon at pH=7.0 and room temperature. Removal efficiency of the adsorbents is enhanced with increasing dose. This is can be attributed to the fact that the higher dose of adsorbents gives better probability of exchangeable sites for the ions in the water solution. Removal efficiency showed slight or no noticeable adsorption change using activated carbon in 9-10g/l range. It is supposed that after a particular concentration of adsorbent, the amount of ions attached and free remains constant even with increasing the concentration of adsorbent.

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3.3.2 Modeling and simulation

In this study, Langmuir and Freundlich models have been applied on PU foam-ground rice straw Biocomposites adsorbents and activated carbon. Fig. 6 and 7 show the fitting of the results using Langumire and Freundlich models respectively. It is depicted that Langmuir model has a better data fitting than Frundlich as the bio-composite former have higher correlation regression coefficient than the latter. This can be explained due to formation of TS monolayer on the surface of adsorbent. This can be obtained when the adsorbent has a low surface area. Therefore, only monolayer of adsorbate is collected on the surface of the adsorbent.

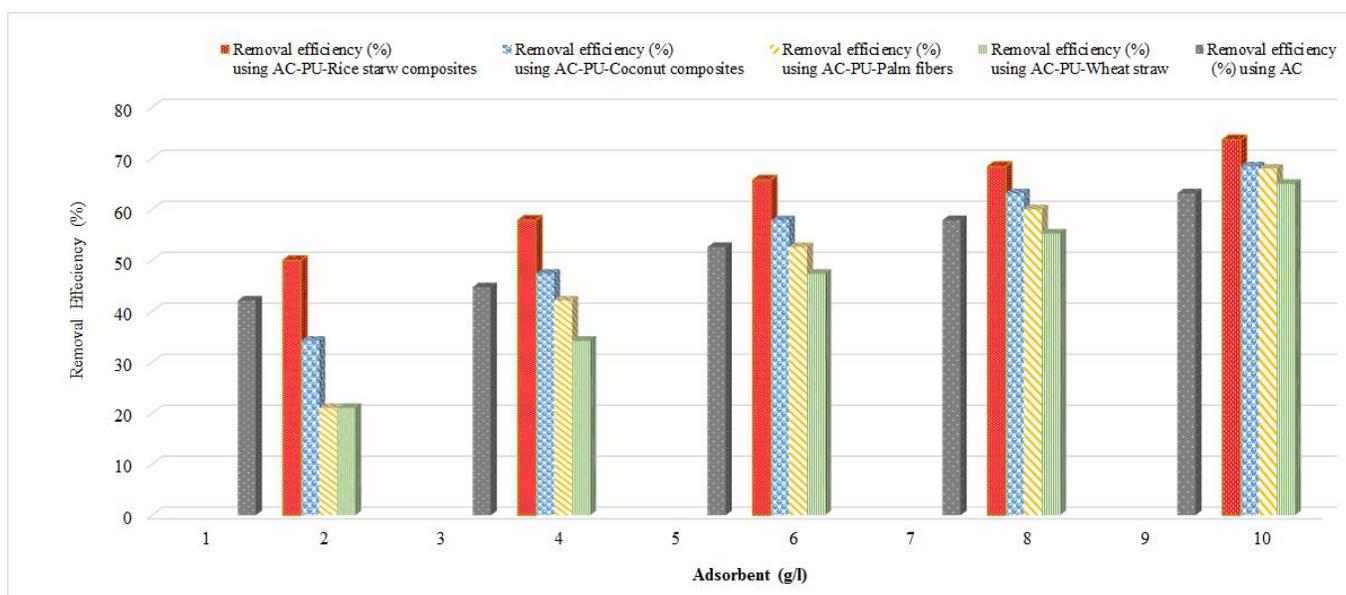


Fig. 5 Bioadsorbents concentration vs removal efficiency

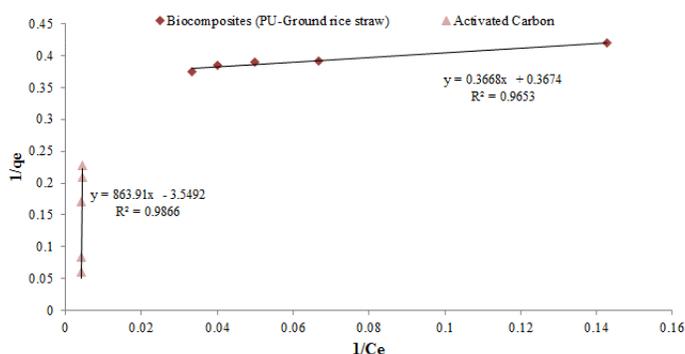


Figure 6 Data fitting to Langmuir Model

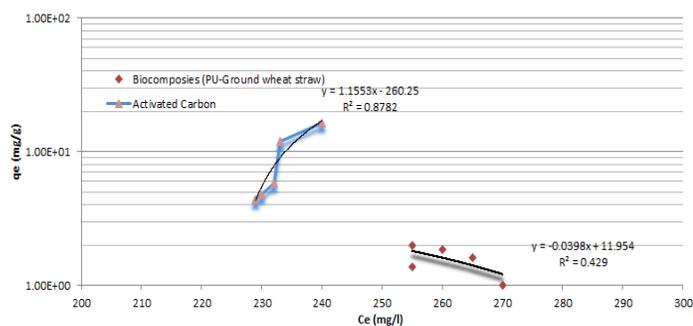


Figure 7 Data fitting to Freundlich model

3.3.3 Sem Analysis

Figure 8 shows the SEM analysis of the fracture surface (PU-biocomposites adsorbents). Average foam cell is 5µm. Ground rice straw particles are well dispersed. Accordingly, this can improve the adsorption process. Additionally, Surface roughness would assist the biocomposite materials to adsorb the inorganic and organic substances contained in the fresh water and created strong interactions.

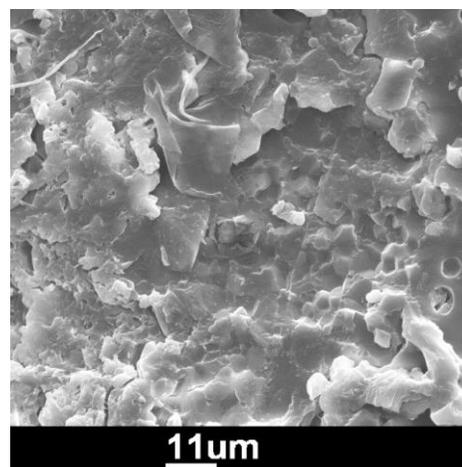


Figure 8 SEM PU-ground rice straw biocomposites

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REFERENCES

- [1] Aksu, Z., Determination of the equilibrium, kinetic and thermodynamic parameters of the batch biosorption of nickel (II) ions onto *Chlorella vulgaris*. *Process Biochem.* 2002, 9938, pp.89. [http://dx.doi.org/10.1016/S0032-9592\(02\)00051-1](http://dx.doi.org/10.1016/S0032-9592(02)00051-1)
- [2] M. H. Abdel-Aziz, I. Nirdosh, G. H. Sedahmed, Ion exchange-assisted electrochemical removal of heavy metals from dilute solutions in a stirred tank electrochemical reactor: A mass transfer study, *Industrial and Engineering Chemistry Research* 52 (2013) 11655 – 11662. <http://dx.doi.org/10.1021/ie400548w>
- [3] G. H. Sedahmed, Y. A. El-Taweel, A.H. Konsowa, M. H. Abdel-Aziz, Mass transfer intensification in an annular electrochemical reactor by an

- inert fixed bed under various hydrodynamic conditions, *Chemical Engineering and Processing*, 50 (2011) 1122 – 1127.
<http://dx.doi.org/10.1016/j.ccep.2011.10.002>
- [4] Babel, S. & Kurniawan, T. A., 2004. Cr (VI) removal from synthetic wastewater using coconut shell charcoal and commercial activated carbon modified with oxidizing agents and/or chitosan. *Chemosphere*, 54 (7), pp. 951-967.
<http://dx.doi.org/10.1016/j.chemosphere.2003.10.001>
- [5] Omar Farouk, the use of rice straw and husk fibers as reinforcements in composites, *Biofiber reinforcement in composite materials*, 1st edition, Woodhead Publishing Limited , , ISBN 1 78242 122 X, ISBN-13: 978 1 78242 122 1, 2014.
- [6] Sayed A.Sherif, M.A.Sadek, F.H.Ashour, M. Bassyouni, 2009. Effects of surface treatment of ground rice husk on the polyurethane based on castor oil. *Polymer & Polymer composites*, 17 (8), pp 467-471.
- [7] M. Bassyouni , Sayed A., Sherif , M.A., Sadek and F.H., Ashour, Synthesis and characterization of Polyurethane – treated waste milled light bulbs composites, *Composites Part B: Engineering*, Volume 43, Issue 3, April 2012, PP1439–1444.
<http://dx.doi.org/10.1016/j.compositesb.2011.08.014>
- [8] M. Bassyouni, Waheed Ul hassan, Farid Nasir bin Ani, M.H. Abdel-aziz, S. M.S Abdel-hamid, date palm waste gasification in downdraft gasifier and simulation using Aspen HYSYS, *Journal of energy conversion and management*, 2014, 88, 693-699, 2014.
- [9] M. Bassyouni, I. Taha, Shereen M.-S. Abdel-hamid and L. Steuernagel “Physico-Mechanical Properties of Chemically Treated Polypropylene Rice Straw bio-Composites”. *Journal of Reinforced Plastics and Composites*, March 2012 31: 303-312, 2012
- [10] Bojic, A.L. Bojic, D. & Andjelkovic, T., 2009. Removal of Cu²⁺ and Zn²⁺ from model wastewaters by spontaneous reduction–coagulation process in flow conditions, *Journal of Hazardous Materials*, 168, pp.213-218.
<http://dx.doi.org/10.1016/j.jhazmat.2009.02.096>
- [11] Cestari, A.R. Vieira, E.F.S. Lopes, E.C.N. & Da Silva, R.G., 2004. Kinetics and equilibrium.
- [12] Chantawong, V. Harvey, N. W.& Bashkin, V. N., 2003.Comparison of Heavy Metals Adsorption by Thai Kaolin and Ballclay. *Water Air Soil Pollution*, 148, pp. 111-125.
<http://dx.doi.org/10.1023/A:1025401927023>
- [13] Chen, J. Yiacoumi, S.& Blydes, T. G., 1996. Equilibrium and kinetic studies of copper adsorption by activated carbon. *Sep. Tech.*, 6, pp. 33–146.
[http://dx.doi.org/10.1016/0956-9618\(96\)00146-4](http://dx.doi.org/10.1016/0956-9618(96)00146-4)
- [14] Corapcioglu, M. O.& Huang, C. P., (1987). The adsorption of heavy metals onto hydrous activated carbon. *Water Res.*, 21(9), pp. 1031-1044.
[http://dx.doi.org/10.1016/0043-1354\(87\)90024-8](http://dx.doi.org/10.1016/0043-1354(87)90024-8)
- [15] Dakiky, M. Khamis, A. Manassra, M. M., 2002. Selective adsorption of chromium (VI) in industrial wastewater using low-cost abundantly available adsorbents, *Adv. Environ. Res.*, 6 (4) (2002) 533–540.
[http://dx.doi.org/10.1016/S1093-0191\(01\)00079-X](http://dx.doi.org/10.1016/S1093-0191(01)00079-X)
- [16] G. Vijaya Lakshmi, N. Chitti Babu, P. V. Ravi Kumar, D. Subba Rao & P. Venkateswarlu,(2008), potential of erythrina variegata orientalis leaf powder for the removal of cobalt(ii), *Chemical Engineering Communications*, Volume 196, Issue 4.
- [17] Ho,Y.S., 2006. Isotherms for the sorption of lead onto peat: comparison of linear and non-linear methods. *Polish journal of environmental studies*, 15(1), pp. 81-86.
- [18] Issabayeva, G. Aroua, M. K. & Sulaiman, N. M., 2007.Continuous adsorption of lead ions in a column packed with palm shell activated carbon. *Journal of Hazardous materials*, 155 (1-2), pp. 109-113.
<http://dx.doi.org/10.1016/j.jhazmat.2007.11.036>
- [19] K.Z. Mohammed, A. Hammdy, A. Abdel-wahab, N .A. Farid. Temperature Effect on corrosion Inhibition of Carbon Steel in Formation Water by Non-ionic Inhibitor and Synergistic Influence of Halide Ions. *Life Sci J* 2012; 9(2):424-434.
- [20] Lee, H. Kuan,Y.C.& Chern, J.M. 2007. Equilibrium and kinetics of heavy metal ion exchange, *Journal of the Chinese Institute of Chemical Engineers*, 38, pp. 71–84.
<http://dx.doi.org/10.1016/j.jcice.2006.11.001>
- [21] Malek, A. & Farooq, S., 1996. Comparison of isotherm models for hydrocarbon adsorption on activated carbon, *AIChE Journal*. 42, pp. 3191–3201.
<http://dx.doi.org/10.1002/aic.690421120>
- [22] Mohan, D. & Pittman, C.U., 2007. Arsenic removal from water/wastewater using adsorbents- A critical review. *Journal of Hazardous materials*, 142, pp.1-53.
<http://dx.doi.org/10.1016/j.jhazmat.2007.01.006>
- [23] Nabi Saheb D., & Jog J. P. 1999. Natural Fiber Polymer Composites: A Review. *Advances in polymer technology*, 18, 351-363.
[http://dx.doi.org/10.1002/\(SICI\)1098-2329\(199924\)18:4<351::AID-ADV6>3.0.CO;2-X](http://dx.doi.org/10.1002/(SICI)1098-2329(199924)18:4<351::AID-ADV6>3.0.CO;2-X)
- [24] Sekar, M. Sakthi,V. & Rengaraj,S., 2004. Kinetics and equilibrium adsorption study of lead (II) onto activated carbon prepared from Coconut Shell,” *J. Colloid Interface Sci.*, 279, pp. 307.
<http://dx.doi.org/10.1016/j.jcis.2004.06.042>
- [25] Shaidan, N.H. Eldemerdash, U. Awad, S., 2011. Removal of Ni(II) ions from aqueous solutions using fixed-bed ion exchange column technique, *Journal of the Taiwan Institute of Chemical Engineers*.
- [26] Sofiane Ben Hamouda, Ali Boubakri, Quang Trong Nguyen, and Mohamed Ben Amor, 2011, PEBA membranes for water desalination by pervaporation process, high performance polymer, 23(2) 170–173
- [27] Volesky, B., 2003. Sorption and Biosorption, BV Sorbex, Inc., 0-9732 983-0-8, Canada.
- [28] Wang, L.H. & Lin, C., 2010. The removal of heavy metal ions from spiked aqueous solutions using solid wastes-Comparison of sorption capability, *Journal of the Taiwan Institute of Chemical Engineers*, 41, pp. 585–590.
<http://dx.doi.org/10.1016/j.jtice.2010.01.005>
- [29] Yuh-Shan Ho , 2006 Polish Journal of Environmental Studies Vol. 15, No. 1 (2006), Isotherms for the Sorption of Lead onto Peat Comparison of Linear and Non-Linear Methods81-86.
- [30] Zvinowanda, C. M. Okonkwo, J. O. Shabalala, P. N.& Agyei,N. M., 2009. A novel adsorbent for heavy metal remediation in aqueous environments. *International Journal of Environmental Science Technology*, 6 (3), pp. 425-434.
<http://dx.doi.org/10.1007/BF03326081>