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ADSORPTION STUDIES OF LEACHATE ON COCKLE SHELLS

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ABSTRACT: Sanitary landfills are important means of disposing municipal solid waste in developing countries. However, these landfills are associated with the generation of leachate, which if untreated may pose severe public health risk and may damage the ecosystem in the long term. In this study, cockle shells were explored as an adsorbent media for the treatment of a stabilized landfill leachate. The optimum shaking speed, pH, and dosage for chemical oxygen demand (COD) parameter removal were investigated using the adsorbent media of particle sizes ranging from 2.00 mm to 3.35 mm. Leachate characteristics were then determined. Results indicated that leachate is non-biodegradable with high concentrations of COD (1763 mg/L), ammonia nitrogen (573 mg/L), and biochemical oxygen demand/COD (0.09). The optimum conditions for shaking were determined at 150 rpm according to the adsorption of COD by the media. Optimum pH and dosage was 5.5 and 35 g/L, respectively. The adsorption isotherms indicated that Langmuir isotherm is better fitted than Freundlich isotherm.

Keywords: Cockle shells, dosage, Isotherm, Leachate, Optimum shaking speed, pH.

1. INTRODUCTION

Leachate is the wastewater generated from the biochemical reaction that occurs inside a waste deposit in a sanitary landfill. The process occurs when waste undergoes physical, chemical, and biological decomposition under aerobic and anaerobic conditions. Leachate usually contains dissolved contaminants, volatile organic acids, toxic heavy elements, and high concentrations of organic matter, chemical oxygen demand (COD), ammonia nitrogen, and biochemical oxygen demand (BOD5) [2–7]. When leachate containing high levels of dissolved contaminants is directly discharged into the environment, it may contaminate soil and water bodies, seriously threatening the environment and public health [8–13].

Many conventional landfill leachate treatments involve high-technology processes. To meet discharge standards, the conventional methods that generate residues are saddled with high initial and operational costs and low applicability to a wide variety of pollutants, among others [14–21]. In recent years, an increasing number of research looks into the potential application of other adsorbents (e.g., agricultural waste or natural polymers and by-products of industrial processes) to achieve appropriate leachate treatment or as an alternative approach to conventional media for the treatment of pollutants that exist wastewater.

For example, gravel sand and peat soil have been explored as a possible treatment of kitchen wastewater, fruit waste has also been analyzed for the removal of heavy metal in wastewater, and the application of certain crops has been postulated for the removal of heavy metal from specific contaminated soils [22–24]. Although adsorption through activated carbon is extremely popular, only a few studies focus on the application of cockle shells (CS) as a substitute of conventional media in landfill leachate treatment. Cockle is small, edible, marine bivalve molluscs living along sandy beaches. In this study, loose CS was experimentally investigated to determine the optimum parameter of agitation speed, pH, and dosage in the removal of COD from a stabilized landfill leachate.

2. MATERIALS AND METHOD

2.1 Sampling

The leachate sample was collected manually from Simpang Renggam municipal landfill site in Johor, located at latitude 10 53’41.64” N and longitude 1030 22’34.68” E in Kluang District. [25]. The initial size of the area was only approximately 8 acres, which was insufficient to accommodate the high volume of waste being transported.

The landfill receives roughly 250 tons of waste every day. Hence, the government has established a new sanitary landfill beside the existing one to cater for the volume of waste transported from the surrounding districts [26].

Raw leachate samples were collected from the influent of the detention pond in clean 20-L high-density polyethylene plastic containers, were transported to the wastewater research laboratory, and were stored at 4 °C in a cold room at Universiti Tun Hussein Onn Malaysia (UTHM) to minimize any change in their initial characteristics. All chemical analyses for leachate characterization were performed within the following 24 h in accordance with the Standard Methods for the Examination of Water and Wastewater [27]. All chemicals used were of analytical grade.

2.2 Adsorbent Preparation

The CS were obtained from several commercial restaurants in Batu Pahat area in Johor. The preparation was conducted according to the procedure outlined by [28, 29]. The CS were brushed and washed thoroughly with tap water, rinsed with distilled water, and air-dried for 24 h. These samples were then oven-dried at 105 °C and air-cooled to room temperature before being pulverized. Subsequently, the shells were sorted into crushed sizes from 2.0 mm to 3.35 mm [13]. The chemical composition of the media was determined using an X-ray fluorescence spectrometry (Model Bruker S4 Pioneer), whereas its density was obtained conventionally (dry weight/volume). Table 2 indicates the composition of the CS.

Formula	Cockle shell (%)
CO_2	0.10
SiO_2	0.30
Fe_2O_3	0.80
K_2O	3.55
CaO	92.00
Na_2O	0.92

2.3 Batch study

The optimum equilibrium conditions for batch study were determined at ambient temperature at a fixed time of 105 min for shaking speed and pH using 8 g of media and 100 ml of raw leachate or 80 g/L of biosorbent concentration. The agitation speed was changed from 50 to 200 using an orbital shaker (DAIKI), and the pH was adjusted from 2 to 10 using sodium hydroxide and hydrochloric acid.

All samples were assessed in triplicate under identical conditions, and the average was obtained. The adsorbent dose was determined by applying 8–64 g/L of the adsorbent. Samples were analyzed for COD, which is one of the major contaminants in leachate. The COD in mg/L was measured using an ultraviolet-visible spectrophotometer (HACH DR6000) [27]. The quantity of the adsorbed COD per unit CS was evaluated using Equation (1).

$$q_e = \frac{(C_o - C_e)\mathrm{V}}{\mathrm{m}} \quad (1)$$

Where C_o = initial concentration in leachate (mg L^{-1}),
C_e = leachate concentration at equilibrium (mg L^{-1}),
V = leachate volume (L),
m = adsorbent mass (g).

The COD percentage removal (%) was evaluated with equation (2).

$$\text{Removal (\%)} = \frac{(C_o - C_e)}{C_o} \text{ x } 100 \quad (2)$$

3. RESULTS AND DISCUSSION

3.1 Chemical analysis of leachate

Numerous published studies describe the variations in leachate quality from different landfills [28]. Table 1 presents the characteristics of the leachate used in this study. The leachate has a high amount of COD, ammonia nitrogen, and iron (Fe) (see Table 1). The average values of BOD5 and COD are 164 and 1763 mg/L, respectively. The biodegradability ratio (BOD5/COD) of a raw leachate ranges from 0.06 to 0.15 with an average of 0.09 (see Table 1). The data of the BOD5 and COD indicate that the leachate is evidently stabilized.

A stabilized leachate usually has high NH3-N (>400 mg/L) and COD (<3000 mg/L) but low biodegradability ratio [2]. The pH of leachate ranges from 7.85 to 8.26 with an average of 8.11, and it usually increases with time, reflecting the decrease in concentration of the partially ionized free volatile fatty acids [3]. A previous research has shown that the pH of a stabilized leachate is greater than 7.5 [30]. Untreated samples in this study indicated a stabilized leachate. The concentrations of Fe are presented in Table 1. The Fe concentration in raw leachate ranges from 2.89 to 9.22, with an average value of 6.79. The amount of Fe falls outside the recommended values of the leachate standard in Malaysia.

Table 1 Characteristics of leachate obtained from Simpang renggam landfill.

Parameter	Minimum Concentration in sample	Maximum Concentration in sample	Average	* Malaysia Leachate discharge Standard (mg/L)
COD (mg/L)	1682	1844	1763	400
BOD5at 20 °C (mg/L)	114	270	164	20
Ammonia Nitrogen (mg/L)	649	541	573	5
SS (mg/L)	585	671	633	50
Color	4615	4721	4676	100
(Platinum unit, Pt-Co)	0.06	0.15	0.09	
BOD5/COD	7.85	8.26	8.11	6.0 – 9.0
pH	9.22	2.89	6.79	5.0

* Acceptable condition for discharging leachate as stated in the 2009 Environmental Quality Regulations, Second Schedule (Regulation 13)

3.2 Effect of shaking speed

Figure 1 illustrates the COD percentage removal in the sample after shaking at 50, 100, 150, and 200 rpm in an orbital shaker. The optimum removal for COD by the adsorbent occurs at 150 rpm. At the beginning of adsorption, the adsorption increases simultaneously with the agitation speed. After reaching 150 rpm, the adsorption dissipates even with a further increase in the shaking speed. Therefore, the adsorption may have attained equilibrium at 150 rpm (28%), such that no further improvement can be attained.

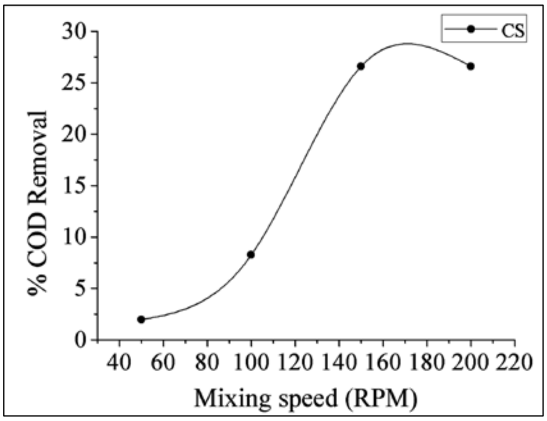

Fig.1 COD removal at 50,100, 150 and 200 shaking speeds

This adsorption behavior may be due to the fact that the initial kinetic energy of the adsorbents and that of the leachate molecules increase as the shaking speed increases. Consequently, the probability of interaction between the molecules and adsorbent becomes significant; hence, the amount of adsorbate increases until it reaches the equilibrium state. After reaching equilibrium, the adsorption diminishes even with the increasing shaking speed. Thus, the condition after equilibrium is possibly caused by the extremely high kinetic energy of the molecules and adsorbent particles that limited their interaction with each other [31]. Hence, 150 rpm was selected for further study.

3.3 Optimum pH

Figure 2 exhibits the percentage removal rate in the sample after the pH is adjusted from 2 to 10 and at an agitating speed of 150 rpm. A gradual increase is evident in the percentage uptake by the adsorbent up to pH5.5 (53%), and the uptake decreases from pH6 to pH10 (see Figure 2).

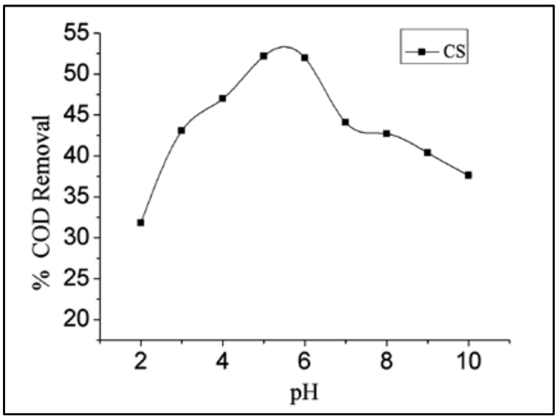

Fig.2 COD removal at pH,2, 3,4,5,6, 7,8,9 and 10

When the pH increases in the solution, the number of negatively charged sites increases, whereas that of the positively charged sites decreases, thereby resulting in an electrostatic attraction between the charged particles. The uptake process increases until it reaches equilibrium.The decrease in the uptake with an increase in pH from pH6 may be caused by the dissociation that occurs at the solid to liquid boundary because of the acid and base interaction [32]. The optimum pH condition for the COD removal is at pH5.5 (see Figure 2).

3.4 Optimum dosage

The effect of the adsorbent dosage on adsorption was evaluated with an agitation speed of 150 rpm, a pH of 5.5, and an adsorbent mass ranging from 8 g/L to 64 g/L. From the beginning, the percentage removal increases with the increase in the adsorbent dose until it reaches an optimum mass of 35 g (55%); then, the percentage removal begins to decrease with a further increment of the adsorbent dose (see Figure 3). This behavior can be explained considering that when the amount of adsorbent increases, the amount of available adsorption sites increases until the optimum mass is reached; any further increase in the adsorbent dose may result in aggregation, which can decrease the probability of molecules contacting all available adsorption sites [33, 34].

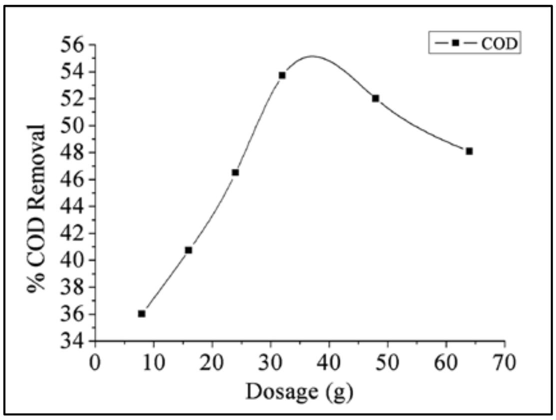

Fig 3. Optimum dosage for COD removal

3.5 Adsorption equilibrium

Adsorption equilibrium is usually plotted in the form of adsorption isotherm (at constant temperature) with the amount adsorbed and mass in the effluent fluid placed on Y- and X- axes, respectively. The isotherm study explains the process of adsorption and the interaction between the adsorbent surface and adsorbate. Langmuir and Freundlich isotherm equations have been widely used for the equilibrium modeling of adsorption systems.

3.5.1 Langmuir Isotherm.

Langmuir isotherm analyzes the formation of a monolayer adsorbate onto the adsorbent surface. This isotherm is based on the assumption that finite adsorption sites are available on the adsorbent surface and that any further adsorption can no longer be completed after these sites are occupied [35,36]. The Langmuir isotherm is represented by Equation (3).

$$\frac{1}{q_e} = \frac{q_m b.C_e}{1+b.C_e} \quad (3)$$

Where
q_e=Equilibrium sorption capacity (mgg^{-1})
C_e=Equilibrium concentration of the adsorbate ($mg\ L^{-1}$)
q_m = maximum amount of adsorbate per unit weight of adsorbent (mgg^{-1})
b = Langmuir constant related to binding sites affinity with adsorbate ($L\ mg^{-1}$)

The linearized Langmuir equation is expressed as follows:

$$\frac{1}{q_e} = \frac{1}{q_m} + \left(\frac{1}{q_m.b}\right)\left(\frac{1}{C_e}\right) \quad (4)$$

The maximum amount of adsorbate (q_m) taken in a given system can be evaluated from the isotherm. A linear plot of $\frac{1}{q_e}$ versus $\frac{1}{C_e}$ gives the slope as $\frac{1}{q_e}$ and intercept $\frac{1}{q_m}$.

3.5.2 Freundlich Isotherm.

Freundlich isotherm is an empirical model that explains heterogeneous surface adsorption in which the surface concentration of the adsorbate on the adsorbent increases with the increase in the initial concentration of the solution [36]. This isotherm can be denoted as

$$\boldsymbol{q_e = K_f . C_e^{1/n}} \quad (5)$$

The linearized equation is as follows:

$$\boldsymbol{q_e = K_f + \frac{1}{n} logC_e} \quad (6)$$

Where
$\boldsymbol{K_f}$ = freudlich constant
$\boldsymbol{n}$ = constant relating to adsorption intensity

A linear plot of $logC_e$ versus $logq_e$ gives the slope as $\frac{1}{n}$ and intercept $logk_f$.

Figures 4 and 5 illustrate the Langmuir and Freundlich isotherms, respectively. The linear plot of both isotherms implies that both are favorable for the experimental data obtained. However, the Langmuir model has higher coefficient of determination (R2) values than the Freundlich model, indicating that the former fits better than the latter. The adsorption on the adsorbent is characterized by a monolayer coverage [26].

4. CONCLUSION

The ability of the CS adsorbent to minimize COD from leachate solution is investigated. The results indicate that the optimum conditions of shaking speed, pH, and dosage for COD removal are 150 rpm, pH5.5, and 35 g/L, respectively.

Table 2. Langmuir and freundlich adsorption isotherm model parameters for COD on cockle shells

Dosage (g/L)	$C_e\ (mg/L)$	$X = (C_o - C_e)$ (mg/L)	$q_e\ (mg/L)$	$1/C_e$	$1/q_e$	$logC_e$	$logq_e$
8	1128.08	634.92	79.37	0.00089	0.01260	3.05234	1.89963
16	1044.90	718.10	44.88	0.00100	0.02228	3.01907	1.65207
24	943.36	819.64	34.15	0.00106	0.02928	2.97468	1.53341
32	816.25	946.75	29.59	0.00116	0.03380	2.91183	1.47108
48	846.44	916.56	19.09	0.00135	0.05237	2.92760	1.28092

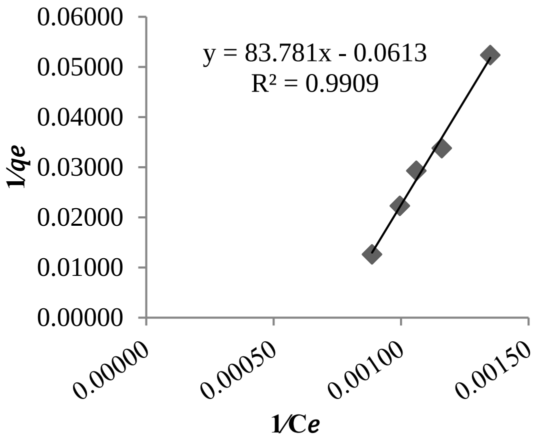

Fig.3. Langmuir isotherm

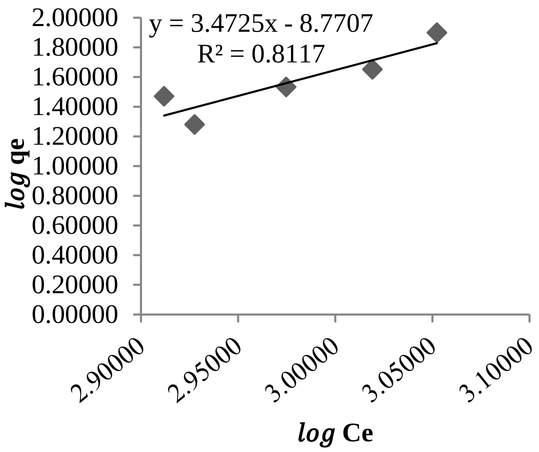

Fig.4 Freundlich isotherm

The adsorption isotherms show that the Langmuir isotherm is better fitted than the Freundlich.

The research findings expand the existing literature on alternative media for leachate treatment, especially in developing countries. Further research is in progress at the UTHM to determine other factors that may affect the field study.

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5. REFERENCES

[1] Bashir MJ, Aziz HA, Amr SS, Sethupathi SA, Ng CA, Lim JW, “The competency of various applied strategies in treating tropical municipal landfill leachate”, Desalination and Water Treatment. 2014, pp.1-4. Available frompp.httppp.//www.tandfonline.com

[2] Aziz HA, Mojiri A, editors. Wastewater Engineering: Advanced Wastewater Treatment Systems. IJSR Publications, 2014.

[3] Abdul Kadir A, Al Bakri Abdullah MM, Sandu AV, Mohamed Noor N, Latif A, Lisanah A, Hussin K, “Usage of palm shell activated carbon to treat landfill leachate”, International Journal of Conversion Science, 5(1), 2014, pp.117-126.

[4] Daud Z, Aziz A, Abdul Latif LM, "Coagulation-Flocculation In Leachate Treatment By Using Ferric Chloride And Alum As Coagulant", Journal of Engineering Research and Applications, 2(4), 2012, pp. 1929-1934.

[5] Azmi NB, Bashir MJ, Sethupathi S, Ng CA, "Anaerobic stabilized landfill leachate treatment using chemically activated sugarcane bagasse activated carbonpp kinetic

and equilibrium study", Desalination and Water Treatment, 2014,pp.1-2. Available frompp.httppp.//www.tandfonline.com.

[6] Takigawa A, Kato K, Nakajima T, Serizawa R, Tamba H, "Landfill waste warter treatment by application of pulsed high voltage", Int. J. of GEOMATE, Vol. 9 No1, 2015, pp. 1375-1379

[7] Papastavrou C, Mantzavinos D, Diamadopoulos E, "A comparative treatment of stabilized landfill leachatepp. Coagulation and activated carbon adsorption vs. electrochemical oxidation", Environmental technology, 30(14), 2009, pp.1547-53. Available frompp.httppp.//www.tandfonline.com.

[8] Saheri S, Mir MA, Basri NE, Mahmood NZ, Begum RA, "Life cycle assessment for solid waste disposal options in Malaysia", Polish Journal of Environmental Studies, Vol.21 No.5, 2012, pp 1377–1382.

[9] Agouborde L, Navia R, "Heavy metals retention capacity of a non-conventional sorbent developed from a mixture of industrial and agricultural wastes", Journal of hazardous materials, 167(1), 2009, pp.536–544.

[10] Zhao R, Novak JT, Goldsmith CD, "Evaluation of on-site biological treatment for landfill leachates and its impact: a size distribution study", water research, 46(12), 2012, pp. 3837–3848.

[11] Nemati S, Tahmoorian F, Mortazavi M, "Environmental problems of iranian landfills at seaside of caspian sea", Int. J. of GEOMATE. 9(2), 2015, pp. 1496 -1501.

[12] Božić D, Stanković V, Gorgievski M, Bogdanović G, Kovačević R, "Adsorption of heavy metal ions by sawdust of deciduous trees", Journal of hazardous materials, 171(1), 2009, pp. 684–692.

[13] Aziz SQ, Aziz HA, Yusoff MS, Bashir MJ, Umar M, "Leachate characterization in semi-aerobic and anaerobic sanitary landfill. A comparative study", Journal of Environmental Management, 91(12), 2010, pp. 2608–2614.

[14] Qi Y, Hoadley AF, Chaffee AL, Garnier G, "Characterisation of lignite as an industrial adsorbent', Fuel, 90(4), 2011, pp.1567–1574.

[15] Cote P, Alam Z, Penny J, "Hollow fiber membrane life in membrane bioreactors (MBR)", Desalination, 288, 2012, pp.145–151.

[16] Pehlivan E, Altun T, Cetin S, Bhanger MI' "Lead sorption by waste biomass of hazelnut and almond shell", Journal of hazardous materials. 167(1), 2009, pp.1203–1208.

[17] Othman E, Yusoff MS, Aziz HA, Adlan MN, Bashir MJ, Hung YT, "The Effectiveness of Silica Sand in Semi-Aerobic Stabilized Landfill Leachate Treatment. Water", 2(4), 2010, pp.904–915.

[18] Mohan S, Gandhimathi R, "Removal of heavy metal ions from municipal solid waste leachate using coal fly ash as an adsorbent", Journal of Hazardous Materials, 169(1), 2009, pp.351–359.

[19] Białowiec A, Davies L, Albuquerque A, Randerson PF, "Nitrogen removal from landfill leachate in constructed wetlands with reed and willow: Redox potential in the root zone", Journal of environmental management, Vol. 97,2012, pp.22–27.

[20] Ali I, Asim M, Khan TA, "Low cost adsorbents for the removal of organic pollutants from wastewater", Journal of environmental management, 113, 2012, pp.170–183.

[21] Witek-Krowiak A, Szafran RG, Modelski S, "Biosorption of heavy metals from aqueous solutions onto peanut shell as a low-cost biosorbent", Desalination, 265(1), 2011, pp.126–134.

[22] Mohamed RM, Chan CM, Ghani H, Yasin MA, Kassim AH, "Application of peat filter media in treating kitchen wastewater", International Journal of Zero Waste Generation, Vol.1 No.1, 2013, pp.11-16.

[23] Othman N, Mohd-Asharuddin S, Azizul-Rahman MF, "An Overview of Fruit Waste as Sustainable Adsorbent for Heavy Metal Removal", InApplied Mechanics and Materials, Vol. 389, 2013, pp.29-35.

[24] Latiff AA, bin Abdul Karim AT, Ridzuan MB, Yeoh DE, Hung YT, "Heavy Metal Removal by Crops from Land Application of Sludge", InEnvironmental Bioengineering, Humana Press.2010, pp. 211-232.

[25] Daud Z, Fatihah N, Hanafi M and Awang H, "Optimization of COD and Colour Removal From Landfill Leachate by Electro-Fenton Method", Australian Journal of Basic and Applied Science,Vol. 7 No.8, 2013, pp.263–268.

[26] Halim AA, Aziz HA, Johari MA, Ariffin KS, Bashir MJ, "Semi-aerobic landfill leachate treatment using carbon–minerals composite adsorbent", Environmental Engineering Science, 29 No.5, 2012, pp.306–312

[27] Standard methods for the examination of water and wastewater. Washington, DC: American Public Health Association (APHA), 2012.

[28] Aopreeya M, Arunlertaree C, Yuwaree C, Boonprasert R, Hutacharoen R, "Blood Cockle Shell: an agro-waste for N and P Removal of Shrimp Farm Effluent", Environment and Natural Resources J. 11(1), 2013, pp.58-69.

[29] Moideen SN, Md Din MF, Ponraj M, Mohd Yusof MB, Ismail Z, Songip AR, Chelliapan S,

"Wasted cockle shell (Anadara granosa) as a natural adsorbent for treating polluted river water in the fabricated column model (FCM)", Desalination and Water Treatment, 29, 2015, pp.1-9.
[30] Foo KY, Hameed BH, "An overview of landfill leachate treatment via activated carbon adsorption process', Journal of Hazardous Materials, 171(1), 2009, pp.54-60.
[31] Jamil N, Khan SM, Ahsan N, Anwar J, Qadir A, Zameer M, Shafique U, “Removal of Direct Red 16 (Textile Dye) from Industrial Effluent by using Feldspar”, J. Chem. Soc. Pak. 36(2), 2014, pp.191.
[32] Ratnamala GM, Brajesh K, “Biosorption of remazol navy blue dye from an aqueous solution using pseudomonas putida”, International Journal of Science, Environment and Technology, 2(1), 2013, pp.80-9.
[33] Soni A, Rai N, Sar SK, “Removal of Anionic Surfactants from Industrial And Domestic Waste Water Using a Bio Adsorbent Embelia Ribes in Region Bilaspur Chhattisgarh, India”, Chem Sci Rev Lett. 4(13), 2015, pp.203-208
[34] Zaker Y., Hossain M.A. and Islam T.S.A, “Effect of Various Factors on the Adsorption of Methylene Blue on Silt Fractionated from Bijoypur Soil, Bangladesh”, Int. Res. J. Environment Sci. 2(6), 2013, pp.1-7.
[35] Shivayogimath CB, Bhandari NB, “Adsorption studies of paper mill effluent on teakwood sawdust activated carbon”, International Journal of Applied Science and Eng. Research, 3(5), 2014, pp.994-1004.
[36] Dada AO, Olalekan AP, Olatunya AM, Dada O, “Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms studies of equilibrium sorption of Zn2+ unto phosphoric acid modified rice husk’, Journal of Applied Chemistry, 3(1), 2012, pp.38-45.

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