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Abstract: Polyaniline-coated lignin-based adsorbent (PLC) was synthesized and used for uptake of reactive dye eosin yellow (EY) from aqueous solution. The adsorption capability of the adsorbent was found to be more effective than the unmodified adsorbent (LC). In particular, the adsorption capability of the PLC was effective over a wider pH range. This could be owing to its higher point of zero charge, which is more favourable for the uptake of the anionic dye. Adsorption isotherm models suggested a monolayer adsorption was predominant. The mean free energy of adsorption (EDR) was found to have values between 8 and 16 kJ.mol-1 which suggests that an electrostatic mechanism of adsorption predominated over other underlying mechanisms. The adsorption process was also found to be spontaneous, with increasing negative free energy values observed at higher temperatures. Chemisorption process was supported by the changes in enthalpy above 40 kJ mol-1 and by the results of desorption studies. This new adsorbent was also reusable and regenerable over four successive adsorption-desorption cycles. The single stage adsorber design revealed that PLC can be applicable as an effective biosorbent for the treatment of industrial effluents containing EY dye.

ABSTRACT

Polyaniline-coated lignin-based adsorbent (PLC) was synthesized and used for uptake of reactive dye eosin yellow (EY) from aqueous solution. The adsorption capability of the adsorbent was found to be more effective than the unmodified adsorbent (LC). In particular, the adsorption capability of the PLC was effective over a wider pH range. This could be owing to its higher point of zero charge, which is more favourable for the uptake of the anionic dye. Adsorption isotherm models suggested a monolayer adsorption was predominant. The mean free energy of adsorption (E_{DR}) was found to have values between 8 and 16 kJ.mol^{-1} which suggests that an electrostatic mechanism of adsorption predominated over other underlying mechanisms. The adsorption process was also found to be spontaneous, with increasing negative free energy values observed at higher temperatures. Chemisorption process was supported by the changes in enthalpy above 40 kJ mol^{-1} and by the results of desorption studies. This new adsorbent was also reusable and regenerable over four successive adsorption–desorption cycles. The single stage adsorber design revealed that PLC can be applicable as an effective biosorbent for the treatment of industrial effluents containing EY dye.

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HIGHLIGHTS

- Polyaniline coated lignin (PLC) was synthesized for uptake of the dye Eosin yellow.

- PLC was more effective than unmodified lignin and works over a wider pH range.

- Electrostatic mechanism of adsorption and monolayer adsorption predominated.

- PLC can be reused and regenerated over 4 cycles.

- Single stage batch adsorber model predicts the amount of PLC required for removal.

1   The Editor in Chief   24/06/2014

2   **International Journal of Biological Macromolecules**

3   Elsevier

4   SUBMISSION OF MANUSCRIPT

5

6   Dear Editor,

7   Please find the manuscript titled "**Single stage batch adsorber design for efficient Eosin**

8   **yellow removal by polyaniline coated ligno-cellulose**", which I submit for consideration of

9   publication in your esteemed journal. In this connection, I report that this is an original work and

10   that the manuscript is not submitted in any other journal for publication. I hereby confirm that all

11   the authors mutually agreed to submit the article in **International Journal of Biological**

12   **Macromolecules** and there is no confliction of interest. The major significance of this work lies

13   in polymer modification of ligno-cellulose isolated from pine cones in a very simple method and

14   the Eosin yellow adsorption efficiency of the polyaniline coated composite increased to a large

15   extent compared to the unmodified one. I hope this article perfectly fits the scope and suitability

16   for **International Journal of Biological Macromolecules**.

17   Your rapid decision will be highly appreciated.

18   With regards,

19   Sushanta Debnath,

20   Department of Applied Chemistry

21   University of Johannesburg

22   South Africa

23

24

25

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27

1

Single stage batch adsorber design for efficient Eosin yellow removal by polyaniline coated ligno-cellulose

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ABSTRACT

Polyaniline-coated lignin-based adsorbent (PLC) was synthesized and used for uptake of reactive dye eosin yellow (EY) from aqueous solution. The adsorption capability of the adsorbent was found to be more effective than the unmodified adsorbent (LC). In particular, the adsorption capability of the PLC was effective over a wider pH range. This could be owing to its higher point of zero charge, which is more favourable for the uptake of the anionic dye. Adsorption isotherm models suggested a monolayer adsorption was predominant. The mean free energy of adsorption (E_{DR}) was found to have values between 8 and 16 kJ.mol^{-1} which suggests that an electrostatic mechanism of adsorption predominated over other underlying mechanisms. The adsorption process was also found to be spontaneous, with increasing negative free energy values observed at higher temperatures. Chemisorption process was supported by the changes in enthalpy above 40 kJ mol^{-1} and by the results of desorption studies. This new adsorbent was also reusable and regenerable over four successive adsorption–desorption cycles. The single stage adsorber design revealed that PLC can be applicable as an effective biosorbent for the treatment of industrial effluents containing EY dye.

1. Introduction

3

76 The presence of colour in any polluted water is visibly detectable and its presence is unpleasant

77 even in very minute amounts [1]. The dye-containing waste water not only pollutes the

78 environment, but also affects the life of aquatic flora and fauna, and directly affects human life

79 [2]. Because of their complex chemical structures, the dyes are heat, chemical and light-resistant,

80 and are difficult to biodegrade [3]. The partially degraded products of the dye are also highly

81 toxic and carcinogenic in nature [4].

82 Eosin yellow (EY) is a highly water-soluble fluorescein class of anionic dye. The IUPAC name

83 of EY is 2-(2,4,5,6-Tetrabromo-6-oxido-3-oxido-3H xanthenes-9-yl) benzoate disodium salt. EY

84 is widely used in the Gram staining of bacterial species because of its red color and strong

85 absorption by red blood cells [5]. Information on the toxicology of EY confirms effects such as

86 severe eye and skin irritation with redness and pain, as well as damage to vital organs like the

87 kidneys, liver and lungs caused by ingestion and inhalation. EY also permanently damages the

88 cornea by destroying the retinal ganglion of the eye [6, 7]. Thus, it is very important to remove

89 the dye from waste water to maintain environmental integrity.

90 Some common methods applicable to the removal of the dye pollutants from waste water are

91 electro-chemical treatment [8], ozonation and oxidation [9], photo-oxidation [10], froth flotation

92 [11] and adsorption [12, 13]. It has been well established that adsorption is the most effective of

93 the available methods in purifying dye-polluted waste water with respect to the complete

94 removal of the pollutant. Several adsorbents have been indicated by researchers for removing

95 toxic dyes from waste water. They include glutaraldehyde cross-linked magnetic chitosan [12],

96 activated carbons from different sources [14,15] and Fe^{3+} grafted clinoptilolite [13]. Recent

97 studies have focused on developing new adsorbents that have a low cost and a high adsorption

98 capacity for the relevant dyes.

99 Lignins and ligno-cellulosic materials derived from various agricultural and forestry sources

100 have gained importance in removing different pollutants form water and waste water [16-20].

101 The benefit of choosing lignins as an adsorbent lies on their easy availability and versatility with

102 respect to the available functional groups, which make it a broad-range biosorbent for different

103 classes of water pollutants [21]. Although several low-cost biosorbents have been used for the

104 removal of EY, lignin-based adsorbents are superior by far because of their oxygen binding sites,

105 which can bind several pollutants. Coating lignin-based adsorbents with polyaniline offers

106 advantages such as a lower cost, enhanced conductivity and mechanical flexibility, which further

4

107 enhances the adsorption capabilities of these adsorbents [22]. Thus, the distinct advantage

108 offered by PLCs over other low-cost adsorbents is their enhanced adsorption capabilities.

109 In this present study, we have exploited the anion-exchanging nature of ligno-cellulose derived

110 from pine cones for the removal of the anionic dye eosin yellow. The ligno-cellulose (LC) was

111 extracted from pine cones through alkaline hydrolysis followed by acid precipitation, and the

112 substance is then characterized using different analytical tools. The isolated ligno-cellulose is

113 further modified by coating it with cheap polymer polyaniline (PLC) to enhance the efficiency of

114 the removal of the dye. The adsorption process was analysed using isotherm and thermodynamic

115 models to evaluate the adsorption constants and parameters. The regeneration and the reusability

116 of the adsorbents were also tested. Furthermore, a single-stage batch adsorber was proposed and

117 a method was developed to predict the amount of PLC and LC required for various amounts of

118 effluent to be treated.

119

120 **2. Materials and methods**

121 Mature pine cones were collected from Monterey Pine (*Pinus radiata*) from a local park in

122 Pretoria, South Africa. Lignin was isolated by alkaline hydrolysis of the scales of these cones.

123 The dye eosin Y (chemical formula = $C_{20}H_8Br_4O_5$, C.I. 45380, FW = 647.89 and λmax = 520

124 nm) was obtained from Sigma Aldrich (analytical grade). Aniline required for polymeric coating

125 of lignin particles was also bought from Sigma Aldrich (analytical grade). The acid and base

126 (HCl and NaOH) used for pH adjustment were of reagent grade. All other reagents used in this

127 study were analytical grade.

128 A stock solution of EY (1000 mg.L^{-1}) was prepared by dissolving 1000 mg of the dye in distilled

129 water and making up the volume to 1000 mL. The working EY solutions used in the experiments

130 were prepared by diluting the stock solution to the required concentration using deionised water.

131 The instruments used for data collection and characterization of the adsorbent were (i) an Orion

132 4-star pH meter (thermo) for adjustment of the pH of the solutions, (ii) a Phillips X-ray

133 diffractometer for the X-ray diffraction (XRD) analysis, (iii) a Perkin Elmer Spectrum 100 for

134 attenuated total reflectance Föurier transform infrared (ATR-FTIR) spectra, (iv) a scanning

135 electron microscope (SEM) (Tescan Vega, UK) for the image of the material for surface

136 morphology, (vii) a Perkin Elmer Raman Station 400 for Raman spectroscopy of the materials

137 (viii) a Malvern Zetasizer NanoS for the zeta potential of the materials and (ix) a UV-vis

138 spectrophotometer (Shimadzu: UV 1800) for colorimetric analysis of EY.

139

140 **2.1 Preparation of LC**

141 LC was isolated from matured pine cone scales by alkali (NaOH) extraction. The scales were

142 cleaned by washing them with distilled water, and they were dried overnight in an oven at 100

143 ^{o}C. The dried scales were crushed in a mechanical crusher and the powder was digested in 2M

144 NaOH at 80 ^{o}C overnight with constant agitation. The resultant dark brown liquor was isolated

145 from the solid particulates by filtration and the filtrate was acidified with concentrated HCl until

146 the pH of the solution was 2.0. The solid precipitate that resulted from the acidification of the

147 filtrate was stirred overnight and finally filtered, washed with distilled water and dried at 60 ^{o}C

148 under a vacuum. This method is a slight modification of the method of lignin isolation reported

149 by Brdar et al., 2012 [17].

150

151 **2.2 Preparation of PLC**

152 The polyaniline (PANI) coating of the lignin particles was achieved by in-situ polymerization of

153 aniline monomers in the presence of lignin particles. Here, 10.0 g LC was taken in 100 mL 0.1M

154 HCl solution with 1 mL aniline and stirred overnight in a mechanical stirrer. Ammonium

155 persulphate solution (0.1M, 10 mL) was added dropwise into the solution and stirred overnight.

156 The reaction was stopped by adding 10 mL acetone into the mixture. The material was filtered

157 and washed with acetone (to remove the oligomers and unreacted aniline monomers) until the

158 filtrate was colourless. Finally, the material was collected and dried at 60 ^{o}C under a vacuum.

159 **3. Results and discussions:**

160 **3.1 Characterization**

161 **Figure 1A** shows the FTIR spectra of PLC, LC and pristine PANI. The prevalent peaks for LC

162 are found to be 1590, 1510, 1460 and 1050 cm^{-1}, which correspond to the C−C aromatic skeletal

163 vibration, C−C ring skeletal vibration, C−H vibration and C−O stretching frequencies,

164 respectively [23]. Weak peaks at 3420 and 2910 cm^{-1} are the characteristic peaks for O−H and

165 C−H stretching frequencies in LC. In PANI, the main peaks are at 1578 and 1497 cm^{-1}, which

166 correspond to the quinonoid and benzenoid ring stretchings of PANI, respectively [24]. The

167 protonation-induced π-electron delocalization of the polymer plain corresponds to the peak at

6

168   1295 cm^{-1}. The 1094 cm^{-1} peak of PANI is assigned for $-NH^+ =$ structure vibration mode of the

169   protonated polymer.

170   The distinguished peaks for PLC are 2910, 1590, 1578, 1497, and 1026 cm^{-1}, which are

171   characteristic peaks for both the LC and PANI. Thus, the PLC is a composite consisting of PANI

172   and LC. The peak at 1295 cm^{-1}, which is the characteristic peak for an induced delocalized π-

173   electron of protonated PANI, is absent in the PLC. This implies that the PANI has interacted

174   with the LC through π–π overlapping of the aromatic rings.

175   **Figure 1B** shows the XRD plot of PLC and LC. The main peak of LC is at 2θ, equal to 22.12^o.

176   This peak is indicative of the distance between the H-bonded sheets in cellulose I. The position

177   of the peak depends on both the moisture content and the crystallite size of the material [25]. The

178   weak peak at 16.21^o indicates the composite peak of the two cellulose allomorphs of IA and IB

179   [25]. The PLC consists of the two abovementioned peaks of LC and also an extra peak at 25.30 ^{o},

180   which is the characteristic peak of PANI. Thus, it can be concluded that during polymerization

181   the PANI coated the LC particles well.

182   **Figure 1C** shows the pH$_{zpc}$ of PLC and LC. The pH$_{zpc}$ of LC and PLC are 3.36 and 4.55,

183   respectively. The low zpc value for both the materials may be because of the fact that they are

184   synthesized at a highly acidic pH and have surface-adsorbed H$^+$ ions on the material. Above

185   pH$_{zpc}$ the surface remains negatively charged and below pH$_{zpc}$ the surface remains positively

186   charged, which makes it favorable for adsorption of anionic dyes like eosin yellow (EY).

187   **Figure 1D** shows the Raman shift of PLC and LC. In the spectra of LC, the peak for lignin at

188   1600 cm^{-1} is less intense, owing to the harsh treatment of the choromophore in acidic conditions

189   [26]. The strong peak at 1099 cm^{-1} is because of the carbohydrate band, which indicates the

190   presence of an adequate amount of carbohydrate in the LC sample [26]. The ratio between the

191   intensity of the peaks at 1600 and 1096 cm^{-1} (I$_{1600}$/I$_{1096}$) is found to be 1.05, which indicates

192   almost equal presence of lignin and carbohydrate in the LC. **Table T1: (Supplementary**

193   **materials)** presents the summary of the peaks and their bond assignments for LC and PLC. From

194   the table it can be seen that LC contains a ligno-cellulosic compound as its constituent material.

195   PLC shows significant peaks from PANI, lignin and cellulose, but with a decreased number of

196   peaks for LC. This confirms the successful coating of LC with PANI.

197 **Figure 2** shows the SEM and EDS images of LC and PLC. The image of LC shows the ribbon-
198 like structure of the cellulosic counterparts of the ligno-cellulose (LC) material. The surface of
199 the material is of irregular morphology, with pores.

200 The SEM image of PLC shows the polymeric formations over the whole material. The cellulosic
201 ribbons are invisible, which implies the successful coating of LC with PANI. The material is
202 much more porous than LC, with average pore diameter 322.78 Å, whereas the pore diameter of
203 LC is 171.12 Å (obtained from BET analysis). Thus, it is expected that PLC is a much better
204 adsorbent for EY than LC, owing to its porous nature.

205 **3.2 Effect of pH**

206 The structural stability of the dye molecule depends on the initial pH of the solution and the
207 surface charge on the adsorbent. Efficient adsorption of the dye depends on the surface charge on
208 the adsorbent and the dissociated form of the dye in the solution at a particular pH. **Figure 3**
209 shows the effect of pH on the adsorption of EY by LC and PLC. The pH of the solution was
210 varied from $1.0 - 8.0$ to observe the effect of pH on the adsorption of EY by LC and PLC. The
211 maximum removals of 99.67 % and 95.91 % were achieved at pH 3.0 for PLC and LC,
212 respectively. The percentage of adsorption decreases drastically for LC and decreases gradually
213 for PLC with an increase in pH. This may be owing to the elevated pH_{zpc} of PLC compared to
214 LC, which makes PLC a better adsorbent for a larger range of pH values than LC. The pH_{zpc}
215 values of LC and PLC are 3.36 and 4.55, respectively. Thus, at pH 3.0 (the optimum pH for EY
216 adsorption by LC and PLC), the surface of both the adsorbents remains positively charged and
217 the anionic form of the dye is feasibly adsorbed. But, owing to higher pH_{zpc} value of PLC when
218 compared to LC, the positive charge density of the PLC surface is higher than the LC surface. As
219 a result, the anionic dye EY becomes electrostatically more attracted by PLC than by LC.

220 **3.3 Adsorption isotherm**

221 In order to utilize the adsorption system for practical applications it is necessary to carry out
222 adsorption isotherm studies based on various adsorption isotherm models. The relation between
223 the amount of adsorption per unit mass of the adsorbent and the equilibrium adsorbate
224 concentration in the reaction solution can be determined. Thus Langmuir, Freundlich, Redlich–

225 Peterson, Temkin and D–R isothermal models are applied to the experimental data obtained

226 during the isothermal adsorption studies.

227 **Figure 4** shows the isotherm equilibrium data points obtained for the adsorption of EY by (A)

228 LC and (B) PLC at temperatures 25, 35, and 45 °C with a maximum fluctuation of ± 1 °C. To

229 evaluate the nature of the adsorption reaction, the data was analyzed with the non-linear fit

230 methods in GraphPad Prism 5 software using equations (1 – 3) [27] shown below:

231 Langmuir model: $q_e = \dfrac{q_m K_a C_e}{1 + K_a C_e}$ (1)

232 Freundlich model: $q_e = K_F C_e^{(1/n)}$ (2)

233 Redlich-Peterson model: $q_e = \dfrac{A C_e}{1 + B C_e^g}$ (3)

234 Temkin model: $q_e = (RT/b_T) ln(A_T C_e) = B_T \, ln(A_T C_e)$ (4)

235

236 where q_e is the adsorption capacity at equilibrium (mg.g^{-1}); q_m is the monolayer adsorption

237 capacity (mg.g^{-1}); C_e is the equilibrium adsorbate concentration (mg.L^{-1}); and K_a (L.mg^{-1}), K_F, A

238 (L.g^{-1}), and B (L.mg^{-1}) are the Langmuir, Freundlich and Redlich-Peterson (R–P) isotherm

239 constants, respectively. A_T (L.g^{-1}) and B_T (J mol^{-1}) are, respectively, the equilibrium binding

240 constants corresponding to the maximum binding energy and the Temkin constant related to the

241 heat of sorption. R (8.314 J mol^{-1} K^{-1}) is the universal gas constant and T (K) is the absolute

242 solution temperature.

243 The non-linear fits of the adsorption data of EY on LC and PLC are also shown in **Figure 4**. The

244 related isotherm parameters with regression coefficients (R^2) and statistical error chi-square (χ^2)

245 obtained from the non-linear plots are summarized in **Table 1**. Based on the regression

246 coefficient (R^2) and the statistical error chi-square (χ^2) values, it can be concluded that the

247 experimental data is best described by the three-parameter R–P isotherm (Eq. 3) ($0.98 \le R^2 \le 0.99$

248 and $\chi2 = 16.07 − 29.58$). The goodness of data fit was fairly favourable, with the two parametric

249 models viz. the Langmuir (Eq. 1) ($R^2 = 0.96 – 0.98$ and $\chi2 = 21.68 – 37.13$) for the range of

250 temperatures studied. The Temkin model parameter is also well fitted so that this model can also

251 be utilized to evaluate the binding energy and the heat of adsorption. The goodness of data fit

252 with the R-P model (Eq. 3) was closer to the Langmuir model (Eq. 1) than the Freundlich model

253 (Eq. 2), with the 'g'-value closer to 1.0, which in turn reduces the R-P equation to the Langmuir

254 equation. The g-values of the R-P model (Eq. 3) increased from 0.84 to 0.95 in the case of PLC

255 and from 0.69 to 0.76 in the case of LC by increasing the reaction temperature from 25 to 45 °C

256 for PLC and LC. The 'g'-values (Table 3) of the R–P model isotherm suggest increasing

257 Langmuir-type monolayer adsorption with increasing temperature on the EY adsorption reaction

258 with LC and PLC. Thus, this indicates surface transformation from slightly heterogeneous to

259 more homogeneous sites with increasing temperature in the reaction, which becomes

260 increasingly monolayer-type with increasing temperatures.

261 The heat of adsorption, evaluated from the Temkin equation, decreases with an increase in

262 temperature for both LC and PLC. This suggests that with increased temperature, less energy is

263 required for the adsorption reaction to occur and the reaction becomes more feasible, which

264 supports the endothermic nature of the reaction.

265 **3.4 Evaluation of adsorption energy**

266 The equilibrium data was analysed using a Dubinin–Radushkevick (D–R) equation [28] (Eq. 5)

267 in order to determine the adsorption energy of the adsorption process.

268
$$\ln q_e = \ln q'_m - K_{DR}\varepsilon^2 \text{,} \tag{5}$$

269 $\varepsilon = RT \, ln(1+ 1/C_e)$ (6)

270 where ε is the Polanyi potential (Eq. 16), q'_m is the D–R adsorption capacity (mol.kg^{-1}), and K_{DR}

271 is a constant related to adsorption energy (mol^2 .kJ^{-2}). The q'_m and K_{DR} parameters were evaluated

272 from the intercepts and slopes of the plots of $ln(q_e)$ versus ε^2 (**Figure S1: Supplementary**

273 **materials**). The mean free energy of adsorption (E_{DR}) is the free energy change when one mole

274 of ions is transferred to the surface of the adsorbent from infinity in the solution [28], and it was

275 calculated using the following equation (Eq. 7):

276 $E_{DR} = (-2K_{DR})^{-1/2}$ (7)

277   The calculated D–R equation parameters and mean free energies evaluated are given in **Table 1**.

278   The magnitude of E_{DR} is useful for determining the type of reaction: values of E_{DR} between 8.0 –

279   16.0 kJ mol^{-1} describe an adsorption reaction that occurs electrostatically [28] for both LC and

280   PLC. The E_{DR} values obtained in this study suggested that EY adsorption on LC and PLC took

281   place through an electrostatic mechanism with some other inherent mechanisms within that [28]

282   The increasing adsorption efficiency accompanying increased temperature can be explained in

283   terms of change in standard thermodynamic parameters like Gibbs free energy (ΔG^{o}), enthalpy

284   (ΔH^{o}), and entropy (ΔS^{o}). The Gibbs-free-energy change of the process is related to the

285   equilibrium constant ($K_a = \dfrac{1000\, q_e}{C_e}$) [29] by the following equation (Eq. 8) [27,30]:

286         $\Delta G^{o} = -RT \ln K_a$ (8)

287         $\ln K_a = \left(\dfrac{\Delta S^{o}}{R}\right) - \left(\dfrac{\Delta H^{o}}{RT}\right)$ (9)

288   The values of ΔH^{o} and ΔS^{o} were calculated from the slope and intercept of the linear plot (R^2 =

289   0.97) of ΔG^{o} versus T (**Figure S2: Supplementary materials**). The slope and the intercept of

290   the plot give the ΔH^{o} and the ΔS^{o} values, respectively. The values obtained are given in **Table 2**.

291   The increasing negative values of ΔG^{o} with increasing temperature indicate the feasibility and

292   spontaneity of the EY adsorption process on LC and PLC. The positive enthalpy change (ΔH^{o})

293   values for the EY adsorption reaction (**Table 2**) indicate the endothermic nature of the process.

294   Low positive enthalpy change ($\Delta H^{o} <$ 40 kJ mol^{-1}) for LC indicates the physical sorption of EY

295   onto the LC surface. However, the change in enthalpy for PLC higher than 40 kJ mol^{-1} indicates

296   the occurrence of chemisorption of EY on PLC, which is further supported by the desorption

297   study. The positive entropy change (ΔS^{o}) for this reaction (**Table 2**) has also indicated the

298   increase in the number of species at the solid-liquid interface, and hence the randomness in the

299   interface presumably stemming from the release of aqua molecules when the aquated EY is

300   adsorbed on the surface of the adsorbent.

301   **3.6 Desorption and reusability study**

302   The desorption trend of EY from both LC and PLC at different pH values was the opposite of

303   that in the adsorption process. An increase in the pH of the desorption solution from 4.0 to 12.0

304 increases desorption efficiency from 34 to 98 % and from 25 to 90 % for LC and PLC,

305 respectively (**Figure 5**).

306 The dye was desorbed to its maximum of 98% when the pH of the solution was 10.0. Further

307 increase in pH does not increase the desorption percentage. Thus, pH 10.0 deionized water was

308 found to be the optimum for EY desorption from both the adsorbents. EY is anionic in nature,

309 and increased adsorption in an acidic medium and increased desorption in an alkaline medium

310 showed that EY was held by the adsorbents, most probably by ion exchange. Usage of 1:1

311 acetone water (v/v) as a desorption solution increased the percentage desorption to 98 and 96 for

312 LC and PLC respectively. Incomplete desorption in an alkaline medium and increased desorption

313 in an organic solvent solution indicate that ion exchange was not the only mode of adsorption. It

314 can be concluded that the third mode of adsorption could be chemisorption [31]. The high ΔH^o

315 value for both LC and PLC also supports this observation. The higher desorption of LC

316 compared to PLC also indicates that PLC is a better adsorbent for EY than LC.

317 The used LC and PLC samples were subjected to adsorption and desorption cycles using a pH

318 10.0 aqueous solution. This process was conducted in triplicate to ensure the reproducibility of

319 the results. After desorption of the EY, the adsorbents were regenerated by equilibrating the

320 adsorbents in pH 3.0 aqueous solutions. It is observed that LC and PLC can retain an adsorption

321 capacity of up to 79.92 % (for LC) and 75.32 % (for PLC) of the initial value in the fourth cycle

322 of regeneration (**Figure S3: Supplementary materials**).

323 Thus, LC and PLC can be used as potential adsorbents of EY for its removal from contaminated

324 water.

325 **3.7 Designing single-stage batch adsorber from equilibrium data**

326 For predicting the design of a single-stage adsorber model for a batch-adsorption study, the

327 adsorption equilibrium data is useful [32, 33]. Designing a batch adsorber model is essential to

328 extrapolate the findings of the lab-bench-scale study to a large-scale one, which in turn could be

329 utilized in designing an industrial waste water treatment system. A schematic diagram of the

330 batch adsorber model is given in **Figure S4: (Supplementary materials).**

331 V (m^3) is the volume of the solution in a batch adsorber system with an initial (EY) dye

332 concentration of C_o (g. m^{-3}) and concentration of dye in the system at any time t of C_t (g. m^{-3}). If

12

333   the mass of the adsorbent (LC/PLC) in the adsorber is M (kg) and the solute loading of the dye at

334   any time t on the adsorbent changes to q_t (g.kg^{-1}) from the initial solute loading of q_o (g. kg^{-1}),

335   then, according to the mass balance (eq. 10),

336    $V(C_o - C_t) = M(q_t - q_o)$ (10).

337   At the initial stage of the reaction, $q_o = 0$. At equilibrium, $C_t = C_e$ and $q_t = q_e$. C_e and q_e are,

338   respectively, the concentration of the dye in the solution and on the adsorbent at equilibrium.

339   Equation 23 reduces to $V(C_o-C_e) = Mq_e$

$$\frac{M}{V} = \frac{C_o - C_e}{q_e}$$

340   (11)

341   The adsorption of EY on LC and PLC is Langmuir-monolayer-type adsorption (confirmed from

342   the adsorption equilibrium study). Consequently, the value of the equilibrium adsorption

343   capacity value (q_e) from the Langmuir equation may be substituted into equation 24 to find out

344   the process parameters of the adsorption of EY by both the adsorbents.

345   **Figure 6** shows the series of plots for the adsorption of EY onto LC and PLC derived from

346   equation 24. The initial concentration of the influent dye was taken as 100 mg.L^{-1} at 35 $^{\circ}$C. The

347   amount of LC and PLC required for reducing the final concentration to $70 - 95$ % for different

348   volumes of the dye solution is shown in **Figure 6**. The design procedure for a single-stage batch

349   adsorber is outlined. The mass of the adsorbent required for removal of the dye from the given

350   volume and concentration of the solution could be calculated from the plot. For instance, if 20 m^3

351   of dye solution has to be treated, the required masses of PLC to decrease the initial dye

352   concentration from 100 mg.L^{-1} to a final concentration of 10, 20 and 30 mg.L^{-1} are 4.11, 3.27 and

353   2.75 kg, respectively.

354   The initial concentration of the influent dye was taken as 100 mg.L^{-1} at 25, 35 and 45 $^{\circ}$C. The

355   amount of LC and PLC required for reducing the final concentration to 5.0 mg.L^{-1} for different

356   volumes of the dye solution is shown in Figure 17. For instance, to purify 50 m^3 of effluent with

357   an initial concentration of 100 mg.L^{-1} of the dye, the required amounts of LC at 25, 35 and 45 $^{\circ}$C

358   are 296.58, 212.21 and 81.41 kg respectively, whereas the required amounts of PLC to remove

359   the same amount of dye in identical conditions are 57.81, 32.94 and 20.56 kg.

360　Similarly, to remove 70, 80 and 90 % of the initial dye concentration (100 mg.L^{-1}) from 50 m^3 of

361　effluent at 35 ^{o}C using LC, the amounts of material required are 13.35, 17.95 and 29.29 kg

362　respectively. To remove the same amount of dye from effluent in identical conditions, the

363　required amounts of PLC are 6.86, 8.17 and 10.28 kg respectively.

Conclusion

364

365　A novel polyaniline-coated lignin-based adsorbent has been synthesized and used for adsorption

366　of the reactive dye eosin yellow (EY). The adsorption was most favorable at pH 3. The PANI-

367　coated adsorbent performed better than the unmodified adsorbent. This is mostly owing to the

368　larger surface area, greater porosity and increased amount of reactive surface functional groups

369　of PLC. The g-values of the R-P model mostly suggest Langmuir-type monolayer adsorption.

370　Both adsorbents were reusable after four successive adsorption-desorption cycles. Modeling of

371　the equilibrium data also revealed that a smaller quantity of PLC was required to remove 90% of

372　the initial dye concentration. Only 6.86 kg of PLC, as opposed to 29.29 kg of LC, was required

373　to reduce the dye concentration from 100 mg L^{-1} to 5 mg L^{-1} using an effluent volume of 50

374　m^{3}at 35°C. This therefore suggests that PLC is a more efficient adsorbent for the removal of EY

375　from industrial effluents.

382　**References**

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Table 1: Parameters for adsorption isotherm analysis for the adsorption of Eosin yellow on PLC and LC at initial pH 3.0 (±0.1)

Model	Temperature					
	25 °C		**35 °C**		**45 °C**	
	PLC	**LC**	**PLC**	**LC**	**PLC**	**LC**
Langmuir						
K_a (L.mg^{-1})	0.1941	0.0449	0.3707	0.0611	0.6608	0.171
q_m (mg.g^{-1})	526.8	388.4	555.7	405.1	605.1	416.4
R^2	0.9757	0.9744	0.9630	0.9756	0.9792	0.9803
χ^2	28.36	21.68	37.13	23.05	29.45	22.13
Freundlich						
K_f (mg.g^{-1})	149.4	48.39	194.2	62.50	227.5	95.36
n	3.536	2.528	3.759	2.756	3.254	2.26
R^2	0.9559	0.9620	0.9597	0.9481	0.9489	0.96.3
χ^2	38.25	26.42	38.74	32.75	46.19	31.45
Redlich Peterson						
A (L.g^{-1})	131.7	29.96	240.1	37.83	377.4	73.77
g	0.9529	0.7262	0.8421	0.7664	0.9035	0.6981
B (L.mg^{-1})	0.2234	0.0601	0.3620	0.07954	0.5436	0.1484
R^2	0.9826	0.9841	0.9804	0.9827	0.9903	0.9914
χ^2	26.34	18.70	29.58	20.73	22.00	16.07
Temkin						
A_T	0.45	0.64	1.23	5.04	41.30	17.44
B_T	41.73	74.27	25.65	72.36	13.25	45.30
R^2	0.7752	0.9906	0.8269	0.9699	0.9223	0.8244
χ^2	86.35	13.18	65.23	24.92	56.95	66.13
Dubinin Radushkevich						
$K_{DR} \times 10^9$	2.63	4.30	2.10	3.52	2.04	2.57
E_{DR}	13.79	10.78	15.43	11.92	15.65	13.95
q'_m (mol.kg^{-1})	2.05	2.59	2.11	2.15	2.88	1.68
R^2	0.9504	0.9217	0.9754	0.8384	0.9668	0.9827
χ^2	0.1517	0.2921	0.1096	0.4259	0.1317	0.1423

Table 2: Thermodynamic parameters for the adsorption of Eosin yellow on PLC and LC at initial pH 3.0 ($\pm$0.1)

Temp	$-\Delta G^o$ (kJ.mol^{-1})		ΔH^o (kJ.mol^{-1})		ΔS^o (kJ.mol^{-1})	
	PLC	LC	PLC	LC	PLC	LC
298	21.40	18.35				
308	23.55	19.32	56.60	10.35	0.2612	0.0963
318	26.63	20.28				
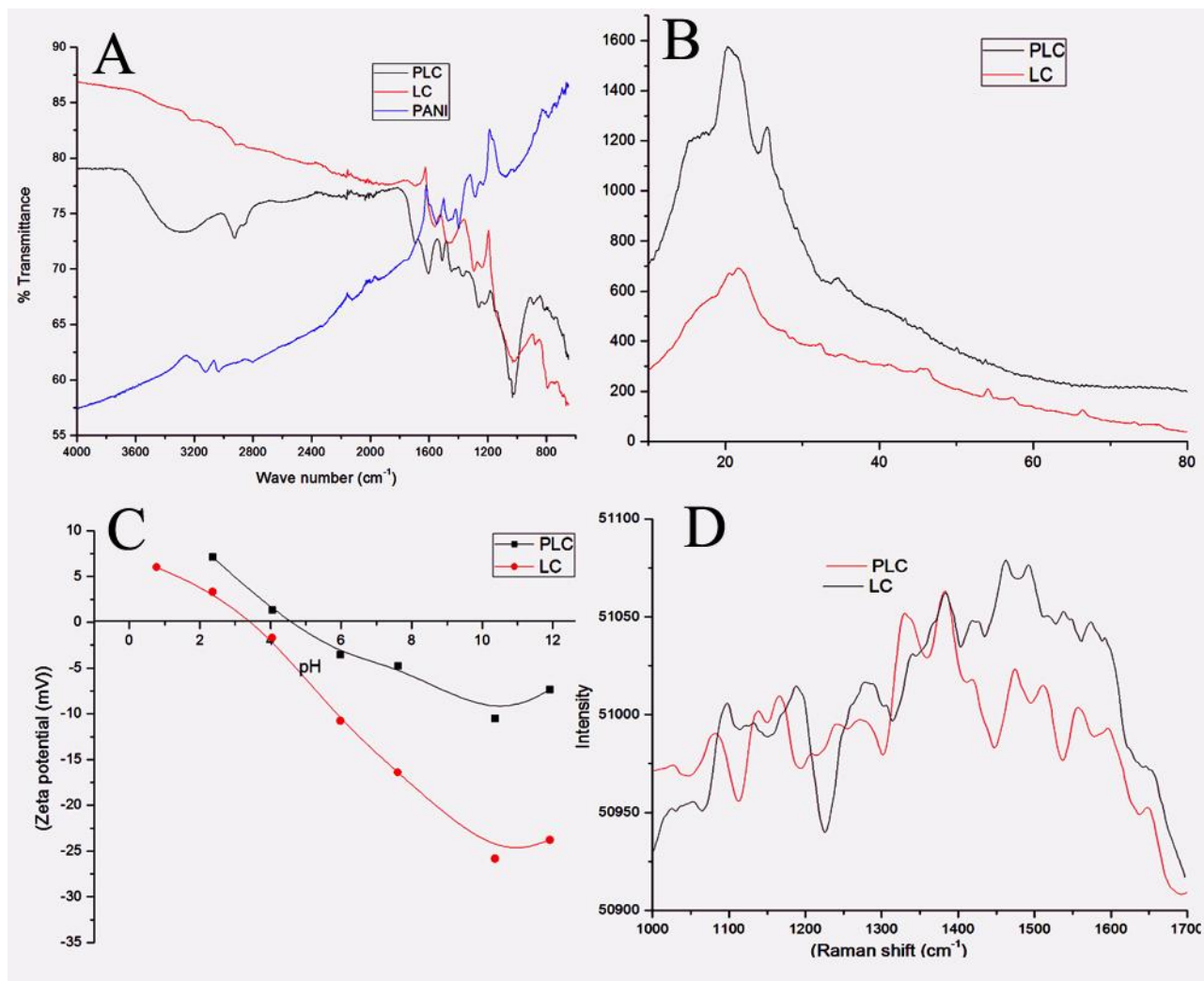
Figure 1: (A) FTIR of LC, PLC and PANI and (B) XRD, (C) point of zero charge (pH$_{zpc}$) and (D) Raman plot of LC and PLC.
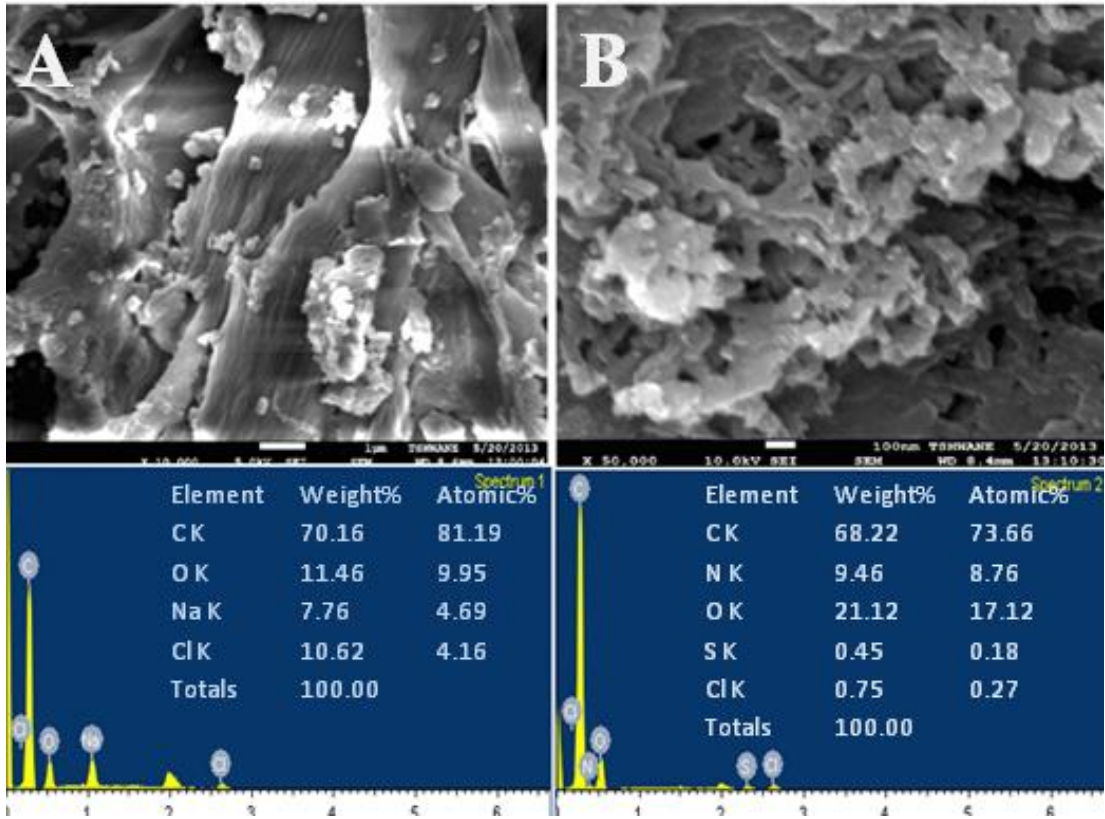
Figure 2: SEM image and EDS spectra of (A) LC and (B) PLC
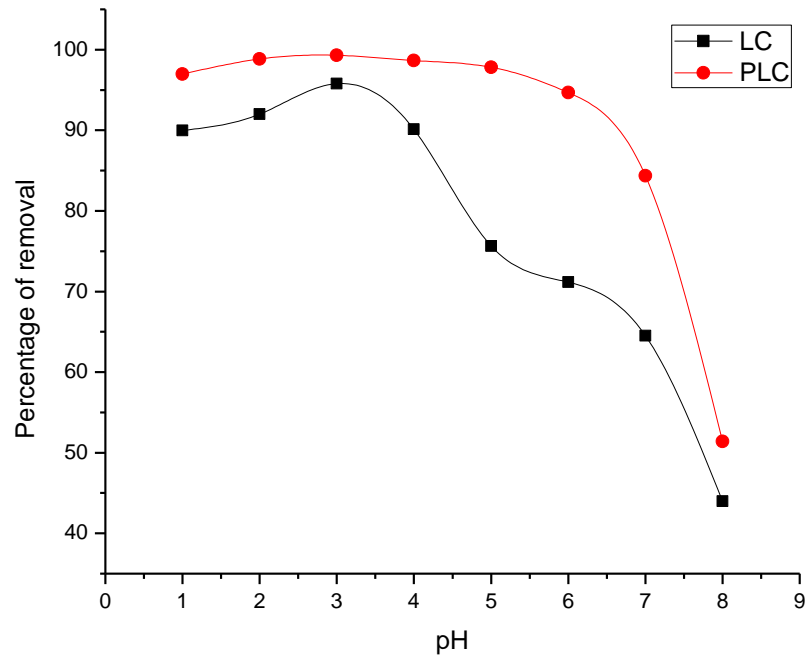
Figure 3: Effect of pH on adsorption of EY by LC and PLC
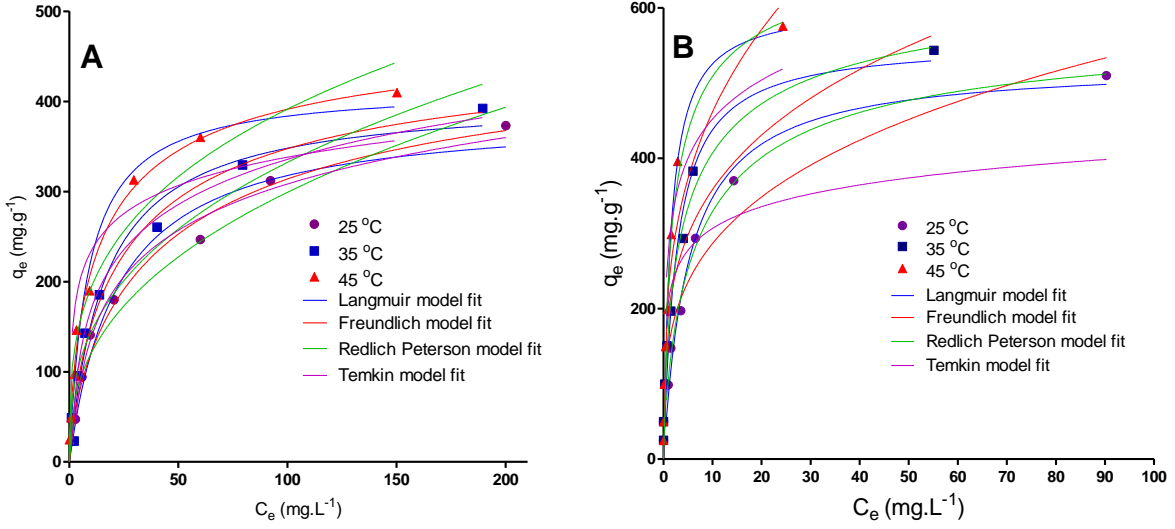
Figure 4: Adsorption isotherm (A) LC and (B) PLC
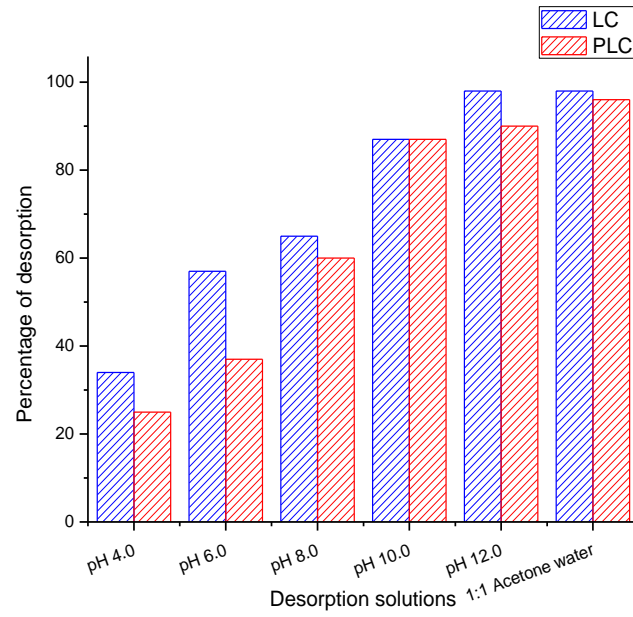
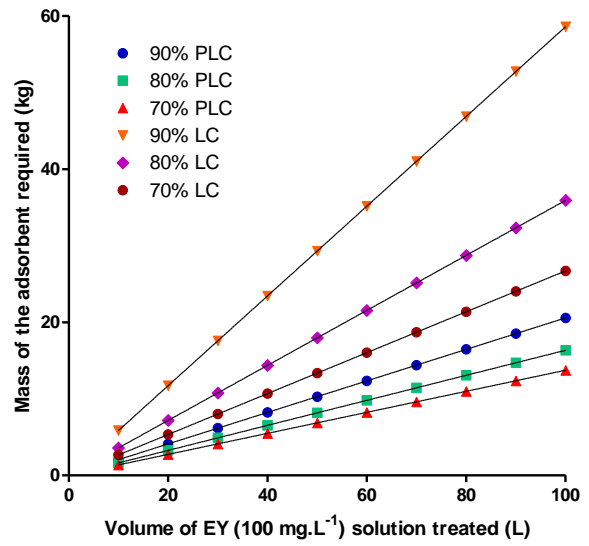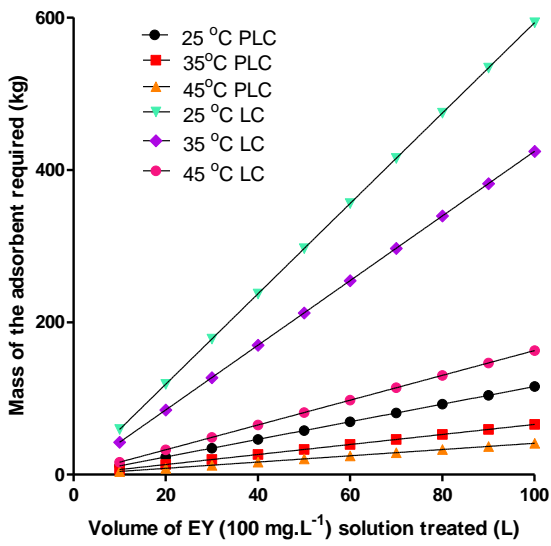**Figure 5: Desorption of EY from LC and PLC using different desorption solution**

Figure 6: Process parameters for adsorption of EY by LC and PLC
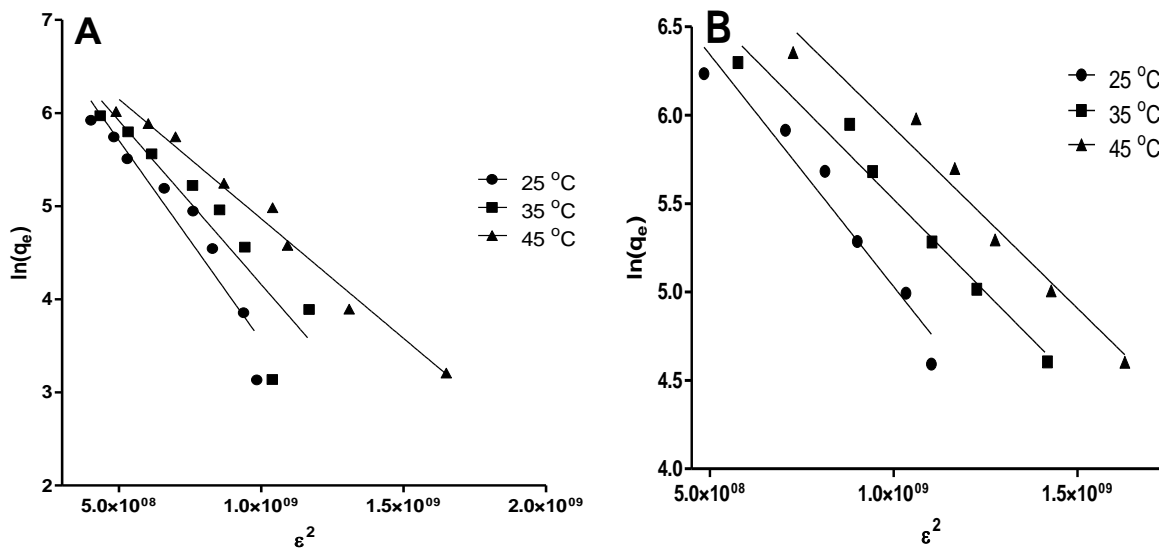
Supplementary Materials

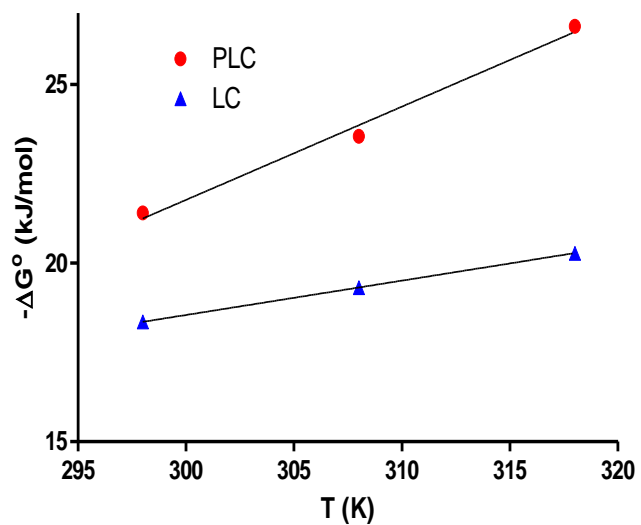**Figure S1: Dubinin Radushkevich isotherm (A) LC and (B) PLC for adsorption of EY**

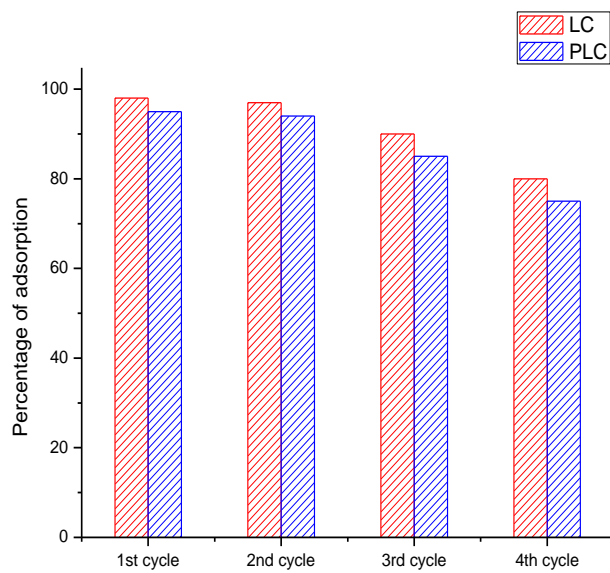**Figure S2: Thermodynamic parameters for adsorption of EY by LC and PLC**

Figure S3: Regeneration of LC and PLC using pH 10.0 aqueous solution.

M kg LC/PLC (q_t g EY kg^{-1} adsorbent)

V m^3 of EY solution

C$_o$ (g.m^3) EY solution

Batch Adsorber system

V m^3 of EY solution

C$_t$ (g.m^3) EY solution
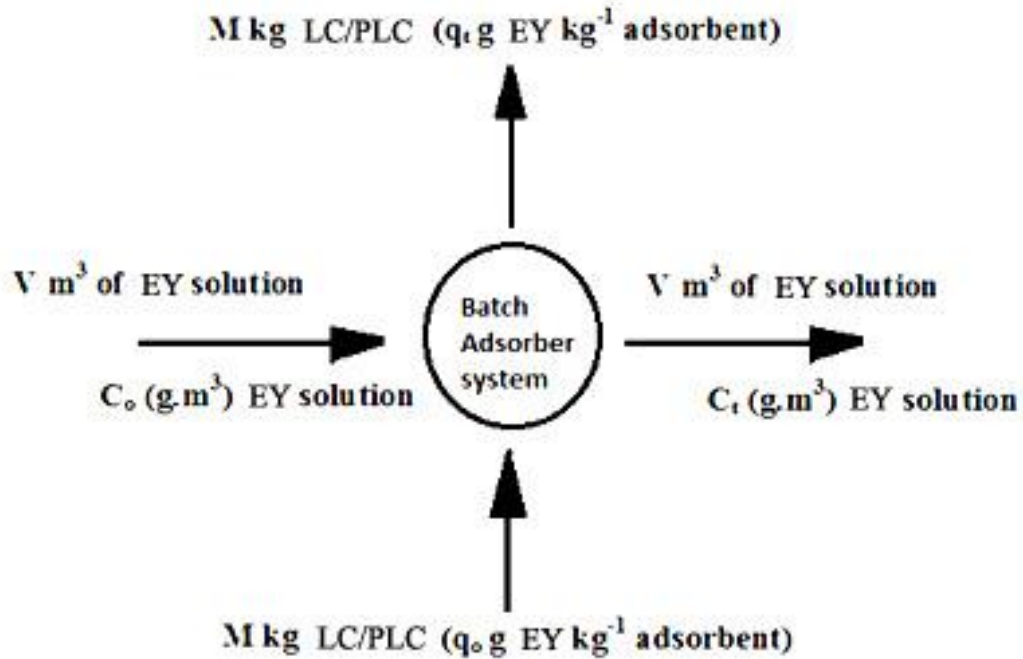
M kg LC/PLC (q_o g EY kg^{-1} adsorbent)

Figure S4: Single stage batch adsorber model for removal of EY by PLC or LC

Table T1: Raman shift (cm^{-1}) and their band assignment for LC and PLC. The constituent of LC or PLC are given in parentheses.

LC (Raman shift (cm^{-1})		PLC Raman shift (cm^{-1})	
1097	C-C and C-O stretching in (cellulose)	1138	A mode of coniferaldehyde (lignin)
1130	Heavy atom (C-C and C-O) stretching (cellulose) A mode of coniferaldehyde (lignin)	1160	β C−H band in PANI
1278, 1382	H-C-C and H-C-O bending (cellulose)	1160, 1490, 1595	quinonoid structure of PANI
1340	A phenol mode (lignin)	1382	H-C-C and H-C-O bending (cellulose)
1419, 1463	guaiacyl ring vibration (lignin)	1487	C=N bond stretching
1492	aryl ring stretching, asymmetric (lignin)	1511	aryl ring stretching, asymmetric (lignin)
1536	aryl ring stretching, symmetric (lignin)		

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