

Biosorption of Basic Black 2XRL from Aqueous Solution and Leather Industry Wastewater Using *Annona squamosa* Bark

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ABSTRACT: Application of *Annona squamosa* bark as biosorbent for the removal of Basic Black 2XRL dye from aqueous solution and leather industry wastewater was investigated. Batch experiments were carried out to determine the effect of pH, particle size, biosorbent dose, contact time and initial dye concentration. Characterization of biosorbent was also done. Maximum dye biosorption of 78.46 % was achieved at pH 7.0, particle size 212 μ m, biosorbent dose of 0.8 g/L, contact time of 120 min and initial concentration of 50 mg/L. The equilibrium biosorption data fitted well to pseudo second order and Langmuir than Freundlich isotherm models. The biosorption results in this study indicated that *Annona squamosa* barks are attractive option for removing basic dyes from the wastewater

KEYWORDS: *Annona squamosa*; Basic Black 2XRL; Biosorption; Isotherm.

I. INTRODUCTION

Leather industries are well known for its effluent problems. The polluting nature of tanneries is obvious from its tarnished odour that specifies tanneries and their zones. Tanneries' liquid effluents which tend to be high in organic and inorganic suspended solids content are also accompanied with dyes. Dyes are basically chemical compounds that can attach themselves to fabrics or surfaces to impart colour due to their complex organic molecules and are resistant to weather, action of detergents, etc. As a result, it is very difficult to degrade it [1]. A series of environmental and health issues are seen as their effect [2, 3, 4]. To overcome this, there are various conventional methods such as chemical coagulation using alum, lime, ferric sulphate [5], oxidation methods using chlorine and ozone [6] biological treatments, floatation [8] and many more which has a draw back as it is expensive, inefficiency and sludge disposal problem [7]. These methods are expensive and industries have been interest to develop technologies which are low cost and eco friendly, among such eco-friendly techniques biosorption is one such technique.

The present study investigates the biosorption of Basic Black 2XRL (BB2XRL) dye from aqueous solution and wastewater using *Annona squamosa* (ASB). Chemical Characterization of ASB and physico-chemical characteristics of leather industry wastewater were studied. The effect of pH, particle size, biosorbent dose, contact time and initial dye concentration of biosorption were studied in detail. Kinetic isotherms, Langmuir and Freundlich isotherm models were used to fit the equilibrium data which revealed pseudo-second order and Langmuir isotherm model fits well.

II. MATERIAL AND METHODS

The Basic black 2XRL (BB2XRL) dye was obtained from Fareeda group, India LTD, Ranipet, Tamil Nadu. Its IUPAC name is 3-Diethylamino-7-(4-hydroxy-phenylazo)-5-phenyl-phenazin-5-ium; chloride. The molecular formula is C₂₈H₂₆ClN₅O, molecular weight is 483.99 [g/mol] and structure of the BB2XRL is shown in Fig 1

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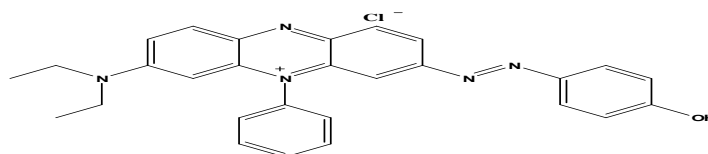


Fig 1: Structure of BB2XRL

A. DYE SOLUTION PREPARATION

An accurately weighed quantity of Basic black 2XRL dye (BB2XRL) was dissolved in double distilled water to prepare stock solution (1000 mg/L) and further diluted to obtain working solutions of lower concentration 50 mg/L which was determined using the absorbance values before and after the biosorption using UV-Vis Spectrometer (HitachiUV-2910). The pH adjustment of solution was carried out using 0.01N HCl and 0.01N NaOH

B. PREPARATION OF BIOSORBENT

This study was focused on investigating biosorption of BB2XRL using *Annona squamosa* barks (ASB). Barks were collected washed thoroughly and dried using sunlight. Subsequently the seeds peels were grounded and sieved to get fine sizes (212µm, 250µm, 355µm, 500µm), according to the standards of ASTM (American Society Testing Materials). And sieved biosorbent was washed thoroughly and constantly several times using double distilled water to remove unwanted particles and dried well in the sunlight, cooled stored the biosorbent in the dry place for experimental use.

C. CHARACTERIZATION OF BIOSORBENT

The FTIR and SEM analyses were carried out by (Shimadzu-IRAffinity-1) FTIR Spectrophotometer and ZEISS, (EVO/LS-15).

D. CHEMICAL CHARACTERIZATION OF BIOSORBENT

Surface area analyses, Elementary analyses were carried out by Quanta chrome Autosorb K and PerkinElmer PE2400, along with analysis of Total ash % and pH of the biosorbent which was also followed by [9,10], respectively. The different chemical constituents of ASB are given in Table 1 along with some other characteristics

Table 1: Chemical characteristics of *Annona squamosa* barks

Parameter	Results
pH	8.12
Total Ash (%)	2.67
Surface Area (m ² /g)	0.42
Elemental Analysis (%)	
C	36.19
H	1.32
N	0.58
S	Below Detective Limit
O	61.91

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Vol. 4, Issue 12, December 2015

E. BATCH EXPERIMENTS

Batch experiments were carried out at room temperature. For experimental run 1000 mg/L of stock solution of BB2XRL was prepared and dilutions were made with double distilled water to determine the effects of different concentrations (10 to 50 mg/L) at required pH level ranging from 2.0 to 10.0 which was determined by using 0.01N HCl and 0.01N NaOH respectively, known amount of biosorbent dose (0.2 g/L to 2.0 g/L) were taken in 250 mL Erlenmeyer flasks and the mixtures were shaken at 170 rpm using mechanical shaker (KEMI KRS 110, India) for a fixed period of time varying from 15 min to 210 min. Mixtures were then filtered from ASB and determined spectrophotometrically using UV-Vis spectrophotometer (HitachiUV-2910) at 670 nm. Determinations of effects pH, particle size, biosorbent dose, contact time and initial dye concentration were done in triplicate average values and then considered. Percentage of biosorption was calculated by the formula

$$\%B = \left(\frac{C_i - C_f}{C_i} \right) \times 100 \quad (1)$$

Where C_i and C_f are the initial and final BB2XRL concentration (mg/L) respectively

F. PHYSICO-CHEMICAL CHARACTERISTICS OF LEATHER INDUSTRY WASTEWATER

The wastewater was collected from leather industry located in Ranipet, Tamil Nadu India. The physico-chemical characteristics were determined using standard method of APHA [11]. The results are presented in Table 2.

Table 2: Physico-chemical characteristics of leather industry wastewater

Characteristics	Contents(mg/L)
Colour	Dark black
pH	6.80
EC(μ s/cm)	8792
Turbidity (NTU)	75.6
TDS	4639
TSS	1801
Total hardness	1524.8
Calcium	706.5
Magnesium	138.4
Chloride	991.2
Sulphate	215.9
Nitrite + Nitrate	169.3
Sodium	1100.7
DO	Nil
BOD	1037.6
COD	2485.1
Iron	8.60
Chromium	1.28

III. RESULT AND DISCUSSION

A. FTIR ANALYSIS

Fig 2a and b shows FTIR spectra of BB2XRL before and after biosorption on ASB. The bands show functional groups of sulphur and carboxylic acids and their derivatives. The peak ranging from 483cm^{-1} is due to S-S bonds in Fig 2a

which are reduced in the Fig 2b as observed; this is due to the biosorption of BB2XRL on ASB. The peaks between 1539 and above 3840 cm^{-1} indicates oxidizing nitrogen functional groups like C=N bonds, O-H stretched bonds and C-N bonds of amine along with overlap C-H stretched bands. The peaks ranging from 2750 to 3500 cm^{-1} which appears as clusters in Fig 2b indicate strong stretching vibration of carboxylic acids groups of amide. An FTIR spectrum of Fig 2b shows peaks in low frequency regions and absence of peaks ranging from 514 cm^{-1} to 720 cm^{-1} because there is a biosorption of BB2XRL on ASB surface, biosorption showed that carbon, hydrogen and atom bonds played major role. Decreased intensity of sharp peaks concluded that BB2XRL has been functionalized by ASB [12].

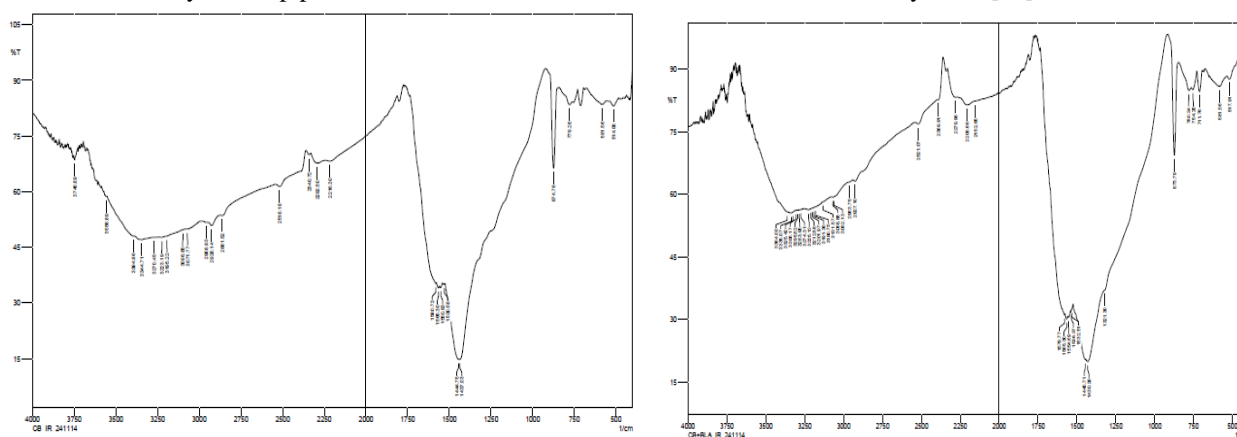


Fig-2 a. FTIR of ASB before biosorption

b. FTIR of ASB after biosorption

B. SCANNING ELECTRONIC MICROSCOPIC STUDIES (SEM)

The ASB morphology was characterized using SEM and the microphotographs, as shown in Fig 3a and 3b. Fig3a shows thick lining with no pores on ASB before biosorption of BB2XRL. However it was not observed after biosorption due to significant changes in the structure of the barks as observed in Fig 3b. They appear cube like deposition along with lining of pore, formation appearing like comb [12, 13]. This phenomenon can be explained by the package of pores involved in dye molecules

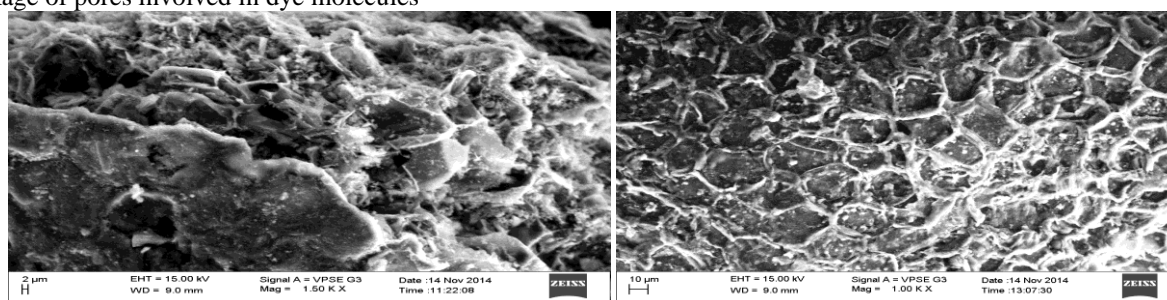


Fig 3 a: *Annona squamosa* (ASB) before biosorption

b: *Annona squamosa* (ASB) after biosorption

C. EFFECT OF pH

The pH of BB2XRL has a great influence on biosorption process of ASB, as it effect on the surface charges of the dye molecules on ASB[8]. Fig 4 shows the effect of pH on the removal of BBX2RL. The percentage of biosorption of BBX2RL increases from 2.0 to 6.0 (31.74% to 75.60 %) and attained maximum biosorption at pH 7.0 (78.46 %) and decreased from 8.0 to 10.0. This is because, at lower pH, ASB is covered with more number of H_3O^+ ions which gets replaced by OH^- ions as the pH increases making the surface negatively charged[14]. Similar results were recorded in malachite green [15], methylene blue [16] and other basic dyes [17,18] in the process of biosorption

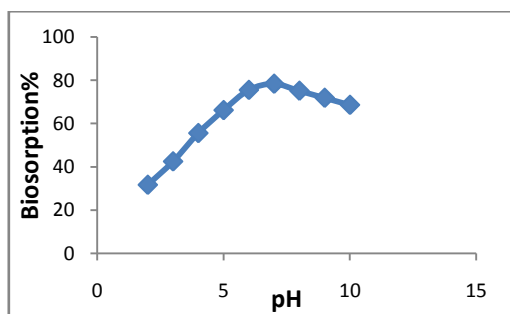


Fig 4: Effect of pH on BB2XRL biosorption on ASB

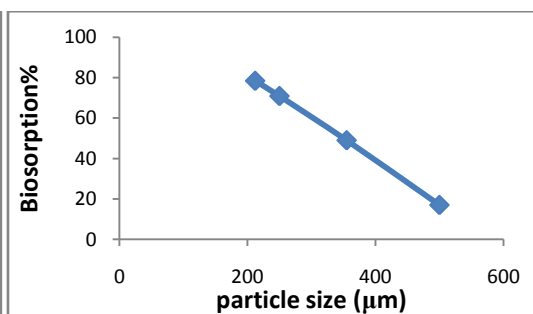


Fig 5: Effect of particle size on BB2XRL biosorption on ASB

D. EFFECT OF BIOSORBENT PARTICLE SIZE

The effects of ASB particle size on biosorption of BB2XRL are shown in the Fig 5. The results describe that the 78.46 % biosorption of BB2XRL was achieved at 212μm. As size increased, biosorption decreased by ASB. It clearly defines that; decrease in particle size would increase the surface area and consequently an increase in BB2XRL biosorption onto the ASB surface. Various factors are responsible for the low biosorption capacity of the BB2XRL on the larger particles size as there may be over saturation of pore sited or high competition for available sites. Similar kinds of result were recorded [19, 20].

E. EFFECT OF BIOSORBENT DOSE

The biosorbent doses on BBX2RL by ASB are shown in Fig 6. The results describe that BBX2RL biosorption increases with increasing biosorbent dose from 0.2 to 0.8 g/L. Maximum biosorption by ASB ranges from 55.22 % to 78.46 %. This is due to increase in surface area and availability of the exchangeable sites on ASB for the biosorption of BBX2RL [21]. Further increase in biosorbent dose beyond 0.8 g/L showed no effect on BBX2RL biosorption, as it attained equilibrium between the liquid and solid phase. Similar results were observed in other basic dyes [22, 23].

F. EFFECT OF CONTACT TIME

The variation of contact time of BBX2RL on ASB is shown in Fig 7. It was clear that maximum biosorption of BBX2RL on ASB (78.46 %) was achieved at 120 min. A rapid biosorption of BBX2RL by ASB took place at 30mins and continued till it reached 75mins and then the biosorption was slow till it reached the equilibrium state. The reason being that, at initial stage there were a more vacant sites for biosorption, which further gets occupied, resulting in slow biosorption. And the biosorption reaches equilibrium state, when contact time and percentage of biosorption becomes constant [24, 25].

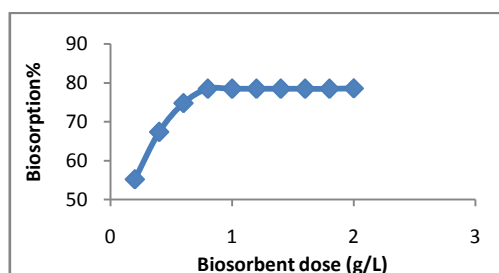


Fig 6: Effect of biosorbent dose of BB2XRL biosorption on ASB

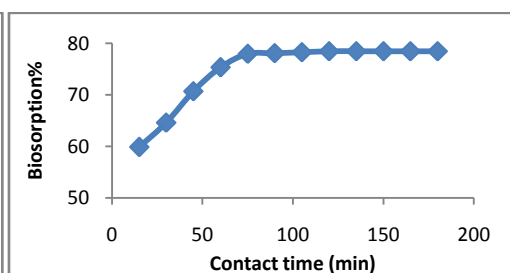


Fig 7: Effect of contact time for BB2XRL biosorption on ASB

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(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 12, December 2015

G. KINETIC ISOTHERMS

The Lagergren's pseudo-first-order model and Ho's pseudo-second-order model [26] have been widely used to predict biosorption kinetics. The pseudo-first order equation is generally applicable to the initial stage of the biosorption processes whereas the pseudo-second order equation predicts the behavior over the whole range of biosorption. These two models were used to fit the present experimental data, whose equations are described in equation (2) and (3)

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t \quad (2)$$

$$\frac{t}{qt} = \left(\frac{1}{k_2 q_e^2}\right) + \left(\frac{1}{q_e}\right) t \quad (3)$$

Where k_1 (min^{-1}) is the rate constant of pseudo-first- order adsorption and k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) is the rate constant of pseudo –second-order adsorption. q_e is amount of dye biosorbed on biosorbent at equilibrium.

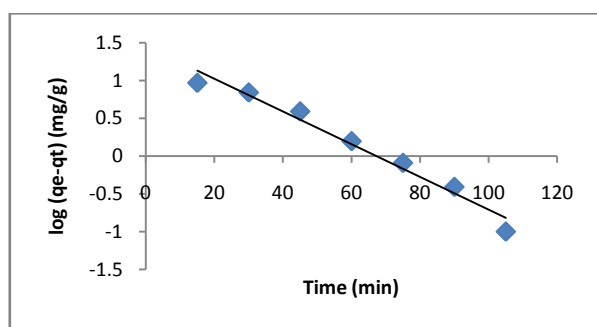


Fig 8: Pseudo-first order for BB2XRL by ASB

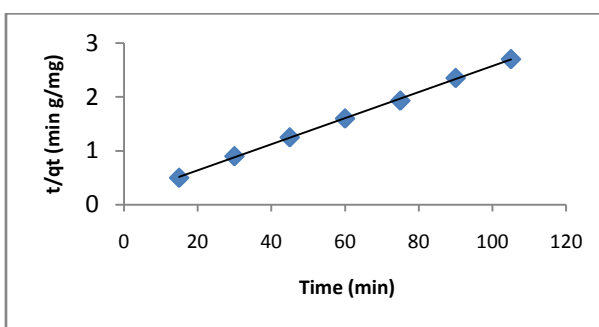


Fig 9: Pseudo-second order for BB2XRL by ASB

Plots of pseudo-first-order and second order are shown in Fig 8 and 9. Results show that pseudo-first-order rate constant (K_1) for BB2XRL biosorption by ASB was $1.17 \times 10^{-3} \text{min}^{-1}$ but $q_{e \text{ cal}}$ values obtained largely different than that of $q_{e \text{ exp}}$ values which indicate the non applicability of pseudo- first order model, whereas higher pseudo-second order rate constant (K_2) of $5.04 \times 10^{-3} \text{g/mg min}^{-1}$ was achieved by ASB, which shows moderate BB2XRL biosorption by ASB. The $q_{e \text{ cal}}$ (27.51 mg/g) values of pseudo- second order are closer to $q_{e \text{ exp}}$ (28.03 mg/g) values and higher regression coefficient (R^2) value was obtained revealing better fitting of equilibrium data to pseudo second order model. This confirmed the involvement of chemical biosorption through exchange or sharing of electrons between biosorbent and biosorbate [25]. Table 3 describes the pseudo-first order and pseudo-second order.

Table -3 Pseudo First Order and Pseudo Second Order Constants Chosen for Biosorption by ASB

Dye	$q_{e \text{ exp}}$ (mg/g)	Pseudo first order			Pseudo second order		
		$K_1(\text{min}^{-1})$	$q_{e \text{ cal}}$ (mg/g)	R^2	$K_2(\text{g/mg min}^{-1})$	$q_{e \text{ cal}}$ (mg/g)	R^2
BB2XRL	28.03	1.17×10^{-3}	25.74	0.971	5.04×10^{-3}	27.51	0.999

H. EFFECT OF INITIAL DYE CONCENTRATION

Initial concentration is also an important parameter in the process of biosorption. Fig 10 shows the initial concentration of BB2XRL by ASB, which describes that, the percentage of biosorption decreases from 99.62 % to 78.46 % with increase in concentration. This is due to the fact that BB2XRL ion concentration causes saturation of biosorption sites on ASB and then blocks further ASB sites as a result the biosorption efficiency decreases [27, 28].

International Journal of Innovative Research in Science, Engineering and Technology

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Vol. 4, Issue 12, December 2015

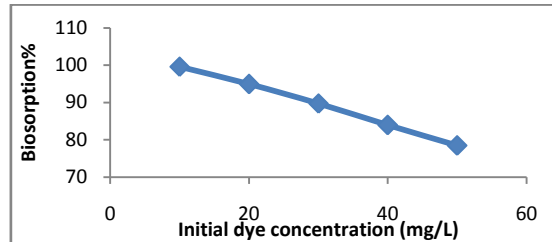


Fig 10: Effect of initial dye concentration BB2XRL biosorption on ASB

I. LANGMUIR AND FREUNDLICH ISOTHERM

The biosorption data was fitted with two isotherms namely Langmuir and Freundlich. The Langmuir [29] and Freundlich isotherm [30] model equations are described in equation (4) and (5) respectively.

$$\frac{C_e}{q_e} = \frac{1}{(b q_{max})} + \frac{C_e}{q_{max}} \quad (4)$$

$$q_e = K_f C_e^n \quad (5)$$

Where, C_e is the equilibrium concentration (mg/L), q_e and q_{max} are the equilibrium and maximum biosorption capacity in (mg/g) respectively, b is the Langmuir constant, K_f and n are the Freundlich constant.

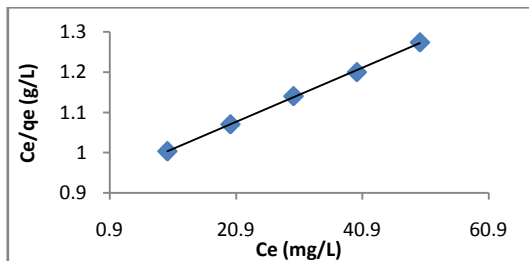


Fig 11: Langmuir isotherm plots for BB2XRL by BB2XRL by ASB

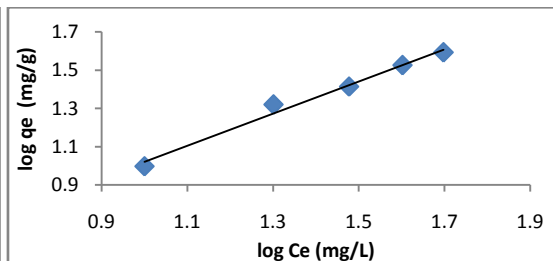


Fig 12: Freundlich isotherm plots for BB2XRL by BB2XRL by ASB

Fig 11 shows the linear plot obtained by plotting C_e/q_e versus C_e . The Langmuir model effectively described the biosorption data R^2 value of 0.999 as given in Table 4. This behaviour indicates monolayer biosorption. The value of b (120.14 L/g) and Q_{max} (58.23 mg/g) indicates maximum interaction and greater affinity of BB2XRL with ASB [31]. Fig 12 shows the linear plot obtained by plotting $\log q_e$ versus $\log C_e$. The Freundlich model parameters like R^2 0.986 values, K_f 11.87 (mg/g) (mg/L)^{1/n} and n (0.80) are given in Table 4. The results indicate that biosorption data for BB2XRL fits well to Langmuir model than Freundlich model. Hence biosorption was monolayer coverage of BB2XRL on ASB [32, 33].

Table -4 Langmuir Isotherms and Freundlich Isotherm Parameters for Biosorption by ASB

Dye	Langmuir isotherm			Freundlich isotherm		
	Q_{max} (mg/g)	b (L/g)	R^2	K_f (mg/g)(mg/L) ^{1/n}	n	R^2
BB2XRL	58.23	120.14	0.999	11.87	0.80	0.986

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 12, December 2015

J. APPLICATION OF LEATHER INDUSTRY WASTEWATER

The practical applicability of ASB for biosorption of BB2XRL from leather industry wastewater was assessed with experiments carried out as follows: 250 mL of Erlenmeyer flask containing 50 mL of wastewater sample which was pre-treated and preserved was taken. To this 212 μm particle size of 0.8 g/L biosorbent dose of ASB was added and pH was adjusted to 7.0 using 0.01N HCl and 0.01N NaOH. After 120 min of agitation, the wastewater sample was filtered and the resultant supernatant solution was analysed by UV-Vis.spectrophotometer (HitachiUV-2910). The result described that BB2XRL biosorption from leather industry wastewater was 70.62% which was less than the aqueous solution. This is due to competition between ions of dyes and co-ions interference for biosorption sites on ASB. Similar results were observed in NNP-bentonite [15], Dairy Sludge [32] and others.

IV. CONCLUSION

The present study investigated the biosorption of BB2XRL by ASB from aqueous media and leather industry wastewater. The biosorption equilibrium was described by the isotherm model. A single-stage batch biosorption system was designed for the BB2XRL removal which was also outlined based on the isotherm model. Langmuir model data fits well than Freundlich model, proving biosorption was monolayer coverage of BB2XRL on ASB. And when the ASB was applied for leather industry wastewater, percentage of biosorption was less compare to aqueous solution as the competition and interaction between ions of BB2XRL and co ions of other dyes. It can be concluded that the efficiency of ASB holds good in biosorbing BB2XRL from leather industry wastewater.

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