Study of bimacid dye removal from aqueous solution: a comparative study between adsorption on pozzolana, bentonite, and biosorption on immobilized anaerobic sulfate-reducer cells

A. Djafer \textsuperscript{a}, S. Kouadri Moustefai \textsuperscript{a}, A. Iddou \textsuperscript{b} & B. Si Ali \textsuperscript{c}

\textsuperscript{a} Laboratoire Eau et Environnement, Université Hassiba Benbouali Chlef, BP 151, 02000, Chlef, Algeria Phone: Tel. +213 55 52 57 450 Fax: Tel. +213 55 52 57 450

\textsuperscript{b} Laboratoire de Valorisation des Matériaux, Université Abdelhamid Ibn Badis de Mostaganem, Bp. 227, Mostaganem, Algeria

\textsuperscript{c} Faculty of Engineering, Chemical Engineering Department, University of Malaya, Kuala Lumpur, 50603, Malaysia

Published online: 28 Aug 2013.

To cite this article: A. Djafer, S. Kouadri Moustefai, A. Iddou & B. Si Ali, Desalination and Water Treatment (2013): Study of bimacid dye removal from aqueous solution: a comparative study between adsorption on pozzolana, bentonite, and biosorption on immobilized anaerobic sulfate-reducer cells, Desalination and Water Treatment, DOI: 10.1080/19443994.2013.833866

To link to this article: http://dx.doi.org/10.1080/19443994.2013.833866

PLEASE SCROLL DOWN FOR ARTICLE
Study of bimacid dye removal from aqueous solution: a comparative study between adsorption on pozzolana, bentonite, and biosorption on immobilized anaerobic sulfate-reducer cells

A. Djafera,*, S. Kouadri Moustefai, A. Iddoub, B. Si Ali

Laboratoire Eau et Environnement, Université Hassiba Benbouali Chlef, BP 151, 02000 Chlef, Algeria
Tel. +213 55 52 57 450; Fax: +21327797795; email: ab-dja@hotmail.fr

Laboratoire de Valorisation des Matériaux, Université Abdelhamid Ibn Badis de Mostaganem, BP. 227, Mostaganem, Algeria

Faculty of Engineering, Chemical Engineering Department, University of Malaya, Kuala Lumpur 50603, Malaysia

Received 4 December 2012; Accepted 5 August 2013

ABSTRACT

The effluents emanating from industries such as paper, plastics, textile, and leather contain many dyes which are toxic and carcinogenic. The treatment of these effluents has become very important to reduce the potential toxicity of their pollutants and minimize their concentration prior to their discharge. This paper presents a comparative study between adsorption and biosorption processes for the red dye bimacid removal from aqueous solution. The experimental results show that the removal efficiency of the red bimacid using biosorption process which uses immobilized anaerobic sulfate-reducer cells onto a physical adsorbent is more significant (up to 91%) as compared to the adsorption process using bentonite and pozzolana powders. The kinetics of biosorption and the adsorption isotherms of the red dye bimacid on these materials showed great affinities to adsorbent-adsorbate. The pH of the aqueous solution influences positively the rate of the dye removal in the case of adsorption; however, it is a limiting factor in the case of biosorption.

Keywords: Dye; Biosorption; Adsorption; Pozzolana; Bentonite; Equilibrium modeling

1. Introduction

Industries such as food processing, textile, leather, tanning, cosmetics, and pharmaceutical use dyes for coloring purposes. These activities generate highly colored wastewaters if not treated thoroughly will affect the environment in many aspects. It is believed that the wastewater discharged from the textile industry contains more than 13% of dyes [1]. The environmental impact of textile industry is associated with its high water consumption and the amount of pollutants released in the effluent [2].

The presence of dyes in the effluent is not only undesirable, but also causes dangerous problems to the receptor’s medium [3]. Dyes are toxic [4,5], they affect several properties of water, amongst others the COD and BOD which impacts the activity of plants and the phytoplankton [6,7].
Dyes are stable and xenobiotic in nature, they are resistant to microbial and physico-chemical attacks, they exhibit the slow degradation rate using conventional methods of wastewater treatment, including biological treatment using activated sludge [8,9]. It is estimated that 50 to 90% of the dyes remain unchanged after treatment [10,11].

The effectiveness of physical and chemical processes for the removal of recalcitrant compounds has been proved by several researchers. These include chemical precipitation, oxidation, ion exchange, reverse osmosis, coagulation and flocculation, adsorption, and membrane technology [12,13]. The drawbacks of these methods are high reagent and energy requirements, generation of toxic sludge and other waste products. These methods are usually very expensive when the pollutants’ concentration are in the range of 10–100 mg L⁻¹ [14]. However, it is possible to use other low-cost methods, using available materials which could adsorb toxic dyes from textile wastewater. Micro-organisms are potent biosorbents for the removal of dyes from wastewater via active or passive uptake action. In general, dyes accumulative bioprocesses fall into one of the two categories: biosorption uptake by non-living cells, non-growing biomass [15] and bioaccumulation by living cells [16,17]. Biosorption and exploitation of cells enzymes for biodegradation can be used to remove dyes effluents from the textile industry. Interactions between dyes and a wide variety of micro-organisms, such as bacteria [18], fungi [19,20], algae [21], and yeast, [22,23] depend on the chemical properties of all the reaction partners. Each dye can have affinity to various micro-organisms. On the other hand, one micro-organism is able to bind to various types of dyes [20]. The effectiveness of accumulative bioprocesses is usually dependent on the parameters such as oxygen level, toxicity of the pollutant, pH of the media, temperature, and availability of nutrients, etc. If the problem of dyes toxicity to the growing cells is overcome using dyes-resistant organisms, the continually self-replenishing system could run continuously for an extended period [24,25].

This work investigates the red bimacid dye removal using the biomass obtained from the domestic wastewater treatment plant of Chlef city/Algeria. In order to obtain a ratio of C/N is 10 [26] and a ratio of C/P is 50 [27]; micro-organisms were grown in anaerobic agitated media containing the following components [28]: glucose (1 g), peptone of casein (0.2 g), NH₄NO₃ (0.0571 g), and KH₂PO₄ (0.035 g). The mixture was dissolved in one liter of tap water.

2.2. Adsorbate

The adsorbate E5R dye (Commercial name = Red bimacid, nature = acid) was procured from a local textile company (SOITEX/Algeria). Amount of red bimacid was dissolved in double distilled water to prepare stock solution of 1,000 mg L⁻¹. Solutions of desired concentration were prepared from the stock solution.

2.3. Batch biosorption studies

Batch study was conducted in an agitated constant temperature reactor (volume = 1,000 mL). The culture media (300 mL) used contains dye and 10% (v/v) of inoculum. Pozzolana (60 g) is used as a support with an average particle size of 30 mm and 4 m² g⁻¹ specific area. The reactor is then put on a rotary shaker at a constant speed of 100 rpm and a constant temperature of 20 ± 2°C. The process was monitored until the substrate limiting conditions reached. Samples were periodically taken and centrifuged at 3,000 rpm for 5 min and the supernatant liquid was separated and analyzed for residual red bimacid concentration. Spectrophotometric titration was carried out using an OPTIZEN 2010 spectrophotometer at 504 nm, and pH measurements were conducted using a HANNA 120 pH-meter.

The chemical composition of bentonite and pozzolana (Table 1) was determined using the XRD Philips PW 3710 X-ray apparatus. Infrared spectra were obtained from (2.5 wt.%) the samples in KBr disks from 500 to 4,000 cm⁻¹ using a Thermo Nicolet Avatar 320 FTIR Spectrometer.

2.4. Batch adsorption

Batch adsorption experiments were performed in a 300-mL reactor containing 60 mL of dye in synthetic wastewater solution. 0.1 g of bentonite and pozzolana powders were added as adsorbent. The solutions were then agitated on a rotary shaker at a constant speed of 100 rpm under a controlled temperature of 20 ± 2°C. The samples were taken at appropriate time intervals and were centrifuged at 3,000 rpm for 5 min. The

2. Materials and methods

2.1. Preparation of the biosorbent

The biosorbent (anaerobic sulfate-reducer cells) was provided by the domestic wastewater treatment
supernatant was used for the analysis of the residual dye concentration. The effect of pH on the dye removal was studied in a range of 2–8. The pH was adjusted using a diluted aqueous solution of HCl (0.1 M) and NaOH (0.1 M).

The adsorption and biosorption kinetic rate prediction is an important parameter in designing batch adsorption systems. The kinetic parameters for the solute uptake are necessary in selecting optimum operating conditions for full-scale batch process. The kinetics of the biosorption and adsorption data were analyzed using two kinetic models: pseudo-first-order and pseudo-second-order models. These models correlate solute uptake, which predict the reactor volume [28]. The models are described as follows:

### 2.4.1. Pseudo-first-order model

The possibility of adsorption data following Lagergren pseudo-first-order kinetic [28–30] is given by Eq. (1):

\[
\log_{10}\left(\frac{q_e}{q_e - q}\right) = \frac{k_1}{2.3} t
\]

where \(q_e\) and \(q\): amounts of the solute adsorbed at equilibrium and at time \(t\), respectively (mg g\(^{-1}\)); \(k_1\): pseudo-first-order rate constant (h\(^{-1}\)); \(t\): time (h)

The pseudo-first-order constant rate \(k_1\) can be obtained from the slope of the plot of \(\log (q_e/(q_e-q))\) vs. time.

### 2.4.2. Pseudo-second-order model

A pseudo-second-order model proposed by Ho and McKay [14,31] can be used to explain the biosorption kinetics. The pseudo-second-order model can be expressed as:

\[
\frac{1}{q_e} = \frac{1}{q_t} + k_2 t
\]

where \(t\) is the contact time (hours), \(q_e\) (mg g\(^{-1}\)) and \(q_t\) (mg g\(^{-1}\)) are the amount of the solute adsorbed at equilibrium and at time \(t\). A plot of \(t/q_t\) vs. \(t\) gives the value of the constant \(k_2\) (g mg\(^{-1}\) h\(^{-1}\)).

The adsorption and biosorption isotherms were then determined by mixing red bimacid solution of different concentrations with known amount of adsorbent till the equilibrium was achieved. The removal efficiency (\(R_E\) (%)) and the dye uptake \(q\) (mg g\(^{-1}\)) were determined using the following equations [28]:

\[
R_E (%) = \frac{(C_0 - C_t)}{C_0} \times 100
\]

\[
q_t = \frac{(C_0 - C_t)v}{m}
\]

where \(q_t\) (mg g\(^{-1}\)) is the amount of dye adsorbed per gram of the adsorbent, \(C_0\) and \(C_t\) are the initial and final dye concentrations (mg L\(^{-1}\)), respectively; \(v\) is the solution volume (L) and \(m\) is the adsorbent mass (g).

### 3. Results and discussion

#### 3.1. FTIR spectra analysis

Figs. 1–3, allow seeing the principal functional groups of the dye and the used materials before and after adsorption of the dye E5R. In fact, the two materials are characterized by bands at 3,400 cm\(^{-1}\) attributed to the hydroxyls groups. The Si-O band at 1,100 cm\(^{-1}\) confirms that the majority of the silica is present in bentonite and pozzolana (Table 1). After adsorption of the dye, it is clear that the increase in the intensities of the absorption bands at 3,400, 1,100 and 1,600 cm\(^{-1}\), and the disappearance of the band at 1,500 cm\(^{-1}\) and the enlargement of the band at 1,000–1,100 cm\(^{-1}\) gives an unequivocal evidence of the fixation of the dye.

<table>
<thead>
<tr>
<th></th>
<th>SiO(_2)</th>
<th>Al(_2)O(_3)</th>
<th>Fe(_2)O(_3)</th>
<th>CaO</th>
<th>MgO</th>
<th>Na(_2)O</th>
<th>K(_2)O</th>
<th>SO(_3)</th>
<th>WL</th>
<th>(S_{BET}) (m(^2)/g)</th>
<th>(V_{pore}) (cm(^3)/g)</th>
<th>(D_{pore}) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pozzolana</td>
<td>46.10</td>
<td>17.50</td>
<td>10.50</td>
<td>5.00</td>
<td>3.00</td>
<td>1.50</td>
<td>0.40</td>
<td>4.41</td>
<td>0.011</td>
<td>109.58</td>
<td>0.062</td>
<td>62.33</td>
</tr>
<tr>
<td>Bentonite</td>
<td>65.20</td>
<td>17.25</td>
<td>1.20</td>
<td>5.00</td>
<td>3.10</td>
<td>3.00</td>
<td>1.70</td>
<td>3.55</td>
<td>0.062</td>
<td>62.33</td>
<td>0.062</td>
<td>62.33</td>
</tr>
</tbody>
</table>

Note: WL: weight loss at 900°C.

The samples were monitored for dye removal using adsorption on bentonite and pozzolana, and biosorption on immobilized cells onto granular pozzolana. Fig. 4 illustrates dye removal experiments using the two tested systems. The removal rate of
immobilized anaerobic sulfate-reducer cells onto granular pozzolana was slower than those obtained using adsorption onto bentonite and pozzolana powders. Initially, higher red bimacid removal efficiency using pozzolana and bentonite was observed; this could be related to the pore structure and chemical
nature of adsorbent surface availability in terms of vacant sites at the initial stage [32]. However, a maximum red bimacid removal was obtained using biosorption as compared to physical adsorption. Furthermore, it is observed that the adsorbents removal efficiency was invariable after 6 h under the conditions of the experiments. This means that active sites of the adsorbent are saturated [33].

The difference in performance between the biosorbent and adsorbents could be due to the structure and composition of the cell wall of the sulfate-reducer. Kulczycki et al. [34] explained that the biosorbent has higher efficiency as compared to the physical adsorbents (such as bentonite and pozzolana) and is related to the specific chemical reactivity of functional groups (e.g. carboxyl and phosphoryl groups) that occur within the structural polymers of cell walls of different kinds of bacteria.

3.3. Effect of pH

Several authors [28,35–37] have studied dyes adsorption and they concluded that the solution pH is the most important factor affecting the adsorption process. This investigation examines the role of hydrogen ion concentration in the adsorption of the red bimacid dye on bentonite and pozzolana in the pH range of 2–8. The data shown in Fig. 5 reveal that the red bimacid adsorption on bentonite and pozzolana increased from 40 to 58% and 45.12 to 67.25%, respectively, for both adsorbents when the solution pH decreases from 8 to 2. The maximum dye sorption was observed at a pH of 2. This phenomenon of adsorption characteristics can be attributed to the higher electrostatic attraction between the positively charged surface of the adsorbent and anionic dyes [28]. The functional groups present in the dyes play a major role in enhancing the dye adsorption process. Relatively less dye sorption was observed at basic pHs. When the initial pH increases, the number of hydroxyl sites on the adsorbent surfaces increases; hence the number of positively charged sites decreases. A negative surface charge of adsorbent does not favor the adsorption of dye anions due to electrostatic repulsion [35]. It is concluded that the presence of positive charges on the adsorbent surface over the investigated acidic pH range is the main reason for the dye adsorption [36,37].

Fig. 4. Adsorption onto bentonite and pozzolana, and biosorption by immobilized cells ($C_i = 60 \text{ mg L}^{-1}$).

Fig. 5. Effect of pH on sorption of dye E5R onto pozzolana and bentonite ($C_i = 60 \text{ mg L}^{-1}$).
3.4. Effect of initial dye concentration on biosorption and adsorption

The removal process efficiency ($R_E$) of the dye E5R depends not only on the properties of the adsorbents and biosorbent, but also on its initial concentration. The initial concentration provides an important driving force for mass transfer resistances between aqueous solution and solid phases [38]. Fig. 6 illustrates the effect of initial dye concentration on the removal efficiency of red bimacid on bentonite/pozzolana and sulfate-reducer cells. The results reveal that the removal efficiencies decrease with increasing initial concentration of red bimacid for both processes. $R_E$ values decrease from 90 to 78% for immobilized anaerobic sulfate-reducer cells, 60 to 51% for pozzolana and 55 to 43% for bentonite. The decrease of the removal efficiencies for biosorption and adsorption with an increase in initial dye concentration may be attributed to the decrease in the availability of surface area in the adsorbent to accommodate and fix more adsorbate in aqueous solution. Ben Hamissa et al. [29] reported that at high initial dye concentrations (>80 mg L$^{-1}$) the biosorbent active sites become saturated and consequently the dye ions cannot easily find an accessible site to bind, and take more time in order to reach another available sites.

4. Adsorption and biosorption kinetics modeling

Fig. 7 shows the Lagergren pseudo-first-order kinetic plot for the adsorption and biosorption of red bimacid on bentonite, pozzolana and immobilized anaerobic sulfate-reducer cells. The calculated values of the rate constant $k_1$ and their corresponding linear regression correlation coefficient ($R^2$) values are given in Table 2. The $R^2$ values found are: 0.95, 0.97 and 0.91 for bentonite, pozzolana and immobilized cells, respectively.

Fig. 8 shows the Ho and McKay model. The pseudo-second-order constant rate $k_2$, the calculated $q_e$ values and the corresponding linear regression correlation coefficient values $R^2$ are given in Table 2. The higher values of ($R^2 = 0.98$) for all adsorbent and the predicted values of $q_e$ nearly fitted the experimental results.
Accordingly, the low correlation coefficients found using Lagergren model suggested that the removal of dye E5R by all adsorbent did not follow the kinetic model. Then, this model cannot be applied to predict the sorption kinetics [39,40]. In fact, the pseudo-second-order kinetic model fits well the sorption data which supports the assumption that the kinetic model of biosorption and adsorption process is a chemisorption process. Similar kinetic results have been reported by Ncibi et al. [41] and Dogan et al. [42].

### 5. Adsorption isotherm

The experimental data were analyzed using linearized Langmuir and Freundlich adsorption isotherms Eqs. (5) and (6), respectively.

\[
\frac{C_e}{q_e} = \frac{1}{bQ_0} + \frac{1}{Q_0}C_e \tag{5}
\]

\[
\ln q_e = \ln K + \frac{1}{n} \ln C_e \tag{6}
\]

---

**Table 2**

Comparison of the kinetic constants for the pre-equilibrium adsorption and biosorption of red bimacid dye onto bentonite, pozzolana, and immobilized anaerobic sulfate-reducer cells

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Experimental ( q_e ) (mg/g)</th>
<th>Pseudo-first-order ( K_1 ) (h(^{-1}))</th>
<th>( R^2 )</th>
<th>Pseudo-second-order ( K_2 ) (g mg(^{-1}) h(^{-1}))</th>
<th>( q_{cal} ) (mg g(^{-1}))</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bentonite</td>
<td>103.78</td>
<td>0.0011</td>
<td>0.95</td>
<td>0.0087</td>
<td>120.00</td>
<td>0.977</td>
</tr>
<tr>
<td>Pozzolana</td>
<td>114.39</td>
<td>0.0028</td>
<td>0.97</td>
<td>0.0119</td>
<td>125.00</td>
<td>0.987</td>
</tr>
<tr>
<td>Immobilized sulfate-reducer</td>
<td>146.4</td>
<td>0.029</td>
<td>0.89</td>
<td>0.0003</td>
<td>166.66</td>
<td>0.98</td>
</tr>
</tbody>
</table>
where \( C_e \): equilibrium dye concentration (mg L\(^{-1}\)); \( q_e \): equilibrium dye uptake on the sorbent (mg g\(^{-1}\)); \( Q_0 \): is the maximum sorption capacity (mg g\(^{-1}\)). \( b \): Langmuir constant related to the affinity between the sorbent and sorbate (L mg\(^{-1}\)). \( K \): Freundlich constant denoting adsorption capacity (mg g\(^{-1}\)); \( n \): empirical constant of Freundlich indicating the adsorption intensity.

The adsorption isotherm’s experiments were carried out with dye solutions of different initial concentrations ranging from 10 to 120 mg L\(^{-1}\). A plot of equilibrium dye concentrations in the solid and liquid phases that is \( q \) vs. \( C_e \) and also \( C_e \) / \( q_e \) vs. \( C_e \) are retrospectively presented in Figs. 9 and 10.

According to the correlation coefficients obtained (Table 3), it could be concluded that the sorption process on pozzolana, bentonite and immobilized cells follows the Langmuir isotherm model. The applicability of this model and the high values of the correlations coefficient \( R^2 \) ranging from 0.97 to 0.99 suggest that favorable monolayer adsorption took place in the adsorption process. Similar observations were reported by Blala et al. [13] and Rathinam et al. [43].

The values of constants \( Q_0 \) and \( b \) were obtained by fitting the experimental data into Langmuir isotherm (Table 3). This data shows that dye uptake \( Q_0 \) is higher 250 mg/g with immobilized cells than 111.1 mg/g with bentonite and 142.85 mg/g with pozzolana. Furthermore, the low values of constant \( b \) indicate that the red bimacid has high affinity towards the immobilized sulfate-reducer cells.

The adsorption capacity of the immobilized cells on pozzolana is much higher than the biosorbents

---

**Table 3**

Sorption isotherm parameters of red bimacid onto pozzolana, bentonite, and immobilized anaerobic sulfate-reducer cells

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Langmuir parameters</th>
<th>Freundlich parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( Q_0 ) (mg/g)</td>
<td>( b ) (L mg(^{-1}))</td>
</tr>
<tr>
<td>Bentonite</td>
<td>111.11</td>
<td>0.21</td>
</tr>
<tr>
<td>Pozzolana</td>
<td>142.85</td>
<td>0.19</td>
</tr>
<tr>
<td>Immobilized cells</td>
<td>250</td>
<td>0.18</td>
</tr>
</tbody>
</table>

**Table 4**

Comparison of maximum sorption capacity of immobilized sulfate-reducer cells with other sorbents

<table>
<thead>
<tr>
<th>( Q_{\text{max}} ) (mg g(^{-1}))</th>
<th>Adsorbent</th>
<th>Authors</th>
<th>( N^* )</th>
</tr>
</thead>
<tbody>
<tr>
<td>148.02</td>
<td>Aspergillus oryzae</td>
<td>Yang et al., 2011</td>
<td>[44]</td>
</tr>
<tr>
<td>106.4</td>
<td>Aspergillus foetidus</td>
<td>Patel and Suresh, 2008</td>
<td>[45]</td>
</tr>
<tr>
<td>33.28</td>
<td>Orange bagasse</td>
<td>L.D. Fiorentin et al., 2010</td>
<td>[46]</td>
</tr>
<tr>
<td>71.43</td>
<td>Algae Azolla rongpong</td>
<td>T.V.N. Padmesh et al., 2006</td>
<td>[47]</td>
</tr>
<tr>
<td>89.351</td>
<td>P. vulgaris L. waste</td>
<td>S.T. Akar et al., 2009</td>
<td>[48]</td>
</tr>
<tr>
<td>43.5</td>
<td>Palm-Trees waste</td>
<td>Z. Belala et al., 2011</td>
<td>[13]</td>
</tr>
<tr>
<td>250</td>
<td>immobilized sulfate-reducer</td>
<td>This work</td>
<td></td>
</tr>
</tbody>
</table>
used by other workers. Table 4 summarizes the comparison of the maximum biosorption capacities of various sorbents.

6. Conclusion

A comparative study between adsorption and biosorption of dye from textile wastewater was carried out. It was found that the use of immobilized living cells (anaerobic sulfate-reducer) for the removal of red bimacid appears to be technically possible and economically attractive for the treatment of dye contaminated wastewater as compared to physical adsorbent such as bentonite and pozzolana. The advantages of the use of biosorption process instead of adsorption process in dye removal from wastewater are the simplicity of the system and the ability to accept a wide variation effluent when their initial concentration is less than 100 mg L\(^{-1}\).

The results from this work indicate that the biosorption by immobilized cells in batch process could be a potential technology to remove dyes from textile effluent. However, further studies are needed to fully optimize this technology for environmental applications. Important questions currently under investigation include the establishment of the exact mechanisms of biosorption by anaerobic sulfate-reducer cells, understanding the dye transformations, and the development of ways to enhance efficiency of the immobilized cells.

Acknowledgments

The authors would like to dedicate this work for the late Mr Prof. Ouali Mohand Said. The authors would like to thank Prof. A. Bentouami and Dr B. Benalioua for their help in FTIR characterization and Dr L.Temdrara for BET Analysis.

References


