Removal of dyes and metals using natural adsorbents

Karthik V.1*, Kamal B.2, Mohammed Haneef M. V.2 and Mannarthippusulthan M. A. M.2

1Department of Industrial Biotechnology, Government College of Technology, Coimbatore, Tamil Nadu, India
2Department of Environmental Engineering, Government College of Technology, Coimbatore, Tamil Nadu, India

ABSTRACT

The present study deals with the comparison of removal of dyes and metals using natural adsorbents such as rice husk, jack fruit leaf powder, coconut shell etc. The study deals with various research papers in which variety of biosorbents are used for the removal of dyes and metals. The entire working principle uses fixed bed column system for isolating and removing the impurities such as dyes and metals from the water sources. Dyes such as acid dyes, reactive azo dyes, food dyes, crystal violet dyes etc. and heavy metals such as lead, copper, cadmium etc. can also be effectively removed by adopting fixed bed column system through different adsorbing materials. The comparison between the various adsorbents is given in table. The adsorbing materials used here are Activated carbon, Rice husk, jack fruit leaf powder, coconut shell etc.

INTRODUCTION

Recent EU environmental policy, including measures affecting all member states, requires that zero synthetic chemical compounds should be released into the marine environment (Min-Yu-Teng et al 2006). Due to their chemical structure, dyes, present in the waste water streams of many industrial sectors, such as dyeing, textile, tannery and the paint industry, are resistant to exposure to light, water and many chemicals is and therefore difficult to decolourise once released into the aquatic environment. Activated carbon is the most efficient adsorbent used widely, but its high cost limits its applicability (F. A. Batzias et al, 2004). Research is currently focusing on the use of low-cost commercially available organic materials as viable substitutes for activated carbon; in fact, sawdust, a relatively abundant and inexpensive material, is being extensively investigated as an adsorbent for removing contaminants from water. Other adsorbent materials that have been studied included wood and agricultural residues, untreated or treated in various ways(Mike A. Acheampong et al 2012).

Many modern technologies such as photo degradation (Sun and Xu, 1997), Coagulation(El-Geundi, 2001), flocculation (Al-Qodah, 2000), chemical oxidation, electro-chemical oxidation (Mustafa Turn et al, 2005), Biological process (Runping Han et al 2006) are all available for the removal of dye from the waste water. (Asok Adak et al, 2005)

Adsorption, which has been extensively used in industrial process for a variety of separation and purification purposes, is rapidly becoming a prominent method of treating aqueous effluents. The colour removal from textile waste water is considered as an important application of the adsorption process using low-cost adsorbents such as shale oil ash (Al-Qodah, 2000), chitosan (Juang et al, 1997), sunflower stalk (Sun and Xu, 1997), natural clay (El-Geundi, 2001) against expensive adsorbents such as activated carbon
EXPERIMENTAL SECTION

The method adopted for standard configuration of fixed bed column studies were done by (McKay and Bino, 1990). A standard rate of flow has been maintained throughout the analysis with a known dye concentration passes through the packed bed of granular activated carbon (GAC). Main adsorbent ingredients used were GAC F 400, Adsorbate, such as acid dye Tectilon orange 3G are used (G. M. Walker et al 1997). The major crises arises in the fixed bed column’s working operation is not deaerated before to the adsorption test, as a result air masses were formed to the column formation of the air masses leads to critics of falling level of pressure, earlier deformation and mass level deformations between the solutions and the carbon (G. M. Walker et al 1997)

2.1. Clays and solutions
The main ingredients are Montmorilloite SAz =\textsuperscript{-1} (Al\textsubscript{2}O\textsubscript{3} .4SiO\textsubscript{2} .nH\textsubscript{2}O) as a source clay mineral element .the composition of the elements includes SiO\textsubscript{2} 60.4% Al\textsubscript{2}O\textsubscript{3} 17.4% Fe\textsubscript{2}O\textsubscript{3} 1.42% MgO 6.42% Na\textsubscript{2}O 0.068% CaO 2.282% (Su-Hsia Lin et al 2004). The clay minerals have found to be effective size of 0.03mm, cation shifting tendency of 120 meg/100g. The cation exchanging tendency of clay minerals were done by using strata of copper (II) ion (0.02 M cu (II) triethletramine) (Min-Yu-Teng et al 2006)

2.2. Adsorbent
Activated carbons extracted from the coconut husks were used. These constitute a minimal iodine number of 850mg of 12g of carbon each. The content of ash was very low (lower than 10%) and a relevant density of 500± 50 kgm\textsuperscript{-3}. The layer of the activated carbon is multilayered packed phase, irrelevant and irregular with a huge BET area (772m\textsuperscript{2}g\textsuperscript{-1}). The porous width of the surface 22.1Å (Anderson Marcos Dias Canteli et al 2013)

2.3. Biomass Preparation
Natural quantitative mass of rice husk were sampled and collected. It is rinsed with distilled water and made it to dry for a period of 8 hours at a temperature of 60°c. Then the biomass was sieved to an effective diameter of (0.5 mm) was used in column studies (Runping Han et al 2006).

2.4. Experimental procedures
The fixed bed tests were carried out in a water-jacketed glass column with an inside diameter of 1.1 cm and a length of 12.8 cm. A typical procedure was as follows. To one end of the column a small glass fibre inserted, aqueous slurry of the clays was then aspirated into the column to obtain the clay bed. A second portion of glass fibre was plugged to another embed the loaded clay in order to prevent the loss of the clay. (Asok Adak et al,2005) The aqueous solution with a known dye concentration was fed to the top of the column at a desired flow rate driven by a micro-metering pump (Cole-Parmer, Master flex 7518-10, USA) until the breakthrough curve was completed. The temperature was controlled at 25 °C. The samples in the outlet were taken at the present time intervals and the concentrations of dye were analysed with an UV– visual spectrophotometer (F.A.Batzias et al, 2004)

2.5. Mathematical description
The break through-curve analysis was used here to study about the column performance based on the shape and time of the curve where it traces over the column bed studies was known. The curve decides the factor of explaining the progress loading behaviour of MB intake from a solution in fixed bed= \( \frac{C}{C_0} \). The factor depends on the function of time, quantity of the solvent, width and height (Runping Han et al 2008).

2.6. Adams-Bohart models
In 1920 Adams and Bohart was found the relationship between \( \frac{C}{C_i} \) and \( t \) in a continuous system, which is applied to gas-solid system. Residual capacity of the solid and the concentration of the sorbed substance proportional to the sorption rate is a main assumption in this model. The Initial part of the breakeven curve can be obtained as above relationship using with following formulae:

\[
\frac{C}{C_i} = \frac{e^{hABG_i}}{e^{kABG_i} + e^{vABG_i}}
\]

(M.Calero et al 2009)

Where, \( C_i \) is the inlet metal concentration in solution in mg/L, \( k_{AB} \) is the kinetics constant in L/mg min, \( N_o \) is the maximum volumetric sorption capacity in mg/L, \( v \) is the linear flow rate in cm/min and \( z \) is the bed depth in the column in cm.
2.7. Thomas model
The Thomas model was mostly used in column performance modelling. Its expression assumes Langmuir kinetics of adsorption-desorption and no axial dispersion so that the driving force for adsorption obeys second-order reversible reaction kinetics. The formulae for the Thomas model for adsorption column is given as (Emmanuel I. Unuabonah et al 2012)

\[
\frac{c_t}{c_0} = \frac{1}{1 + \exp\left[\frac{k_{Th} q x}{Q} - k_{Th} c_0 t\right]}
\]

Where \(k_{Th}\) is the Thomas rate constant \([\text{mL/(h \text{ µmol})}]\), \(q_e\) is the equilibrium uptake capacity \((\text{µmol/g})\), \(x\) the mass of sorbent packed in the column \((\text{g})\) and \(Q\) is the volumetric flow rate \((\text{mL/h})\); \(c\) and \(c_0\) are the concentration \((\text{µmol L}^{-1})\) of PCP in the effluent and in the influent at any time \((h)\), respectively. (Mouloud Lezehari et al 2012)

2.8. Yoon-Nelson model
The model states the relation between the probability of adsorption of adsorbate molecules and adsorbate absorption they were directly proportional to one another. The model is not a complex one in nature and not requires information related to type of adsorbent or else the properties of column bed (Emmanuel I. Unuabonah et al 2012). The Yoon-Nelson model not only was less difficult than other models, but also necessitates no detailed data concerning the characteristics of adsorbate, the physical properties of the adsorption bed and the type of adsorbent. The Yoon-Nelson formulae for a single component system was. (Runping Han et al 2008)

\[
\frac{c_t}{c_0} - c_t = \exp(KYN t - \tau KYN)
\]

The approach involves a plot of \(\ln \left[\frac{C_t}{C_0 - C_t}\right] \) Vs sampling time \((t)\) according to the equation. The parameters of \(KYN\) and \(r\) can be obtained using the nonlinear regressive method (Mike A. Acheampong et al 2012)

2.9. Dynamic adsorption models
The dynamic adsorption models nominated, Bed-depth-service-time (BDST), Thomas and Yoon–Nelson was employed to represent the experimental breakthrough curves. The BDST model elucidates a relation between the time and the packed-bed depth of the column where \(K\) is the adsorption constant rate, \(N0\) is the adsorption capacity, \(h\) is the bed depth of fixed-bed \((\text{cm})\), and \(u\) is the linear flow rate. (Mustafa turan et al, 2005)

RESULT AND DISCUSSION

3.1. Effect of bed height
The adsorption column used in this study was designed to contain sampling points at 5 cm interval, to facilitate the study of the effect of bed height on the life-span of the column. This flow profile has been observed previously by other researchers for the adsorption of Cu (II), Ni (II) and Cd (II) onto banana pith and moss (S.Y. Quek et al 2006); The property of adsorbent present inside the column bed plays a major role in the separation of metals bed height of 10cm, 20cm and 30cm to produce an yield of isolation of metals 3.5, 7.0, 10.5 g adsorbent material were used. The break through curve is plotted for material of varied quantity at a flow rate of 10 ml/min and 100 mg/L initial nickel compactness for waste tea biomass (Emrine Malkoc et al 2006)

3.2. Effect of dye concentration
The break analysis curve increases by increases in inflow quantity of adsorbate concentration whose volume was minimized before the carbon regeneration. Increase in the dye concentration of inlet at constant rate reduces the output. This is due to more adsorbate a component isolating the activated carbon rapidly thus reduces the break even time (G.M. Walker et al 1997)

3.3. Application of Thomas and Yoon-Nelson model
The adsorption phenomenon was examined by adopting Thomas and Yoon Nelson models at different flow rates. The Thomas equation relates the break even time and the isolation time of the adsorption in column. It shows a reasonable experimented \(R_2\) values varied from 0.96 to 0.98 for VBC-NMG and 0.94 to 0.97 for GMP-PVC (Esra Bilgin Simsek et al 2014). The kinetic constant, \(K_T\), tends to increase as the flow rate increases, while \(q_e\), cal becomes smaller, as obtained by other researchers. Moreover, the maximum column capacities calculated from the
Thomas model (qe, cal, and mg/g) are very close to the experimental column capacities (qe, exp, and mg/g). (Baudu et al, 2012)

3.4. Regeneration of column
M.L.G. Vieira et al 2013, these method is very essential in industrial aspects as it’s effectively minimal the cost of the operation. NaOH solution was carried out for the azo dyes used in the method. The output obtained was same for FD&C red40, FD&C yellow5, FD&C yellow6 for a NaOH solution of 1.0 mol L⁻¹ at a flow rate of 5 ml min⁻¹. The study conducted after 20 mins noted that all the dyes were removed. The efficiency obtained in removed of dyes were 99.3%, 97.5%, 95%, 92.1% and 90.3% for the five corresponding adsorption elution cycles

3.5. Adsorption kinetics
The modeling of the adsorption kinetics may be described by two common models, namely, the pseudo-first-order Lagergen rate model and a pseudo-second-order model. Lagergen’s kinetics equation had been most widely used for the adsorption of an adsorbate from an aqueous solution. (Yu-Na et al 2011). Adsorption was a time-dependent process and the rate of pollutant removed from aqueous solution is essential in order to design suitable sorption treatment plants. Moreover, the study of adsorption kinetics of in waste water treatment provides helpful insights into the mechanism of sorption reaction (Esra Bilgın Simsek et al 2014)

Table 1: Removal of Metals using with different adsorbents

<table>
<thead>
<tr>
<th>Heavy metal</th>
<th>Adsorbent</th>
<th>pH values</th>
<th>Temperature</th>
<th>% of Removal</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boron</td>
<td>Selective polymeric resins</td>
<td>3-8</td>
<td>95</td>
<td>98</td>
<td>EsraBilgınSimsek et al, 2014</td>
</tr>
<tr>
<td>Cadmium</td>
<td>Noval polymer clay</td>
<td>5.5</td>
<td>85</td>
<td>87.4</td>
<td>Emmanuel I. Unuabonah et al, 2010</td>
</tr>
<tr>
<td>Cadmium</td>
<td>Protonated sargassum muticum</td>
<td>3.5 &amp; 4.5</td>
<td>60-100</td>
<td>89.5</td>
<td>P.Lodeiro et al, 2006</td>
</tr>
<tr>
<td>Cobalt (II)</td>
<td>Natural hemp fibers</td>
<td>1-5</td>
<td>75</td>
<td>86.5</td>
<td>LaviniaTofan et al, 2013</td>
</tr>
<tr>
<td>Cobalt (II)</td>
<td>Sunflower biomass</td>
<td>3-5</td>
<td>95</td>
<td>88</td>
<td>EnsarOguz et al, 2013</td>
</tr>
<tr>
<td>Copper</td>
<td>Chitosan immobilized on bentonite</td>
<td>4.5-8</td>
<td>40-110</td>
<td>92</td>
<td>Cybelle Morales Futalan et al, 2010</td>
</tr>
<tr>
<td>Chromium</td>
<td>Olive stone</td>
<td>4-5.5</td>
<td>50</td>
<td>91.5</td>
<td>M.Calero et al, 2009</td>
</tr>
<tr>
<td>Lead</td>
<td>Zeolite and Sepiolite</td>
<td>8-11</td>
<td>40-80</td>
<td>94</td>
<td>Mustafa Turn et al, 2005</td>
</tr>
<tr>
<td>Nickel (II)</td>
<td>Waste tea</td>
<td>4</td>
<td>25</td>
<td>89%</td>
<td>EmmeMalkoc et al, 2005</td>
</tr>
</tbody>
</table>

Table 2: Removal of Dyes using with different adsorbents

<table>
<thead>
<tr>
<th>Dyes</th>
<th>Adsorbent</th>
<th>pH values</th>
<th>Temperature</th>
<th>% of Removal</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Food azo dye</td>
<td>Glass beads coated with chitosan</td>
<td>3.5, 4.5 and 6</td>
<td>50°C</td>
<td>40.9-74.7%</td>
<td>M.L.G.Vieira et al, 2013</td>
</tr>
<tr>
<td>Methyl Orange</td>
<td>Montmorillonite</td>
<td>4</td>
<td>60°C</td>
<td>76%</td>
<td>Min-YuTeng et al, 2005</td>
</tr>
<tr>
<td>Methyl blue</td>
<td>Phoenix tree leaf powder</td>
<td>4-10</td>
<td>50-110</td>
<td>60.7%</td>
<td>Runping Han et al, 2007</td>
</tr>
<tr>
<td>Toluenediamine</td>
<td>Activated carbon</td>
<td>4-10</td>
<td>30-50°C</td>
<td>72.43%</td>
<td>Yu-Na Hu et al, 2011</td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td>Granular activated carbon (Coconut husk)</td>
<td>8.4</td>
<td>20.15°C</td>
<td>88%</td>
<td>Anderson Marcos et al, 2014</td>
</tr>
<tr>
<td>Acid dye</td>
<td>Pristine &amp; acid activated clay</td>
<td>3.5-9</td>
<td>65°C</td>
<td>78.42%</td>
<td>Su-Hua Lin et al, 2004</td>
</tr>
<tr>
<td>Reactive azo dye</td>
<td>Argano-zeolite</td>
<td>3-10</td>
<td>85-125°C</td>
<td>81.24%</td>
<td>y.e.Benkli et al, 2007</td>
</tr>
<tr>
<td>Tectilon blue</td>
<td>Granular activated carbon</td>
<td>7.4</td>
<td>140°C</td>
<td>85.2%</td>
<td>G.M.Walker et al, 1996</td>
</tr>
<tr>
<td>Crystal violet dye</td>
<td>Surfactant modified alumina</td>
<td>3.5, 8 &amp; 11.5</td>
<td>44-85°C</td>
<td>74.6%</td>
<td>Asok Adak et al, 2008</td>
</tr>
<tr>
<td>Acid dye</td>
<td>Activated carbon</td>
<td>3.5-9</td>
<td>74°C</td>
<td>86.8%</td>
<td>G.M.Walker et al, 1998</td>
</tr>
<tr>
<td>Methylene blue&amp;red22</td>
<td>Beech saw dust</td>
<td>3-5</td>
<td>23°C &amp; 100°C</td>
<td>68-74%</td>
<td>F.A.Batzias et al, 2004</td>
</tr>
<tr>
<td>Methylene blue</td>
<td>Rice husk</td>
<td>7.5 &amp; 9</td>
<td>70-140°C</td>
<td>84.6%</td>
<td>Runping Han et al, 2006</td>
</tr>
<tr>
<td>Methylene blue</td>
<td>Jack fruit leaf powder</td>
<td>3.9-10</td>
<td>50-120°C</td>
<td>87.4%</td>
<td>Md. TamezUddin et al, 2008</td>
</tr>
<tr>
<td>Pentachloro phenol</td>
<td>Alginate-encapsulated pillar clay</td>
<td>5.3</td>
<td>35°C</td>
<td>70.25%</td>
<td>MouloudLezehari et al, 2012</td>
</tr>
</tbody>
</table>

3.6. Effects of electrolyte
Calculated values for some operating characteristics of the npolymer–clay composite adsorbent premodified with 0.1MNaNO3 and 0.1M Ca(NO3)2 for the adsorption of Cd2+. The results showed that at the same initial Cd2+ concentration, polymer–clay composite adsorbent treated more volume of the metal ion solution at breakthrough than with polymer–clay composite adsorbents pre-modified with electrolytes. (Emmanuel I. Unuabonah et al 2010)
3.7. Effect of flow rate

The effect of flow rates from 5 to 20 mL min⁻¹ on breakthrough curves can be observed as expected, an increase in flow rate produces a diminution in breakthrough and exhaustion times, and as a consequence, the curves become steeper with a shorter mass transfer zone (P. Lodeiro, et al 2006) an increase in flow rate from 0.20 mL/min to 0.60 mL/min increases the volume of effluent treated from 165.40mL to 247.00mL but decreases the Cu(II) removal efficiency as well as the uptake capacity of Cu(II). At lowest flow rate of 0.20 mL/min, the highest Cu(II) removal of 80.20% and highest bed adsorption capacity at breakthrough and exhaustion is obtained at 15.80 mg/g and 26.52 mg/g, respectively (Cybelle Morales Futalan et al 2010)

CONCLUSION

In this work, continuous biosorption operation in a fixed-bed column had been performed for heavy metals and dyes biosorption by varying adsorbent. This paper shows that the varying adsorbent could be used as an effective biosorbent for aqueous solutions containing these metals and dyes. The continuous laboratory scale studies suggested the following conclusions. First, the influence of various operational parameters on solute uptake by biosorbent in the contactor had been presented. The flow rate was decreases with the increases of the break through and saturation time. When the bed depth was increased, the same affect of decrease the flow rate. On the other hand, the breakthrough and saturation time decreases as the inlet concentration increases, for the same flow rate and bed depth. The capacity of removal obtained at optimum conditions was close to 0.800mg of metal/g biosorbent. Adams–Bohart, Thomas, Yoon–Nelson and Dynamic adsorption models were applied to experimental data obtained from dynamic studies performed on fixed column to predict the breakthrough curves and to determine the column kinetic parameters. The initial region of breakthrough curve was defined by the Adams–Bohart model. The analysis of the pH evolution during the operation of the column showed a pH increase at the beginning of the test due to the H⁺ ions being sorbed in the matrix of the biosorbent. When the sites in the bed were saturated, no more protons were sorbed and the pH tends to the initial value.

REFERENCES