STUDY OF LOW COST CELLULOSE AND DERIVATIVES AS BIOSORBENT FOR CATIONIC AND ZWITTERIONIC DYES

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ABSTRACT
Biosorption of Cationic dye and Zwitterionic dye on cellulose extracted from eucalyptus bark and its grafted derivatives has been investigated. Several experiments have been carried out by using batch adsorption technique. Basic Red 12 and Basic violet 10 have been used as model cationic and zwitterionic dyes. The effect of process variables like adsorbent dosage, pH, contact time, temperature; initial dye concentration has been evaluated. The adsorption of dyes was found to take place at pH>pH_{pzc} for all the adsorbents. Thermodynamic parameters like ΔG, ΔH and ΔS were determined and the processes were found to be spontaneous for both dyes, the processes were exothermic with negative entropies suggesting that ionic dye adsorption on cellulose and derivatives was enthalpy driven in nature. The study highlighted the application of low cost renewable adsorbents for the removal of dyes from aqueous medium by the ion exchange process. Kinetic models like Lagergren, Pseudo second order and Elovich were evaluated and pseudo second order fitted the data well. Langmuir, Freundlich and Temkin isotherm models were evaluated and the Langmuir isotherm model fitted the data well suggesting monolayer and chemisorption of dyes on adsorbents. Scanning electron microscopic analysis and Fourier transform infra red spectroscopy (FTIR) revealed a noticeable surface morphology change after surface grafting.

Keywords: Adsorption, Cellulose Grafting, Kinetic Models, Isotherm Models, Thermodynamics

INTRODUCTION
Rapid industrial growth of countries like India has brought economical revolution in all the parts of world and industrial waste water treatment is an important task due to environmental concerns. Thousands of dyes are prepared for printing and dyeing industries from coal tar based hydrocarbons such as benzene, anthracene, naphthalene, xylene, toluene etc. Dyes are used in industries like paper, textile, cosmetics, rubber, food, drug and plastics. According to an estimate 10,000 different types of commercial dyes are present and 7X10^5 tones of dyes are produced annually worldwide. This is observed that aerobic biodegradation has very less color removal efficiency. Most of the treatment technologies work on biological treatment processes. Other physical and chemical methods like coagulation, oxidation, filtration, membrane separation and adsorption are in practice. Adsorption is a procedure of choice due to its simplicity, efficiency and cost efficacy. Activated carbon is the best adsorbent but its higher cost and difficult regeneration has encouraged many workers for the research of new adsorbents. Many Investigators have studied the feasibility of using low cost adsorbents such as Eucalyptus bark (Morais et al., 2002; Dave et al., 2011) tea waste (Tamezuddin et al., 2009; Khosla et al., 2013) bagasse fly ash (Mall et al., 2006) coir pith (Namasiyam and Kavitha, 2002) peat (McKay et al., 1981) orange and banana peel (Annadurai et al., 2002) saw dust and rice husk (Malik, 2003) grass waste (Hameed, 2009) maize cob (Geunidi and Aly, 1992) deoiled soya and bottom ash (Mittal and Gupta, 2010) cotton waste (McKay et al., 1999) slag (Ramakrishana and Viraraghavan, 1997) sugar cane stalk (Sayed et al., 2011) dried mango seeds (Itodo et al., 2011) ashoka leaf powder (Shelke et al., 2011) activated carbon from low cost wood (Sivakumar and Palanisamy, 2010) and sewage sludge (Dave et al., 2011a) etc. Consequently the interest in search for more economical and effective adsorbents has continued to grow. Cellulose is a very important and fascinating biopolymer and an almost inexhaustible and renewable raw material. The trend towards this kind of resources and the tailoring of innovative products for science, medicine and technology has led to a global renaissance of interdisciplinary cellulose research and to the extended use of this abundant organic polymer over the last decade (Ciocanu and Popa, 2010). In the present study
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cheap source derived cellulose has been used as a biosorbent in raw and grafted form for the removal of cationic dye basic red-12 and a zwitter ionic dye basic violet-10 for exploring the kinetics and thermodynamics of the adsorption process. In grafting reaction, the accessibility of cellulose molecules to the reagent is highly important in the process and efficiency of modification. Cellulose is assumed to be stable chemically with hydroxyl (-OH) as a main functional group which can be modified with suitable reagents as per requirements. In our work the cellulose is used for adsorption of dyes from aqueous solution with and without surface modification to generate a low cost surface tailored adsorbent which can be used for dye adsorption in energy efficient and environmentally benign way.

MATERIALS AND METHODS

Cellulose Extraction and Surface Modification by Grafting and Carboxylation

_Eucalyptus citriodora_ trees are commonly grown in India sheds off their barks often. The cellulose extraction from field waste EB gives the possibility of conversion to a low cost ion exchanger which can bind with the dye molecules to form a floc which can be separated by filtrations. Cellulose was extracted from Eucalyptus tree bark (EB) as it contained around 40% cellulose. The extraction was carried out by following standard protocol (Brendel and Schrag, 2004). 15.0 g EB was heated with 120 mL of 80% glacial acetic acid and 12 mL of 69% nitric acid for 30 min at 403 K on heating block in a round bottom flask by using water condenser. The solution was then cooled and transferred to a centrifugation tube. The supernatant was removed carefully followed by washings with ethanol and double distilled water till white fluffy cellulose was obtained. The extracted cellulose was finally washed with acetone and dried under vacuum and stored in desiccators till further use.

Cellulose (Cell) obtained above was grafted by a method proposed by Raji and Anirudhan (2001). 20.0 g of cellulose was treated with 300 mL of solution containing 5.0 g of N, N-Methylenebisacrylamide and 2.0 g of potassium peroxy sulphate. 7.5 g of acrylamide was added and the mixture was refluxed at 343 K for 2 h. The grafted product was washed with acetone to remove monomer. This was cooled and filtered by using Buchner funnel. The grafted cellulose (PAG-Cell) was dried at 353 K for 6 h. This was stored in desiccator till further use. PAG-Cell was carboxylated by treating 10.0 g of it with 10.0 mL of ethylene diamine and 10.0 mL of toluene at 373 K for 2 h followed by refluxing with succinic anhydride in 1, 4-dioxane at pH 4.0. PAG-Cell-COOH was filtered and washed with 1, 4-dioxane followed by washing with ethanol. The material obtained was dried in hot air oven at 353 K and stored in desiccators till further use.

Preparation of Dye Solutions

1000 mg L⁻¹ stock solution of dyes viz; basic red-12 (BR-12) and basic violet-10 (BV-10). 1000 mg L⁻¹ solutions were prepared by dissolving appropriate amount of dye in deionized water and stored in dark colored bottles and diluted by adding suitable amount of water to the stock solution as per requirement. Basic Red-12 (BR-12) is a cationic dye while Basic violet 10 (BV-10) is a zwitterionic dye. The structure of these dyes are shown in Figure 1. The dye concentration before and after adsorption was determined by converting the optical density to corresponding concentration. The dyes were analyzed at their respective λₘₐₓ.

Analysis of Adsorbents

The FTIR of Cell and surface derivatives was carried out with Perkin Elmer spectrophotometer in the range 400-4000 cm⁻¹ using perkin elmer spectrophotometer. The adsorbent was mixed with anhydrous KBr to make a pellet and simultaneous 400 scans were carried out to give the average FTIR scan. The adsorbent samples were also characterized by powder X-ray diffractometry using an X’PERT PRO PANalytical with Cu-Kα radiation. SEM was carried out by using ZEOL scanning electron micrograph. The images allowed us to view samples on a molecular level, making it possible to analyze structure and texture. BET surface area measurement was carried out by using micromeritics surface area analyzer. This also gave monolayer volume of N₂ and pore volume of the adsorbents. The density of the adsorbents was determined by using standard protocol. 10 ml graduated and dry cylinder was filled with 5.0 ml of...
DDW carefully with a syringe. The mass of graduated cylinder and water was recorded; then adsorbent was added carefully so that no water was lost to raise the level of water by 2.0-3.0 ml. After this addition the mass and volume of cylinder and solid was determined carefully. Knowing the mass and volume of adsorbent, the density was calculated. The surface acidity and basicity was determined by using Bohem titration method (Bohem, 1966).

**Batch Experiments**

The series of experiments were conducted by placing 50 ml of dye solution in an Erlenmeyer flask and adding the required amount of adsorbent to that in water bath incubator shaker. The pH of different solutions was adjusted with 0.1 N HCl and 0.1 N NaOH. After attainment of equilibrium the aqueous phase was analyzed for residual dye concentration using UV visible spectrophotometer. From the absorbance data $q_e$ (mg g$^{-1}$) was determined using equation 1.

$$q_e = \frac{(C_0 - C_e)V}{W}$$

(1)

Where $C_0$ is initial dye concentration, $C_e$ is final dye concentration, $V$ is volume of dye in liters and $W$ is mass of adsorbent in g. Duplicate experiments were performed to get concordant results. The results showed variation in the range of ±5%. The kinetics of dye removal was studied using required dye concentration. The samples were withdrawn at regular intervals and residual concentration was analyzed after centrifugation using ultracentrifugation at 1000 rpm. The isotherms were studied by using 50 ml of dye solution within optimum range of concentration at 303 K, 313 K and 323 K. After the attainment of equilibrium the residual dye concentration was analyzed spectrophotometrically. The pH of dye solutions and pH$_{zpc}$ were determined by using pH meter by Toshvin (TMP-85). An auto arranging conductivity meter TCM+15, provided with temperature compensator made by Toshnival, India was used for determination of surfactant characteristics and nature of the filtrate of adsorbent and its derivative washings. The weighing was carried out on a digital weighing balance of accuracy up to 0.1 mg by Citizen Co.

**RESULTS AND DISCUSSION**

**Surface Area Analysis**

Surface chemistry of the adsorbents such as specific surface area, pore volume distribution and pore diameter have been measured. Pore volume has been determined by the same technique. The zero point charge (pH$_{zpc}$) of the adsorbents and derivatives has been determined by solid addition technique. The results of the surface area analysis, pore volume, bulk density and pH$_{zpc}$ have been given in Table 1. The surface area is an important parameter for the sorption capacity of adsorbents. The adsorption occurs mainly at the liquid-solid interface. The surface area available to the dye molecule determines the efficacy of the adsorbent. Generally, larger the surface area, higher the adsorbent's capacity is.
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and its derivatives is very low (0.998 m\(^2\)g\(^{-1}\) -1.649 m\(^2\)g\(^{-1}\)) with small pore volume though it increases with grafting and carboxylation after surface modification. The degree of linearity of \(\alpha\)-cellulose enables it to approach together to give a compact structure which is less porous. The cellulose has high cohesive energy which is enhanced by the fact that the hydroxyl groups are capable of forming extensive hydrogen bonded network between the chains and within the chains. Due to this reason the cellulose is crystallized in the form of crystallites.

Table 1: Physicochemical properties of Cell, PAG-Cell and PAG-Cell-COOH

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Surface Area(m(^2)g(^{-1}))</th>
<th>Bulk Density(g.ml(^{-1}))</th>
<th>Pore Volume(cm(^3)g(^{-1}))</th>
<th>pH(_{zpc})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell</td>
<td>0.998</td>
<td>0.371</td>
<td>0.032</td>
<td>7.21</td>
</tr>
<tr>
<td>PAG-Cell</td>
<td>1.128</td>
<td>0.415</td>
<td>0.003</td>
<td>7.03</td>
</tr>
<tr>
<td>PAG-Cell-COOH</td>
<td>1.649</td>
<td>0.524</td>
<td>0.010</td>
<td>6.24</td>
</tr>
</tbody>
</table>

Cellulose obtained from EB is significantly fibrous material (Figure 2) with rough surfaces which shows the regions of grafting after reaction with polyacrylamide. The treatment of PAG-Cell with succinic anhydride makes the coating of acid on the surface of grafted polymer in a uniform manner. The XRD spectra of adsorbents (Figure 3) helps to find the coherence length, which is determined by using Debye-Scherrer equation (equation 2).

\[
L = \frac{0.9 \lambda}{\beta \cos \theta}
\]

(2)

Where, \(\lambda\) is wave length \((1.5406 \text{ Å Cu-K}\alpha)\), \(\theta\) is angle of diffraction and \(\beta\) is full width half maximum (FWHM). The XRD spectra suggests that Cell is amorphous in nature which remains amorphous even after grafting and carboxylation. The peak intensities for Cell, PAG-Cell and PAG-Cell-COOH are different.

Figure 4 shows the FTIR spectra of Cell and its derivatives. The FTIR spectra of Cell reveal that O-H stretching appears at 3400 cm\(^{-1}\). The bands at 2810 cm\(^{-1}\) appears due to C-H stretching and at 1430 cm\(^{-1}\) is due to C-H bending. The band at 890 cm\(^{-1}\) indicated the C-O-C stretching in \(\beta\) (1-4) linkage of cellulose which remained intact after grafting also.

In PAG-Cell additional bands appears at and 1500 cm\(^{-1}\) due to N-H stretching in primary amide involving coupling of N-H bending with other vibrations. A band at 1690 is due to >C=O stretching of amide in PAG-Cell. The carboxylated derivative of PAG-Cell represents a band at 1400 cm\(^{-1}\) due to symmetric stretching (Silverstein and Webster, 2009).

The carboxylate group gives rise to two bands around 1650 cm\(^{-1}\) and 1550 cm\(^{-1}\). The FTIR spectra has revealed that Cell contains –OH as a main functional group, the –CONH\(_2\) group appears after grafting with poly acrylamide and –COOH group arises after carboxylation, these three groups make the adsorption of dyes with different charges feasible.

Figure 2: SEM of Cell and Derivatives; (a) SEM of Cell at Magnification 1200x (b) SEM of PAG-Cell at Magnification 1500x (c) SEM of PAG-Cell-COOH at Magnification 1500x [15kV]
Effect of Adsorbent Dose

Cell is very efficient adsorbent as it can remove BR-12 (250 mg.L⁻¹) and BV-10 (250 mg.L⁻¹) up to an extent of 102.2 mg.g⁻¹ and 24.1 mg.g⁻¹ with adsorbent dose of 7.5 g.L⁻¹ and 5.0 g.L⁻¹ respectively. Cellulose has the basic molecular format of C₆H₁₀O₅, which is also called anhydro glucose unit. The cellulose molecule is linked in the form of β-1, 4-glucan. Figure 5 is the schematic molecular structure of cellulose. Generally, 20-30 cellulose units give cellulose properties. Each cellulose chain has two ends, one with an original C₄-OH group is called the non reducing end and the other with an original C₁-OH is called the reducing end. Additional functional groups can be introduced onto cellulose by chemical treatment. Many characteristic properties are determined by the molecular structure, including hydrophilicity and degradability. The multiple -OH groups on Cell molecule and its linear structure enable the formation of crystalline fiber bonded by extensive hydrogen bonds. Cell upon grafting with polyacrylamide form PAG-Cell, which upon carboxylation increases the surface area of Cell from 0.998 m².g⁻¹ to 1.128 m².g⁻¹ and 1.649 m².g⁻¹ respectively. The adsorption capacity of PAG-Cell and PAG-Cell-
COOH for BR-12 (250 mg.L⁻¹) is 84.53 mg.g⁻¹ and 38.93 mg.g⁻¹. The cationic dye can bind to ionised Cell better than grafted and carboxylated cellulose. The adsorbent dose required for removal of BR-12 by Cell, PAG-Cell and PAG-Cell-COOH is 7.5 g per 100 ml while for removal of BV-10 this dose is 5.0 g per 100 ml. PAG-Cell-COOH could not remove BV-10, probably due to like charges on dye and adsorbent surfaces. Due to the same reason anionic dyes could not be removed by the Cell and its derivatives.

**Effect of pH**
Surface change is the most important parameter for ionic dye adsorption. The dye adsorption is affected by solution pH and in the present study the effect of pH is studied in the range of 2-9. Cell, PAG-Cell and PAG-Cell-COOH have pH_{zpc} values 7.21, 7.03 and 6.24 respectively. This may be attributed to the reason that the functional groups such as hydroxyl groups, glycosidic linkages, amido groups and carboxyl groups are affected by the pH of solutions. Cell can remove BR-12 and BV-10 at pH 8.0 and 2.0 respectively. Cell is protonated and suitable for binding BV-10 at pH 2.0 and ionizes at pH 8.0 to develop negative oxygen ends which can bind with cationic dye like BR-12. Cell develops –NH₂ groups after grafting with acrylamide and pH_{zpc} decreases causing binding of cationic dye BR-12 at pH 7.0, dipolar dye BV-10 at pH 2.0. The carboxylation of PAG-Cell decreases pH_{zpc} further and binds with dyes through ion exchange mechanism. BR-12 being cationic binds better at pH 9.0 after ionization of –COO⁻ and BV-10 could not bind due to negatively charged surface. The dipolar structure of BV-10 is shown in Figure 6.

**Effect of Contact Time**
The contact time is of utmost importance for designing batch sorption systems, consequently it is important to establish the time dependence of such systems under various process conditions. The optimum time required for removal of BR-12 is 2h which increases to 3h after acrylamide grafting and decreases after carboxylation to 1h, the equilibrium time required for removal of BV-10 on Cell is 2h while the PAG-Cell is extended than this. The PAG-COOH could not remove BV-10. The dye is transferred from the bulk solution to the external surface of the adsorbent material. In the second step, the
dye molecule diffuses from the relatively small area of the external surface (a few square meters per gram) into the macropores, transitional pores, and micropores within Cell and its derivatives. Most adsorption occurs in the micropores because the majority of available surface area is there (hundreds of square meters per gram). In the third step, the dye molecule adsorbs to the surface in the pore due to the presence of appropriate functional group. Figure 7 explains the schematic and adsorption process proceeding through overall mass transfer and diffusion.

Figure 7: Predicted Mechanism of Dye Diffusion from Aqueous Solution to Adsorbent (Khosla et al., 2014)

Kinetics of Adsorption Processes
Adsorption kinetics depends upon the adsorbent-adsorbate interface and system condition, the adsorption kinetics has been investigated for their suitability and application in water pollution control. Two vital appraisal elements for adsorption process operation unit are the mechanism of adsorption and the reaction rate.

Dye uptake rate determines the dwelling time required for completing the adsorption process till attainment of equilibrium, which can be cataloged from kinetic analysis. In order to investigate potential rate controlling steps such as mass transport and chemical reaction processes four kinetic models; Lagergren pseudo first order, Ho and McKay’s pseudo second order and Elovich have been used to test the experimental data following the linear regression methodology.

Lagergren Pseudo First Order Kinetics
The first order rate expression of Lagergren (1898) based on the solid adsorption capacity is generally expressed by equation 3.

\[ \log (q_e - q_t) = \log q_e - \left( \frac{k_1}{2.303} \right) t \]  

(3)

Where, \( q_e \) and \( q_t \) are the amount of dye adsorbed at equilibrium and time \( t \) (min) respectively and \( k_1 \) is the rate constant of pseudo-first order rate constant (min\(^{-1}\)). The values of \( k_1, q_e, R \), for dye binding on Cell and derivatives are given in Table 2. The adsorption of BR-12 on Cell, PAG-Cell and PAG-Cell-COOH fits the data well.

BV-10 also binds with PAG-Cell following the same kinetic model, while Cell adsorbs BV-10 slowly and does not fit into this model. The value of rate constant for adsorption of BR-12 is 0.0164 min\(^{-1}\) and 0.0299 min\(^{-1}\) for adsorption on Cell and PAG-Cell respectively. The value of rate constant for adsorption of BR-12 on PAG-Cell-COOH is 0.1332 min\(^{-1}\) i.e. much higher than the values of rate constant for adsorption of same dye on Cell and PAG-Cell indicating the better fit of this model for adsorption of BR-12 on PAG-Cell-COOH.
This behavior of anionic dyes have been explained on the basis of fact that the anionic dye ions used in this study are very weakly adsorbed on Cell and its derivatives also show a good fit in Lagergren model. The rate constant of BR -12 removal by PAG -COOH is high in Lagergren model, though the equilibrium adsorption capacity of BR -12 on Cell and its derivatives also show a good fit in Lagergren model. The rate constant of BR -12 removal by PAG -Cell is comparable in both the models while the rate constant for removal of BR -12 on PAG -Cell-COOH is high in Lagergren model, though the equilibrium adsorption capacity of pseudo second order kinetic model is also very high in comparison to the adsorption capacity determined by Lagergren model. The rate constant of BR -12 removal by PAG -Cell is comparable in both the models while the rate constant for removal of BR -12 on PAG -Cell-COOH is high in Lagergren model, though the equilibrium adsorption capacity of pseudo second order model is high due to the reason that these two biopolymers offers complementary possibility of dye ion binding with them. The Cell is an acidic biosorbent as it can liberate free oxygen binding sites after ionization of protons from the surface of Cell. The binding of cationic dye is fast on Cell and grafted Cell (PAG -Cell) is weakly alkaline due to amido group on the surface, hence, it binds with cationic dye ions in near neutral solutions as at pH near 7.0. The protonation and deprotonation of amido groups may take place; moreover the degree of polymerization also effects the binding of dye ion on cellulose and PAG -Cell. The binding of dye ions on PAG -Cell can take place through different mechanisms; complexation on nitrogen and possibly due to formation of ternary complexes or through ion exchange. The deprotonation of amido group and binding with dye ion control the rate of reaction. The mechanism is essentially active in near neutral solution. The adsorption of BV -10 on Cell very poor fit on Lagergren model but the regression coefficient for the removal in pseudo second order equation lies in the range 0.999 indicating chemisorptions of BV -10 over the surface of natural polymer while after polymer grafting and carboxylation of grafted polymer Lagergren binding preferably takes place. The functional group which is mainly responsible for dye binding is amido group in PAG -Cell and carboxylate groups PAG -Cell-COOH. The hydroxy group is responsible for stability of bonded dye ions to the polymer. The amido group seems to be ineffective against anionic dyes even at low pH; this behavior of anionic dyes have been explained on the basis of fact that the anionic dye ions used in

Table 2: Lagergren Pseudo First Order Kinetics Data for Dye Interactions on Cellulose and its Derivatives

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Dye</th>
<th>( q_e )</th>
<th>( k_1 )</th>
<th>( R )</th>
<th>SEE</th>
<th>RSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell</td>
<td>BR-12</td>
<td>0.852</td>
<td>0.0164</td>
<td>0.9683</td>
<td>0.0871</td>
<td>0.031</td>
</tr>
<tr>
<td>PAG-Cell</td>
<td>BR-12</td>
<td>2.546</td>
<td>0.0299</td>
<td>0.9886</td>
<td>0.0956</td>
<td>0.037</td>
</tr>
<tr>
<td>PAG-Cell-COOH</td>
<td>BR-12</td>
<td>6.801</td>
<td>0.1332</td>
<td>0.9539</td>
<td>0.2571</td>
<td>0.066</td>
</tr>
<tr>
<td>Cell</td>
<td>BV-10</td>
<td>1.005</td>
<td>0.0347</td>
<td>0.7309</td>
<td>0.3732</td>
<td>0.277</td>
</tr>
<tr>
<td>PAG-Cell</td>
<td>BV-10</td>
<td>2.916</td>
<td>0.0051</td>
<td>0.9899</td>
<td>0.0212</td>
<td>0.002</td>
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</table>

Table 3: Pseudo Second Order Kinetics Data for Dye Interactions on Cellulose and its Derivatives

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Dye</th>
<th>( k_2 )</th>
<th>( q_e )</th>
<th>( R )</th>
<th>SEE</th>
<th>RSS</th>
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</thead>
<tbody>
<tr>
<td>Cell</td>
<td>BR-12</td>
<td>0.0553</td>
<td>18.077</td>
<td>0.9999</td>
<td>0.0780</td>
<td>0.037</td>
</tr>
<tr>
<td>PAG-Cell</td>
<td>BR-12</td>
<td>0.0291</td>
<td>34.377</td>
<td>0.9998</td>
<td>0.0627</td>
<td>0.024</td>
</tr>
<tr>
<td>PAG-Cell-COOH</td>
<td>BR-12</td>
<td>0.0548</td>
<td>18.255</td>
<td>0.99906</td>
<td>0.9436</td>
<td>0.890</td>
</tr>
<tr>
<td>Cell</td>
<td>BV-10</td>
<td>0.0839</td>
<td>11.912</td>
<td>0.9999</td>
<td>0.0902</td>
<td>0.051</td>
</tr>
<tr>
<td>PAG-Cell</td>
<td>BV-10</td>
<td>0.0191</td>
<td>52.265</td>
<td>0.9983</td>
<td>0.4605</td>
<td>1.061</td>
</tr>
</tbody>
</table>

Pseudo Second Order Kinetics
The pseudo second order kinetic model of Ho and McKay (1998) is given by equation 4.

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e}t
\]

(4)

Where, \( k_2 \) is rate constant of pseudo second order adsorption (g. mg\(^{-1}\).min\(^{-1}\)). This model predicts the behavior over whole range of adsorption and is in agreement with an adsorption mechanism being the rate controlling step. The applicability of this model has been verified by plotting \( t/q_t \) against time as per equation 4. The adsorption of BR -12 on Cell and its derivatives also show a good fit in this model (Table 3) than Lagergren model. The rate constant \( k_2 \) has value 0.05 g mg\(^{-1}\).min\(^{-1}\) which is much higher than \( k_1 \) (0.0163 min\(^{-1}\)) obtained in Lagergren model. The equilibrium adsorption capacity of pseudo second order kinetic model is also very high in comparison to the adsorption capacity determined by Lagergren model. The rate constant of BR -12 removal by PAG -Cell is comparable in both the models while the rate constant for removal of BR -12 on PAG -Cell-COOH is high in Lagergren model, though the equilibrium adsorption capacity of pseudo second order model is high due to the reason that these two biopolymers offers complementary possibility of dye ion binding with them. The Cell is an acidic biosorbent as it can liberate free oxygen binding sites after ionization of protons from the surface of Cell. The binding of cationic dye is fast on Cell and grafted Cell (PAG -Cell) is weakly alkaline due to amido group on the surface, hence, it binds with cationic dye ions in near neutral solutions as at pH near 7.0. The protonation and deprotonation of amido groups may take place; moreover the degree of polymerization also effects the binding of dye ion on cellulose and PAG -Cell. The binding of dye ions on PAG -Cell can take place through different mechanisms; complexation on nitrogen and possibly due to formation of ternary complexes or through ion exchange. The deprotonation of amido group and binding with dye ion control the rate of reaction. The mechanism is essentially active in near neutral solution. The adsorption of BV -10 on Cell very poor fit on Lagergren model but the regression coefficient for the removal in pseudo second order equation lies in the range 0.999 indicating chemisorptions of BV -10 over the surface of natural polymer while after polymer grafting and carboxylation of grafted polymer Lagergren binding preferably takes place. The functional group which is mainly responsible for dye binding is amido group in PAG -Cell and carboxylate groups PAG -Cell-COOH. The hydroxy group is responsible for stability of bonded dye ions to the polymer. The amido group seems to be ineffective against anionic dyes even at low pH; this behavior of anionic dyes have been explained on the basis of fact that the anionic dye ions used in

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present investigation have large polar surface area. The degree of complexation of Cell and derivatives depends upon the association of dye with the polymer chain. The plot of time vs. $t/q_t$ for the removal of dyes by Cell and its derivatives is shown in Figure 8.

![Figure 8: Pseudo Second Order Kinetic Model for Adsorption of Dyes over Cellulose and Derivatives](image)

**Elovich Kinetic Model**

Elovich kinetic model (Hameed et al., 2008) is followed in the reactions involving chemisorptions of dye ions on solid surface of adsorbent without desorption of products, the adsorption rate decreases with increase of time due to an increased surface coverage of the adsorbent. Elovich model is the most useful model to evaluate chemisorption and the Elovich model is given by equation 5.

$$qt = \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\beta} \ln t$$

(5)

Where, $\alpha$ is initial rate of adsorption (mg g$^{-1}$ min$^{-1}$) because when $dq/dt$ approaches $\alpha$ then $q_t$ approaches to zero and the parameter $\beta$ is related to the extent of surface coverage and the activation energy for chemisorption.

The adsorption of ionic dyes on Cell, PAG-Cell and PAG-Cell-COOH (Table 4) suggests that the initial rate of binding $\alpha$ of dye BR-12 decreases drastically after polymer grafting due to increased selectivity of the surfaces containing $\text{–CONH}_2$ and $\text{–COOH}$ functional groups. The value of $\alpha$ for adsorption of BV-10, the initial rate of binding increases after polyacrylamide grafting. The values of Elovich constant $\beta$ show a decrease after polymer grafting and carboxylation of Cell suggesting that with the increase in number of functional groups on the surface.

The constant $\beta$ increases for adsorption of BV-10 on PAG-Cell than Cell. The Elovich model does not seem to fit well on adsorption of BR-12 on PAG-Cell-COOH and BV-10 on Cell as is clear from low values of regression coefficients.

**Isotherm Analysis of Adsorption Processes**

The adsorption isotherm gives the relationships between the amount of dye adsorbed on the adsorbent and the concentration of adsorbed dye in the solution phase at equilibrium. In this study the adsorption mechanisms and characteristic parameters for the present processes were analyzed by two parameter isotherms i.e. Freundlich, Langmuir and Temkin isotherm models. These models are used to explain the experimental results within wide range of concentration and temperatures.
The exponential decaying adsorption site energy distribution that can be applied to non ideal sorption on heterogeneous surfaces as well as multilayer sorption and is expressed by equation 6.

\[ q_e = K_f \cdot C_e^{\frac{1}{n}} \]  

(6)

Where \( C_e \) is equilibrium liquid phase concentration of dye (mg.L\(^{-1}\)); \( q_e \) is equilibrium solid phase concentration (mg.g\(^{-1}\)), \( K_f \) and \( n \) are indicative adsorption isotherm parameters of adsorption capacity (L.g\(^{-1}\)) and intensity (mg.e\(^{-1}\)) respectively. This equation assumes that the strong binding sites of the adsorbent are occupied on priority and the binding strength decreases with the increase in degree of site occupation. The equation can also be represented in linear form as equation 7.

\[ \log q_e = \log K_f + \frac{1}{n} \log C_e \]  

(7)

The adsorption parameters represent quasi-Gaussian energetic heterogeneity of adsorbent surface. The adsorption isotherm data of ionic dyes on Cell, PAG-Cell and PAG-Cell-COOH is fitted in Freundlich model and this was found that the isotherm model fits the data well as the values of R are very high for adsorption of BR-12 and BV-10. The Freundlich parameters for adsorption of ionic dyes on Cell and derivatives are given in Table 5. The intensity of adsorption \( K_f \) is higher for adsorption of BR-12 than BV-10. The value of \( K_f \) for BR-12 adsorption is increasing with the increase of temperature for Cell and
decreasing for adsorption on PAG-Cell and PAG-Cell-COOH indicating that the binding of BR-12 on grafted and carboxylated cellulose is purely electrostatic in nature. The highest value of $K_f$ for BR-12 adsorption is observed for cellulose as the ionization of Cell in aqueous medium at appropriate pH, negative surfaces of Cell with higher surface area and exposed pores are blocked after grafting and carboxylation leading to compact structure, forming thin layers of dye ions on surface of adsorbent. The N-ends of PAG-Cell can form weaker bonds than its back bone of Cell due to less hydrophilicity of PAG-Cell than Cell. The adsorption of BV-10 on Cell and PAG-Cell divulge that the adsorption intensity of zwitter ionic dye is lesser than cationic dye. The value of $K_f$ is decreasing with the rise of temperature due to weak binding between dye ions and adsorbent. The Freundlich plots for adsorption of BR-12 on Cell and its derivatives are shown in Figure 9.

**Figure 9**: (a) Freundlich Plots for Sorption of BR-12 on Cell (b) Freundlich Plots for Sorption of BR-12 on PAG-Cell-COOH (c) Freundlich Plots for Sorption of BR-12 on PAG-Cell at 303K, 313K and 323 K

**Langmuir Isotherm**

This is probably the best known and most widely applied adsorption isotherm. It was developed in 1916 for gas solid phase adsorption on to activated carbon and is traditionally used to quantify and contrast the performance of different adsorbents. This model assumes the monolayer adsorption (Langmuir, 1918) on definite localized sites which are identical and equivalent. This model assumes that there are no lateral interactions or steric hindrance between the adsorbed dye molecules even on adjacent sites. In the derivation of this isotherm this is assumed that the adsorption is homogeneous and all sites have equal affinity towards the dye molecules. Due to this reason each molecule has constant enthalpy and sorption activation energy with no transmigration of adsorbate in the plane of the surface. Graphically it is characterized with a plateau, an equilibrium saturation point where once a molecule occupies a site, no further adsorption can take place. The Langmuir theory is related to rapid decrease in intermolecular attractive forces to the increase of distance. The mathematical model of Langmuir isotherm is given by equation 8.

$$q_e = \frac{Q_o b C_e}{1 + b C_e} \quad (8)$$

The above equation can be linearized as follows
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\[
\frac{1}{q_e} = \frac{1}{Q_o} + \frac{1}{bQ_oC_e}
\]  
(9)

Where \( Q_o \) and \( b \) are Langmuir constants, the constant \( Q_e \) is related to the monolayer adsorption capacity in mol.g\(^{-1}\) and \( b \) is the binding constant in L.mol\(^{-1}\) related to equilibrium enthalpy constant. The adsorption of dyes over different adsorbent is studied and this was found that the Langmuir isotherm model fitted the data well on most of the adsorption studies of the present work. The adsorption isotherm data of ionic dyes on Cell, PAG-Cell and PAG-Cell-COOH are fitted in Langmuir model and this was found that the model fits better than Freundlich model as is evident from higher values of \( R \) and less values of SEE and \( RSS \). The values of Langmuir parameters are shown in Table 6. The values of monolayer adsorption capacity \( Q_o \) is increasing for adsorption of BR-12 on Cell with the increase of temperature while it decreases for adsorption of BR-12 on PAG-Cell and PAG-Cell-COOH. The spatial arrangement of different dye ions is different on Cell, PAG-Cell and PAG-Cell-COOH due to different types of functional groups and binding capabilities. The Cell and its derivatives act as chelating ion exchanger. The adsorption of bigger BV-10 dye ion is weaker than smaller BR-12 ion as the adsorption capacity of Cell and derivatives, the porosity of Cell and its derivatives is different thus the monolayer adsorption capacities are different. The value of monolayer adsorption capacity BV-10 on Cell is increasing with the increase of temperature and decreases for adsorption on PAG-Cell. The Langmuir plots for adsorption of BR-12 on Cell and derivatives are shown in Figure 10.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Dye</th>
<th>Temperature(K)</th>
<th>( Q_e \times10^3 )</th>
<th>( b )</th>
<th>( R )</th>
<th>SEE</th>
<th>RSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell</td>
<td>BR-12</td>
<td>303</td>
<td>0.0541</td>
<td>5467.12</td>
<td>0.9982</td>
<td>0.0042</td>
<td>0.000</td>
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<tr>
<td>Cell</td>
<td>BR-12</td>
<td>313</td>
<td>0.0593</td>
<td>15178</td>
<td>0.9995</td>
<td>0.0022</td>
<td>0.000</td>
</tr>
<tr>
<td>Cell</td>
<td>BR-12</td>
<td>323</td>
<td>0.0643</td>
<td>15541</td>
<td>0.9961</td>
<td>0.0048</td>
<td>0.000</td>
</tr>
<tr>
<td>PAG-Cell</td>
<td>BR-12</td>
<td>303</td>
<td>0.0523</td>
<td>3118.82</td>
<td>0.9966</td>
<td>0.0064</td>
<td>0.000</td>
</tr>
<tr>
<td>PAG-Cell</td>
<td>BR-12</td>
<td>313</td>
<td>0.0254</td>
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<td>0.9846</td>
<td>0.0148</td>
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<tr>
<td>PAG-Cell</td>
<td>BR-12</td>
<td>323</td>
<td>0.0182</td>
<td>8883.92</td>
<td>0.9876</td>
<td>0.0118</td>
<td>0.001</td>
</tr>
<tr>
<td>PAG-Cell-COOH</td>
<td>BR-12</td>
<td>303</td>
<td>0.0265</td>
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<td>0.9443</td>
<td>0.1736</td>
<td>0.151</td>
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<tr>
<td>PAG-Cell-COOH</td>
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<td>0.0183</td>
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<td>0.9815</td>
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<td>0.006</td>
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<td>BR-12</td>
<td>323</td>
<td>0.0173</td>
<td>2546.85</td>
<td>0.9769</td>
<td>0.0275</td>
<td>0.004</td>
</tr>
<tr>
<td>Cell</td>
<td>BV-10</td>
<td>303</td>
<td>0.0312</td>
<td>1338.33</td>
<td>0.9904</td>
<td>0.0235</td>
<td>0.003</td>
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<tr>
<td>Cell</td>
<td>BV-10</td>
<td>313</td>
<td>0.0342</td>
<td>507.17</td>
<td>0.9757</td>
<td>0.0314</td>
<td>0.005</td>
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<tr>
<td>Cell</td>
<td>BV-10</td>
<td>323</td>
<td>0.0383</td>
<td>1427.73</td>
<td>0.9773</td>
<td>0.0294</td>
<td>0.004</td>
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<td>PAG-Cell</td>
<td>BV-10</td>
<td>303</td>
<td>0.5155</td>
<td>242.96</td>
<td>0.9604</td>
<td>0.0220</td>
<td>0.002</td>
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<td>PAG-Cell</td>
<td>BV-10</td>
<td>313</td>
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<td>698.66</td>
<td>0.9964</td>
<td>0.0069</td>
<td>0.000</td>
</tr>
<tr>
<td>PAG-Cell</td>
<td>BV-10</td>
<td>323</td>
<td>0.1213</td>
<td>850.28</td>
<td>0.9806</td>
<td>0.0171</td>
<td>0.001</td>
</tr>
</tbody>
</table>

Temkin Adsorption Isotherm

Temkin isotherm assumes that the fall in heat of adsorption (function of temperature) would decrease linearly for the dye and adsorbent interactions (Padmesh et al., 2006). The isotherm can be represented by equation 10.

\[
q_e = \frac{RT}{b_1} \ln(a_1C_e)
\]  
(10)

Where, \( b_1 \) is temkin constant related to the heat of sorption (J mol\(^{-1}\)) and \( a_1 \) is temkin isotherm constant (L.g\(^{-1}\)). The isotherm contains a factor that takes into account the adsorbate adsorbent interactions. This
isotherm is applicable on intermediate range of concentration only. This isotherm assumes uniform
distribution of binding energies up to some maximum extent. This isotherm is more appropriate when
adsorbate is bound tightly with identical orientation on the surface of adsorbent. The constant \( b_t \) is directly
proportional to enthalpy of adsorption but it is not absolute enthalpy of adsorption. The Temkin isotherm
model is applied on adsorption of BR-12 and BV-10 on Cell and derivatives and the Temkin parameters
are given in Table 7.

The Temkin constant related to heat of sorption is highest for adsorption of BR-12 on PAG-Cell-COOH.
The value of constant \( b_t \) increases with the rise of temperature for Cell and PAG-Cell-COOH and
decreases for PAG-Cell. The nature of PAG-Cell is different from other due to high hydrophilicity and
more nitrogen content. The adsorption involves energetically favorable processes like entrapping of dye
ion in rearranged polymer chain around dye ion creating favorable Vander Waal interactions and
Hydrogen bond formation. The energy changes during these interactions decide the magnitude of Temkin
constant \( b_t \) for the dye binding with adsorbent particles. The Temkin plot for adsorption of BR-12 on Cell
and derivatives are given in Figure 11. The adsorption of BV-10 on Cell and derivatives reveals that the
value of \( b_t \) are decreasing with the increase of temperature for adsorption of BV-10 on Cell and remains
almost constant for adsorption of BV-10 on PAG-Cell. The hydrophobic micro fibril of Cell may interact
with aromatic rings of the dyes by proper orientation of non polar C-H groups of cellulose with dye ions.
The surface hydroxyl group of cellulose also binds with the polar sites of dye ions by electrostatic
interactions.

**Thermodynamics of Adsorption**

The original concepts of thermodynamics believe that in an isolated system, where energy cannot be
gained or lost, and the entropy change is driving force. In environmental engineering practice, both
energy and entropy factors must be considered in order to consider various processes occurring
simultaneously among adsorbent and adsorbate.

The spontaneity is judged from the net negative values free energy, \( \Delta G^\circ \) at given temperature. The thermodynamics of a process can relate seemingly unrelated properties, and the thermodynamics applies
to equilibrium adsorption isotherms. The equilibrium is said to be attained in sorption processes if that
point is attained by raising or lowering the concentration of dye in the system. The application of Langmuir isotherm on the given set of data gives us the value of adsorption equilibrium constant \( b \).

Thermodynamic parameter \( \Delta G^o \) is calculated by using equation 11.

\[
\Delta G^o = -RT \ln b
\]  

(11)

The Langmuir equilibrium constant was calculated at three different temperatures, i.e. 303K, 313K and 323K. \( \Delta H^o \) and \( \Delta S^o \) are calculated by using Clausius-Clapeyron equation 12. The slope and intercept of the equation gives the value of these parameters respectively.

\[
\ln b = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \cdot \frac{1}{T}
\]

(12)

The thermodynamic parameters for adsorption of BR-12 and BV-10 on Cell and derivatives are shown in Table 8.

The adsorption of BR-12 and BV-10 with Cell and derivatives are enthalpy driven processes. The enthalpy of adsorption is high when opposite charges are present on adsorbent and dye ions. The adsorption of BR-12 on PAG-Cell-COOH and BV-10 on PAG-Cell at optimum pH is most favorable energetically forming stable adsorbate adsorbent complexes.

### Table 7: Temkin Parameters for Adsorption of Ionic Dyes over Cell and Derivatives

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Dye</th>
<th>Temperature(K)</th>
<th>( a_T )</th>
<th>( b_T )</th>
<th>R</th>
<th>RSS</th>
<th>SEE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell</td>
<td>BR-12</td>
<td>303</td>
<td>0.1397</td>
<td>292.70</td>
<td>0.9933</td>
<td>0.2908</td>
<td>0.423</td>
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<tr>
<td>Cell</td>
<td>BR-12</td>
<td>313</td>
<td>0.2316</td>
<td>398.81</td>
<td>0.9941</td>
<td>0.2689</td>
<td>0.362</td>
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<tr>
<td>Cell</td>
<td>BR-12</td>
<td>323</td>
<td>0.4060</td>
<td>527.13</td>
<td>0.9880</td>
<td>0.3795</td>
<td>0.720</td>
</tr>
<tr>
<td>PAG-Cell</td>
<td>BR-12</td>
<td>303</td>
<td>0.0944</td>
<td>374.57</td>
<td>0.9944</td>
<td>0.2227</td>
<td>0.248</td>
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<tr>
<td>PAG-Cell</td>
<td>BR-12</td>
<td>313</td>
<td>0.0933</td>
<td>285.11</td>
<td>0.9980</td>
<td>0.1500</td>
<td>0.113</td>
</tr>
<tr>
<td>PAG-Cell</td>
<td>BR-12</td>
<td>323</td>
<td>0.0951</td>
<td>233.58</td>
<td>0.9979</td>
<td>0.1669</td>
<td>0.139</td>
</tr>
<tr>
<td>PAG-Cell-COOH</td>
<td>BR-12</td>
<td>303</td>
<td>0.0328</td>
<td>564.61</td>
<td>0.9876</td>
<td>0.1969</td>
<td>0.194</td>
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<td>PAG-Cell-COOH</td>
<td>BR-12</td>
<td>313</td>
<td>0.0523</td>
<td>582.89</td>
<td>0.9959</td>
<td>0.1117</td>
<td>0.062</td>
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<tr>
<td>PAG-Cell-COOH</td>
<td>BR-12</td>
<td>323</td>
<td>0.0633</td>
<td>594.66</td>
<td>0.9961</td>
<td>0.1332</td>
<td>0.089</td>
</tr>
<tr>
<td>Cell</td>
<td>BV-10</td>
<td>303</td>
<td>0.0466</td>
<td>729.19</td>
<td>0.9586</td>
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<td>0.613</td>
</tr>
<tr>
<td>Cell</td>
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<td>0.0537</td>
<td>719.33</td>
<td>0.9622</td>
<td>0.3171</td>
<td>0.503</td>
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<tr>
<td>Cell</td>
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<td>0.9989</td>
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<tr>
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<td>0.0755</td>
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<tr>
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<td>0.3132</td>
<td>0.490</td>
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<tr>
<td>PAG-Cell</td>
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<td>0.0627</td>
<td>501.53</td>
<td>0.9716</td>
<td>0.4477</td>
<td>1.002</td>
</tr>
</tbody>
</table>

### Table 8: Thermodynamic Parameters for Adsorption of Dyes on Cell and Derivatives

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Dye</th>
<th>( \Delta H^o )</th>
<th>( \Delta G^o )</th>
<th>( \Delta S^o )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell</td>
<td>BR-12</td>
<td>-72.696</td>
<td>-24.217</td>
<td>-0.155</td>
</tr>
<tr>
<td>PAG-Cell</td>
<td>BR-12</td>
<td>-73.025</td>
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<td>PAG-Cell-COOH</td>
<td>BR-12</td>
<td>-85.281</td>
<td>-20.825</td>
<td>-0.142</td>
</tr>
<tr>
<td>Cell</td>
<td>BV-10</td>
<td>-69.097</td>
<td>-17.958</td>
<td>-0.163</td>
</tr>
<tr>
<td>PAG-Cell</td>
<td>BV-10</td>
<td>-76.850</td>
<td>-16.332</td>
<td>-0.193</td>
</tr>
</tbody>
</table>
Figure 11: (a) Temkin Plots for Sorption of BR-12 on Cell (b) Temkin Plots for Sorption of BR-12 on PAG-Cell-COOH (c) Temkin Plots for Sorption of BR-12 on PAG-Cell at 303K, 313K and 323 K

Conclusion
The research work presented here shows that ionic dyes can be successfully removed from the aqueous solution by adsorption on Cellulose. The adsorbents derived from Cell, PAG-Cell and PAG-Cell-COOH are low cost and are useful and valuable mean for controlling water pollution due to dyes. The main characteristics and results of the study suggests that the batch adsorption experiments show that the adsorption of the BR-12 and BV-10 over Cellulose and its derivatives is dependent on pH, amount of adsorbent, concentration, contact time and temperature.

In the present study, a correlation kinetic approach is applied to sorption processes and Lagergren kinetic model, Pseudo second order kinetic model and Elovich models are applied for adsorption processes. The kinetics of dye adsorption has been found different for cationic and zwitter ionic dye adsorption on Cell and its derivatives. The results of kinetic experiments show that, for all adsorbents, the adsorption proceeds through pseudo second order kinetics at lower and higher concentrations. The thermodynamic parameters obtained in both cases confirm the feasibility of the process at each concentration. The Enthalpy of adsorption has shown an increase with surface modification and adsorption has been found to be more exothermic for adsorption of BR-12 than BV-10. Langmuir isotherm model fitted best for binding of dyes on Cell and surfaces. From this study, it can be concluded that Cellulose and its derivatives are inexpensive and environmentally benign and can be used as excellent adsorbents for removal of dyes aqueous medium.

REFERENCES

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