



**ADSORPTION MECHANISM OF CHITOSAN, ACTIVATED CARBON, AND MAGNETIC CHITOSAN-
ACTIVATED CARBON COMPOSITES ON TO THE DYES WITH DIFFERENT POLARITIES:
ADSORBENT OPTIMIZATION STUDY**

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ABSTRACT

Textile effluent contains dyes of different ionic charges; therefore, it is most important to identify the efficiency of bioadsorbent with respect to their ionic charges and the mechanism of adsorption to ensure the maximum treatment. Thus, this research mainly focuses on adsorption of dyes with different net charges using three types of bioadsorbents, namely chitosan, activated carbon, and chitosan-activated carbon composites. Chitosan was extracted from the crab shells and activated carbon was synthesized from Luffa sponge. Composites of magnetic chitosan and activated carbon were also prepared from the known methods. For adsorption studies, three dyes, Basic Red 18, Acid Yellow 17, and Disperse Blue 106 were selected with positive, negative, and neutral charges, respectively. Results showed that negative dye was maximum adsorbed by chitosan at optimized conditions, while positive and dispersed dye adsorptions were significantly less, whereas adsorption of negative dye was maximum when activated carbon used at optimized parameters; but the rate of adsorption of negative and dispersed dye was considerably less. When composites used, all the dyes were adsorbed at maximum at low concentrations compared to chitosan and activated carbon. Therefore, this research infers that magnetic chitosan-activated carbon composites can be used as a promising low-cost bioadsorbent for textile effluent that contains dyes with different charges in one step.

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INTRODUCTION

Synthetic dyes are most important and are widely used in many industries such as leather, textiles, leather, printing, wool, printing, paper, cosmetics, paper, pharmaceutical, and food industries. There are about 100,000 commercial dyes are available. Textile and dyeing industries uses abundant amount of fresh water and approximately 10 – 15% dyes are wasted in effluents during dyeing processes. Once this effluent left untreated or not properly treated and discharged in to water resources, water quality could be highly affected significantly by reducing the dissolved oxygen contents in water and inhibit sunlight into water sources⁴. Dyes usually have complex aromatic molecular structures since they become more stable and difficult to biodegrade (Blanca *et al*, 2006). Based on the charges, dyes can be classified in to three types as discussed below”

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Cationic or Basic Azo Dyes

Cationic dyestuffs are water-soluble dyes with bright colors. In water, they ionize into cationic ions which dye the fibers by forming ionic linkage with the acid groups on the fibers through the function of electric charge. Acrylic fiber is mainly dyed using basic dyes; it can also be used to modify the dyeing and printing of the polyester and nylon

Anionic or Acid Azo Dyes

Acid dyes have sulfonic or carboxylic acid groups attached to their aromatic rings. They are typically soluble in water and have affinity for amphoteric fibers. In acidic media, they are attracted to protonated amino groups of protein, in case of wool and silk. A carboxylic acid may not be entirely ionized at the pH of the dye bath.

Disperse Dyes

Disperse dyes have low solubility in water, but they can interact with the polyester chains by forming dispersed particles. Mostly they are used in dyeing polyesters and

minimally used in dyeing cellulose acetates and polyamides. Disperse dyes are usually small, planar, and non-ionic, with attached polar functional groups like -NO₂ and -CN. Disperse dyes are less soluble in water and used for dyeing synthetic textile materials such as dyeing polyester yarn of fabric.

Therefore, proper techniques are necessary for efficient removal of these toxic chemicals from before shedding in to external water resources. There are numerous physicochemical processes such as adsorption, reverse osmosis, coagulation/flocculation, electrochemical, photochemical and photocatalytic degradation, advanced oxidation processes, etc., have been proposed and applied for treatment of dye wastewater. Among these, adsorption is found to be very effective, because of their excellent mechanical and chemical stability, high specific surface area and resistance to biodegradation. Therefore, this research aims at using magnetic chitosan-activated carbon composites for treating synthetic dyes with different charges. The results are also compared with adsorption efficiency of activated carbon and chitosan to justify the composite can be used to adsorb dyes with different charges in a single step.

MATERIALS AND METHODS

Preparation of Adsorbents

Activated carbon was synthesized from Luffa sponge using H₃PO₄ and chitosan was extracted from crab shell using mild chemical treatment. Magnetic chitosan and activated carbon composites were prepared following the method of Kyzas *et al*, 2014.

Preparation of the Dye Solution

A stock solution of dyes (1000 ppm) was prepared by dissolving 1 g of the respective dye in the distilled water and then made up to 1000 mL using double distilled water. The samples were stored in a volumetric flask for making other dilute solutions.

Adsorption experiments

Adsorption of three different dyes on to different adsorbents was carried out using a bath experiments method. 50 mL dye solution and known amount of adsorbents were added, respectively, into the flasks. Then the flasks were agitated on the magnetic stirring apparatus at a constant speed of 500 rpm. Since the adsorption process here mainly depends on ionic charge, pH of the reaction solution was optimized first, over a pH range of 2–10. The pH was adjusted by adding the dilute aqueous solutions of 0.1N HCl or 0.1N NaOH. Further, effect of contact time on adsorption of each dye was studied by taking spectroscopic values every 10 min up to 120 min. Then the effect of different concentrations of adsorbents was examined using the adsorbents concentration varying from 10 to 150 mg/L. Initial dye concentrations were optimized further using 10, 40, 80, 120, and 150 mg/L of dye solutions. After the defined time intervals, samples were withdrawn from the shaker, centrifuged and the supernatant solution was analyzed for residual dye concentration using a UV-Visible spectrophotometer. After optimizing pH, initial dye concentration, and adsorbent rat, effect of temperature on the process was determined by varying the temperature from 27 to 60 C. Temperatures were maintained using ice and hot water bath with inserted thermometer. And finally, effect of contact

time was also calculated from 10 to 120 min. The dye removal percentage can be calculated as follows:

$$(\%) \text{ of dye removal} = \frac{(C_0 - C_e)}{C_0} \times 100$$

where C₀ and C_e are the initial and final concentrations(mol/L) of the dye, respectively.

Analytical Method

The samples of batch experiments were first vacuum filtered with to remove the adsorbent and then free adsorbent solution was analyzed by a UV-Vis Spectrophotometer to determine the remaining dye concentration.

RESULTS AND DISCUSSION

Dye adsorption properties of chitosan, activated carbon, and composites were examined using batch process for 2 hrs at room temperature (37 C). Rate of adsorption was different for different materials with respective to their physical and chemical properties and nature of the dyes. Different parameters such as pH, adsorbent concentration, initial dye concentration, temperature, and contact time were optimized in order to maximize the adsorption rate

Effect of pH

While treating dyes based on their charges, pH has an important role in adsorption. The pH of the dye solution affects the surface charge of the adsorbent, the degree of ionization of the materials, and the dissociation of functional groups on the active sites of the adsorbent. It also affects the structure of the dye molecules (Wawrzekiewicz and Hubicki, 2009). Table 1 shows different dye absorption natures of biomaterials.

Table 1 Adsorption of Anionic, Cationic, and Disperse dyes by different bioadsorbents at different pH

Chitosan						
Dye	2	4	6	7	8	10
Chitosan	15.3	68	66.1	30	22.8	10.5
Activated Carbon	66.7	60.1	50.6	41	30.9	21.4
Composites	75.7	98.3	78.6	75.4	60	50.4
Activated Carbon						
Chitosan	5.9	10.8	13.4	15.2	48.9	65.6
Activated Carbon	15	21	35	40.2	61	69.9
Composites	80.6	97.6	50.4	70.8	75.6	70.6
Composite						
Chitosan	9.9	16.4	28.7	5	59.4	68.6
Activated Carbon	69.8	72.2	20.9	15.2	16.5	10.4
Composites	80.6	97.6	50.4	70.8	75.6	70.6

Table 2 Adsorption of Anionic, Cationic, and Disperse dyes by different concentrations of bioadsorbents

Dyes mg/l	Anionic				Cationic				Disperse						
	20	40	60	80	100	20	40	60	80	100	20	40	60	80	100
Chitosan	50.5	53.8	56.2	59.5	61.2	36.5	44.5	58	62.8	54.1	35	40.9	52.6	59.2	63.4
Activated Carbon	50	54.2	57.8	60	62.9	59.9	63	66	69	71.2	37	42.1	48	52.5	58.8
Composites	91.7	94.2	96.8	98.5	98.9	92.5	95.1	97.8	99.2	98	90	93.1	94.6	98.2	99

Adsorption of Different Dyes by Chitosan

Adsorption of Anionic Dye

From the results, below pH 3, adsorption of anionic dye decreased to 15.3 %; because at high acidic conditions, there may be increase in the hydrogen ion concentration and as a result repulsion of ions occur that lead to gel formation between dye and chitosan. At pH 4, adsorption of dye markedly increased from 15.3 to 64%. At this stage, amino groups become free from protonation, which reduces the concentration of hydrogen ions leading to the decrease in

competition of H⁺ with the dye solution for sorption sites by electrostatic force of attraction, resulting increase in the adsorption efficiency. These results are in agreement with the work of (T. Santhi and S. Manonmani 2009). At pH 7, adsorption was 30%. At neutral pH, the electrostatic balance between anionic and cationic groups on chitosan would make it less favourable for dye binding. At pH above 8, there was significant decline in dye adsorption to 10.5%; the increased negative charges on the adsorbent surface decreased the attraction of oxyanions of the dye on the adsorbent, leading to decreased electrostatic force and slowdown the adsorption efficiency. These results are in agreement with the work of (S. Sugashini and K. Begum 2013; Wang *et al.*, 2005; Dada *et al.*, 2012; Ahmed *et al.*, 2016).

Adsorption of Cationic Dye

In case of cationic dyes, the process is vice versa, i.e., adsorption increases with increasing pH (2–10) from 5% to 65%. The logic behind the process is quite simple. When pH is acidic, it forms more number of hydrogen ions, i.e., the system is already protonated, in addition to that when cationic dye and chitosan with positive charge react, a strong electrostatic repulsion between the positive charges occur and thus hinders the adsorption process.

Adsorption of Dispersed Dye

Adsorption in case of disperse dye is different. Disperse dyes have neutral charge in water. At pH 7, see Table 1, adsorption is very less, i.e., 5% because there is no electrical repulsion and packing density on the surface of adsorbent and dye molecules. When pH of the system increased from 7 to 10, adsorption rate increased parallelly from 5 to 68%. Because, negative charge is formed on the surface of disperse dye and this causes chitosan to adsorb the molecules on to their surface through electrostatic force. But when pH is decreased from 7 to 2, positive charge is thus formed and adsorbent rate was only 10% may be due to physical adsorption but not based on the ionic charge.

Adsorption of different Dyes by Activated Carbon

Adsorption by activated carbon is vice versa. The surface of carbon is negatively charged (Bean *et al.*, 1964) and the mode of adsorption differed respective to the dye charge.

Adsorption of Anionic Dye

The removal of anionic dyes at alkaline pH, where the adsorbent is negatively charged cannot be explained based on the electrostatic attraction; another mechanism of adsorption like ion exchange or chemisorption might be operative. Activated carbon below pH 5 becomes positively charged and above pH 6 becomes negatively charged. Therefore, adsorption of anionic dye increased at low pH from 41 to 66% and decreased with increase in pH from 50 to 21, because of the presence of excess OH⁻ ions competing with the dye anions for the adsorption sites. Similar results are also obtained by (40–42). A similar trend was observed for the adsorption of Congo red on activated carbon prepared from coir pith (Namasivayam *et al.*, 2002); Adsorption of Acid Brilliant Blue (Namasivayam *et al.*, 1993a) and Acid Violet (Namasivayam *et al.*, 1993b) on a biogas residual slurry; and adsorption of Congo Red on waste orange peel (2003d) and banana pith (Namasivayam *et al.*, 1996).

E.Oyelude and F. Appiah-Takyi 2012 also evidenced that while increasing pH, more amount of H⁺ ions are formed and may exert electrostatic repulsion with the positive charged dye thereby decreasing the adsorption efficiency.

Adsorption of Cationic Dye

In case of cationic dye, when pH is increased from 7 to 10, adsorption percentage increased from 40 to 69%, due to the fact that with increase in ionic strength there is a partial neutralization of the positive charge on the adsorbent surface. The high ionic strength enhances the hydrophobic–hydrophobic interactions by the compression of electric double layer that of pH solution. And when pH decreased from 7 to 2, adsorption rate also decreased from 40 to 15%. This is because at low pH, a number of cationic ions increases and lowers the adsorption sites and electrostatic force.

Adsorption of Disperse Dye

Results also show that acidic pH is favorable for disperse dye. Rate of dye adsorption increased from 20 to 69 % with the decrease in pH from 7 to 2. And there was a decrease in adsorption from 20 to 10% when pH increased from 7 to 10. These results corroborate with the work of Ozokar and Sengil, 2004. Generally, electrostatic interaction between activated carbon and dye molecules was the main force controlling the adsorption process. The protonated groups of activated carbon were mainly carboxylic group (-CO-), phenolic 2OH+(-OH2+) and chromenic groups (O+) and the de-protonated groups of reactive dyes were probably the sulphonate groups (-SO3-). In the pH range of 4.5–6.0, the surface of activated carbon is negatively charged (pHpzc=4.4) and reactive dyes are positively charged (pKa=5-6). Therefore, the strong electrostatic attraction favored the adsorption of reactive dyes onto activated carbon, resulting in the high removal efficiency of dyes.

Adsorption by Composites

Adsorption rate of all the three dyes by composite was different from the above. The optimized pH for the adsorption of all the three dyes was 4. At pH 4, adsorption rate of cationic dye was maximum of 97.6%. Anionic dye was about 98.3%, and disperse dye was about 96.4%. The reasons can be as follows: At acidic pH, cationic dye and disperse molecules were attracted by activated carbon, whereas anionic dye molecules were adsorbed maximum by magnetic chitosan by electrostatic forces. Results also show that only highly alkaline conditions are not preferable for dye adsorption. At acidic and mild acidic conditions, adsorption of all the three dyes was maximum. We can infer from the results that irrespective of charges, the composite obtained from this study can effectively adsorb dye molecules with different charges.

When we compare the efficiency of chitosan, activated carbon and composites, the composites showed highest adsorption property.

Effect of Adsorbent Dose

The concentration of the adsorbent should be optimized in order to carry out maximum adsorption process. Because, the biomaterial used should have the efficiency to remove the dye molecules at one step in comparatively less quantity.

The effects of different concentrations of chitosan, activated carbon, and composites on the uptake of three different dye

molecules were studied in detail and the results are shown in Table 2. The concentrations of adsorbents, chitosan, activated carbon, composites, respectively, were increased from of 20 to 100 mg in 10mL of different dye solutions. From the results obtained above, it can be clearly inferred that percentage removal increases with the adsorbent dose and there was a linear relation between them, but after certain concentration it became constant. After optimizing pH of the adsorbing system, it is very important to optimize concentration of the adsorbent. Because, the biomaterial used should have the efficiency to adsorb the dye molecules at one step in comparatively less quantity.

Adsorption by Chitosan

Adsorption of negative dye was spontaneous with the increase in the concentration of chitosan; When the concentration increased from 20 to 100 mg/L, the rate of adsorption also increased from 50.5 to 61.2%; because, there may be increased availability of active sites for anionic dye and increase of amine groups in chitosan, whereas in case of positive dye there was increase in the rate of adsorption up to 80 mg/L with 62% but above that decrease in the adsorption rate, 54%, was observed due to charge repulsion of positive dye and chitosan. In case of disperse dye, adsorption rate gradually increased with increase in concentration, from 35 to 63% with 20 to 100mg/L increase in concentration, respectively; because the concentration of ionic charges between the dyes and adsorbents increase and thus aids in adsorption.

Adsorption by Activated Carbon

Similar mechanism was observed in activated carbon but in the opposite direction due to negative charges. That is, adsorption of cationic dye was higher from 59.9 to 71%, when compared to anionic dye, when the concentration increased from 20 to 100mg/L, respectively. Adsorption rate of disperse dye by activated carbon was also slightly higher than the chitosan. We can also see that concentration of chitosan required for complete adsorption of dyes was slightly high when compared to activated carbon and composites which may be due to the lesser number of active sites.

Adsorption by Composites

Rate of adsorption by composites was significantly high when compared to chitosan and activated carbon. The concentration required for adsorption of maximum amount of dyes were also comparatively less. Results show that 91.7% of anionic dyes were adsorbed at minimum concentration, 2mg/L, whereas at the maximum concentration 98.9% of the dye was adsorbed. Similarly, 20mg/L of composites could effectively remove 92.5 and 89 % of cationic and disperse dyes, respectively, whereas maximum of 98 and 99 % of the respective dyes removed efficiently at the maximum concentration, i.e., 100mg/L.

The reasons may be at the optimized pH, magnetic chitosan and activated carbon together would efficiently act on the dye molecules in the solution and due to strong electrostatic forces, they could be adsorbed at the maximum. At the concentration of 100mg/l, composites effectively adsorbed 99 % of anionic, cationic and disperse dyes. The increase in percentage removal could be explained by the fact that with an increase in adsorbent dosage, increase in the surface area and availability of active sites to the dye molecules. But after certain concentration, there is saturation in the adsorption because of

overlapping of active sites at high doses that decreases the surface area adsorbents and particle interactions such as aggregation (Rao *et al*, 2008). The results also correlate with the works of Namasivayam and Sangeetha, 2004; Vadivelan and Vasanthkumar, 2003; and Yu *et al*, 2003. Stephan Inabaraj *et al.*, 2002 also evidenced that at high concentration the available sites of adsorption becomes fewer and hence the percentage removal of dye depends upon initial concentration.

Effect of initial dye concentration

In order to calculate the maximum adsorption capacity of all the three adsorbents, determining the equilibrium sorption data at various initial dye concentrations is most important. Initial concentration of dye is one of the most important reasons to determine the percentage adsorptively, because the concentration of dye has direct influence on its removal in the aqueous phase. It also provides necessary driving force to overcome the resistance to the mass transfer between the aqueous and solid phases (Bulut and AydIn, 2006). In this study, initial dye concentration was examined for all the three sorbents, namely chitosan, activated carbon, and composite.

The effect of dye concentration on the efficiency of adsorption was investigated by increasing the dye concentration from 20 to 100mg/L and the results are shown in Table 3. From the results obtained, it is concluded that with the increase in initial dye concentration, the percentage of dye adsorption also decreased (Arivoli *et al*, 2007; Qin *et al*, 2009) and the actual amount of dye uptake increased. [Balasubramani K and Sivarajasekar (2014).

Table 3 Adsorption efficiency of different bioadsorbents at various initial dye concentrations (Anionic, Cationic, and Disperse)

Dyes	Anionic					Cationic					Disperse				
	20	40	60	80	100	20	40	60	80	100	20	40	60	80	100
mg/l	20	40	60	80	100	20	40	60	80	100	20	40	60	80	100
Chitosan	60	52.1	48.3	43.9	31	36	34.2	31	27.8	24	64.1	60	56.8	52.1	40.9
Activated Carbon	64.1	70.2	61	67.2	62.8	40	76.5	72.4	69.6	62.2	58	79.5	61	55.4	51.6
Composites	91.	90.2	88.6	85.4	83.7	92.5	90	86	85.6	82	97	95	92.2	89.2	84.7

When the concentration of cationic dye increased from 20 to 100 mg/L, the percentage removal by chitosan, activated carbon and composites also decreased but the composites comparatively removed higher percentage of dye. We can observe that when the concentration of dyes slightly increased, adsorption properties of both the chitosan and activated carbon gradually decreased because of increased repulsive force between the adsorbents and dye molecules.

When the concentration of anionic dye increased from 20 to 100 mg/L, there was decline the adsorption efficiency from 60 to 31%, similarly adsorption rate decreased from 36 to 24 and 64 to 40% when the concentration of cationic dye and disperse dye, respectively, increased from 20 to 100mg/L. Rate of adsorption of all the three dyes by magnetic composites was appreciably high even at the highest dye concentrations. Adsorption rate of composites even at the maximum dye concentration was above the average. That is, composites was capable of removing 83.7, 82 and 84 % of dye at the highest dye concentration, 100mg/L. The obtained results confirmed that minimal concentration of composites was required for maximum adsorption of all the dyes. Overall, we can infer that the adsorption capacity is directly proportional to the dye concentration and with the increase in dye concentration,

adsorption increases; because at this stage, the surfaces of adsorbents were highly available to the dyes molecules, till the saturation level (R. Gottipati and S. Mishra, 2010); therefore, interaction between the ions and the adsorbent molecules increased and the mass transfer resistance between the aqueous and solid phase becomes less (Maarof *et al*, 2003). As a result, with the increase in number of collisions between the dye molecules and the surface area of adsorbent, the adsorption of dye molecules increases (Masrosemal *et al*, 2009).

However, above the saturation level (Eren and Acar, 2006), higher dye concentration, the colour removal percentage decreases because of the availability of limited active sites on the adsorbate to remove dye molecules and no more free binding sites for further adsorption.

Effect of time

The influence of contact time on the dye uptake from the aqueous solution by three different bioadsorbents was studied and the results are shown in Table 4. Rate of adsorption greatly varied according to the net ionic charge of the dye molecules and bioadsorbents used. It was also evidenced that adsorption in all the dyes was rapid at the initial stages and became slower in later stages till the saturation point

Table 4 Adsorption of Anionic, Cationic, and Disperse dyes by different concentrations of bioadsorbents at various temperatures

Temperature (C)	Anionic			Cationic			Disperse		
	27	40	65	27	40	65	27	40	65
Chitosan	30.47	68.1	40.2	30.57	68.9	15.27	32.7	64.6	14.4
Activated Carbon	32.32	61.5	52.1	34.4	64.6	56.45	30.8	62.3	55.8
Composites	56.44	98.2	87.23	55.67	99.1	59.87	57.8	99.4	79.4

Adsorption by Chitosan

In chitosan, the rate of anionic dye adsorption was very fast and reached equilibrium at around 70 min may be due to availability of the negatively charged surface of dye. The rate of cationic and disperse dye adsorptions was comparatively slower than that of negative dye and equilibrium was gradually attained after 80 min.

Adsorption by Activated Carbon

Adsorption rate of activated carbon on negative dyes were similar but in the opposite to that of chitosan, i.e., adsorption of cationic dye was rapid at the initial stage and attained equilibrium around 50 min, whereas rate of adsorption was very slow in case of anionic and disperse dye, but the equilibrium achieved at around 80 min. This may be because of slow pore diffusion due to less electrostatic force between the dye molecules and adsorbent.

Adsorption by Composites

In case of composites, since the adsorption was rapid for all the three dyes, equilibrium achieved at 20 min, i.e., after 20 min maximum of the dye molecules were adsorbed. Therefore, it can be clearly seen that time required for adsorption of dyes by composites were significantly less compared to chitosan and activated carbon. Results evidences that rate of adsorption rate of composites were significantly constant and quick when compared to chitosan and activated on all the three dyes, respectively.

The difference in the adsorption rate by different adsorbents may be due to the net charges of the dye molecules and the adsorbents itself. In detail, when chitosan, positive charge, interacts with cationic dye, rate of adsorption is spontaneous and attains saturation in lesser time. But in case of anionic and disperse dyes, the adsorption rate is less and very slow when compared to the above process due to charge repulsion and lack of charge, respectively. While using composites over three dyes, there was comparatively efficient adsorption when compared to chitosan and activated carbon at lesser time, because it provides adsorption sites for dyes with different polarities.

Mode of Dye Adsorption

The mode of adsorption is clearly explained as follows. The cationic, anionic, and disperse dye molecules first interact with the composites in a aqueous phase and encounter the boundary layer effect where they get adsorbed from the surface and finally diffuse into the porous structure of the composites (Malik, P.K, 2003) and a monolayer is formed on the surface (Malakootian *et al.*, 2011). The reason for this rapid adsorption at initial stage may be due to increased availability of adsorption sites on the adsorbents as stated by Pathania *et al.* (2013). At this time increased concentration gradient between adsorbate in solution and adsorbate on the adsorbent will occur. As a result, strong attractive forces formed between them, which lead to fast diffusion into the interparticle matrix to attain rapid equilibrium.

After the certain point, enough amounts of dye molecules might have diffused in to the interior parts of the adsorbents and the active sites do not allow further adsorption to take place. Therefore saturation state attained and no more adsorption occurs. To ensure the equilibrium, the duplicated were left for 24 hours and the results were ensured.

Effect of temperature

Optimization of the system’s temperature is one of the most important criteria; because, temperature has an important role in all kinds of reactions. Therefore, in this research, the effect of temperature on the percentage removal of cationic, anionic and disperse dyes by different adsorbents has been studied at different temperatures, viz., 27, 40, and 60° C as shown in Table 5.

Table 5. Adsorption of Anionic, Cationic, and Disperse dyes by different concentrations of bioadsorbents from 10 to 120 min

Time (min)	10	20	30	40	50	60	70	80	100	120
Anion										
Chitosan	67.23	74.89	80.32	89.65	94.35	100	100	100	100	100
Activated Carbon	46.12	51.74	59.32	63.89	79.45	85.1	92.36	98.65	100	100
Composites	71.56	89.20	98.7	100	100	100	100	100	100	100
Cation										
Chitosan	40.82	50.89	57.22	61	78.91	81.78	90.50	99.23	100	100
Activated Carbon	66.89	75.10	83.58	90.36	96.87	100	100	100	100	100
Composites	70.89	90.10	98.10	100	100	100	100	100	100	100
Disperse										
Chitosan	50.7	57.4	62.8	78.6	84.8	95.10	99.1	100	100	100
Activated Carbon	58.87	67.5	71.98	82.3	89.65	97.4	100	100	100	100
Composites	79.36	86.20	97.10	100	100	100	100	100	100	100

Results show that in anionic dye with the increase in temperature from 27 to 40° C, the removal percentage of anionic dye by chitosan increased from 30.47 to 68.1 %, cationic dye adsorption increased from 30.57 to 68.9 % and disperse dye removal increased from 32.7 to 64.6.

Likewise, activated carbon also showed increase in the adsorption rate with the increase in the temperature from 27 to 40. Adsorption of anionic, cationic, and disperse dyes by activated carbon increased from 32.32 to 61.5, 34.4 to 64.6, 30.8 to 62.3.

Among the three, magnetic composites exhibited highest adsorption rate with the increase in temperature from 27 to 40 C. Rate of adsorption of anionic dye increased from 65 to 98.2%, adsorption of cationic dye increased from 55 to 99.1%, whereas disperse dye adsorption rate increased from 57 to 99.4.

Overall, magnetic composites exhibited best adsorption property among all the three. Therefore, the results also conclude that the temperature has positive correlation with the efficiency of dye adsorption, i.e., the removal percentage of dye increases when the temperature of the system increased from 27 to 40° C, which indicates that adsorption of dyes in this system was an endothermic process.

With an increase in temperature, up to certain point, 60 C, there may be increase in the mobility of the large dye ions. Thus, sufficient energy to interaction with active sites at the surface dyes could be provided by increasing number of molecules. Furthermore, increasing temperature also causes swelling of internal structures of chitosan and activated carbon that enables dyes to penetrate further, Iscen *et al*, 2007; Won *et al*, 2006; Vijayaraghavan and Yun, 2007.

From the graphs we can see that beyond particular temperature, 60° C, there was considerable decrease in the adsorption rate which may be due to the damage of active binding sites and weakening of binding forces between the dye molecules and adsorbent and may be due to denature of chitosan in the composite. Similar types of results have also been reported by Li *et al.*, 2010; Senthil Kumar, 2014; Salleh *et al.*, 2011.

Therefore, from the results, we can clearly infer that magnetic composites were efficient among the three. By adjusting the pH to 4, system temperature at 40 C, initial dye concentration to 100 mg/L, initial composite concentration to 20 mg/L and the reaction time to 20, we can attain the maximum adsorption of all the three dyes.

CONCLUSION

Results clearly inferred that the rate of adsorption and mode of adsorption greatly depend on the charge of bioadsorbent used and also the net charge of the dye. Among different bioadsorbents, magnetic composites are most effective in removing all the three dyes with different charges.

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References

- Arivoli Shanmugam M (2009). Thenkukuzhali and P. Martin Deva Prasath. Adsorption of rhodamine B by acid activated carbon: Kinetic, Thermodynamic and Equilibrium Studies. *The Electronic Journal of Chemistry*. 1(2), 138-155.
- Ahmed MB, Zhou JL, Ngo HH, Guo W (2016). Insight into biochar properties and its cost analysis *Biomass Bioenergy*, 84, pp. 76-86
- Balasubramani K and Sivarajasekar N (2014). Adsorption Studies of Organic Pollutants onto activated Carbon. *International Journal of Innovative Research in Science, Engineering and Technology*. 3:10575- 10581
- Bean EL, Campbell SJ and Anspach FR (1964). *J Am Wat Works Asso*, 56.
- Bulut, Y and Aydin H (2006). A kinetics and thermodynamics study of methylene blue adsorption on wheat shells. *Desalination*, 194(1-3), 259.
- Dada AO, Olalekan AP, Olatunya AM and Dada O (2012). Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms studies of equilibrium sorption of Zn²⁺ onto phosphoric Acid modified rice husk. *Journal of Applied Chemistry*, 3(1), 38-45
- Eren Z, Acar FN (2006). Adsorption of reactive black 5 from an aqueous solution: equilibrium and kinetic studies. *Desalination* 194, 1– 10.
- Gottipati R and Mishra S (2010). Application of biowaste (waste generated in biodiesel plant) as an adsorbent for the removal of hazardous by emethylene blue-from aqueous phase. *Brazilian Journal of Chemical Engineering*. 27(2): 357-367.
- Isцен CF, Kiran I, and Ilhan S (2007). Biosorption of Reactive Black 5 dye by *Penicillium restrictum*: the kinetic study. *Journal of Hazardous Materials*, 143(1-2): 335-340.
- Jia Yu, Li and Shukla, Shyam and Dorris L, Kenneth and Shukla, Alka and Margrave J (2003). Adsorption of Chromium from Aqueous Solution by Maple Saw Dust. *Journal of hazardous materials*. 100. 53-63.
- Karaer, Hatice and Kaya, Ismet (2016). Synthesis, characterization of magnetic chitosan/active charcoal composite and using at the adsorption of methylene blue and reactive blue4. *Microporous and Mesoporous Materials*. 232.
- Namasivayam C and Kadirvelu K (1997). Activated carbons prepared from coir pith by physical and chemical activation methods. *Bioresource Technology*. 62. 123-127.
- Namasivayam C, Yamuna RT (1993a). Colour removal from aqueous solutions by biogas residual slurry. *Toxicol Environ Chem.*, 38; 131-43
- Namasivayam C, Yamuna RT (1993b). Utilizing biogas residual slurry for dye adsorption. *Am. dyestuffRep*. 83 22-8
- Namasivayam C, Kanchana N, Yamuna RT ((1993c). Waste banana pith as adsorbent for removal of Rhodamine B from aqueous solutions. *Waste management*, 13(1993c) 89-95.
- Namasivayam C, Muniasamy N, Gayathri K, Rani M, Ranganathan K (1993d). Removal of dyes from aqueous solutions by cellulosic waste orange peel. *Bioresource Technology*, 57(1996) 37-43.

- Namasivayam C and Sangeetha D (2006). Removal and recovery of vanadium (V) by adsorption onto ZnCl₂ activated carbon: Kinetics and isotherms; *Adsorption*. 12:103–117
- Oyelude EO and Appiah-Takyi F (2012). Removal of methylene blue from aqueous solution using alkali-modified malted sorghum mash. *Turkish J. Eng. Env. Sci.* Vol.36, pp.161 – 169.
- Ozacar M, Sengil IA (2004). Application of kinetic models to the sorption of dispersed dyes onto alunite, colloids and surfaces, *Physicochem. Aspects* 242: 105-113.
- Qin Q, Ma J, Liu K (2009). Adsorption of anionic dyes on ammonium-functionalized MCM-41. *J. Hazard. Mater.* 162, 133– 139.
- Rao C R N, and Karthikeyan J (2008). Adsorption of fluoride by gamma alumina. 12th International Water Technology Conference (IWTC12), Alexandria, Egypt, pp.141-151
- Pathania D, Sharma S, Singh P (2013). Removal of methylene blue by adsorption onto activated carbon developed from *Ficus carica* bast, *Arabian Journal of Chemistry*(0).
- Li Q, Yue Q, Su Y, Gao B, Sun H (2010). Equilibrium, thermodynamics and process design to minimize adsorbent amount for the adsorption of acid dyes onto cationic polymer-loaded bentonite. *Chem. Eng. J.*, 158 (2010), pp. 489-497.
- Maarof HI, Hameed BH and Ahmad A L (2003). Adsorption equilibrium of phenols from aqueous solution using modified clay. *Jurnal Jurutera Kimia Malaysia*. 3: 85-94.
- Masrosemal H, Mas H and Kathiresan S (2009). The removal of methyl red from aqueous solutions using banana pseudostem fibers. *American Journal of Applied Sciences*. 6(9): 1690-1700.
- Malik PK (2003). Use of activated carbons prepared from sawdust and rice-husk for adsorption of acid dyes: A case study of Acid Yellow 36. *Dyes Pigments*, 56, 239–249.
- Malakootian M, Moosazadeh M, Yousefi N and Fatehizadeh A (2011). Fluoride removal from aqueous solution by pumice: case study on Kuhbonan water. *African J. Envir. Sci. Tech.* 5:299
- Senthil Kumar P, Sebastina Anne Fernando P, Tanvir Ahmed R, Srinath R, Priyadarshini M, Vignesh AM and Thanjlappan A. Effect of Temperature on the Adsorption of Methylene Blue Dye onto Sulfuric Acid-Treated Orange Peel. *Chem. Eng. Comm.*, 201:1526–1547.
- Salleh MAM, Mahmoud DK, Karim WAWA, Idris A (2011). Cationic and anionic dye adsorption by agricultural solid wastes: a comprehensive review. *Desalination*. 280(1–3):1–13.
- T. Santhi S. Manonmani, and Ravi S (2009): Uptake of Cationic Dyes from Aqueous Solution by Biosorption onto Granular *Muntingia calabura*. *E-Journal of Chemistry*. 6(3), 737-742
- Sugashini S and Meera Sheriffa Begum K M (2013). Column Adsorption Studies for the Removal of Cr(VI) Ions by Ethylamine Modified Chitosan Carbonized Rice Husk Composite Beads with Modelling and Optimization. *Journal of Chemistry* Volume, 11 pages
- Stephan Inabaraj K, Selvarani and Sulochana NJ (2002). *Sci. Ind. Res.* 61, 971 – 978
- Vijayaraghavan K and Yun YS (2008). Biosorption of C.I. Reactive Black 5 from aqueous solution using acid-treated biomass of Brown seaweed *Laminaria* sp. *Dyes and Pigments*, 76, 726-732
- Vadivelan V and Vasanthkumar K (2005). Equilibrium, kinetics, mechanism and process design for the sorption of methylene blue onto rice husk, *J Colloid Interface Sci*, 286, 91.
- Wang S, Zhu Z H, Coomes A, Haghseresht F, Lu GQ (2005). The physical and surface chemical characteristics of activated carbons and the adsorption of methylene blue from wastewater. *Journal of Colloid and Interface Science*, v. 284, n. 2, p. 440–446.
- Wawrzkievicz M, Hubicki Z (2009). Removal of Tartrazine from aqueous solutions by strongly basic polystyrene anion exchange resins. *J. Hazard. Mater.*, 164, p. 502
- Won SW, Wu G, Ma H, Liu Q, Yan Y, Cui L and Yu YS (2006). Adsorption performance and mechanism in binding of Reactive Red 4 by coke Waste. *J. Hazard. Mater.* 138, 370–377.

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