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Removal of azo dye from water by adsorption using waste residue from alum manufacturing process

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Adsorption techniques are widely used to remove certain groups of pollutants such as dyes which are not amenable to biodegradation and environmentally very problematic. Although commercial activated carbon is a preferred sorbent for color removal, its widespread use is restricted due to high cost. As such, alternative non-conventional sorbents should be investigated. It is well-known that natural materials, waste materials from industry and agriculture, and bio sorbents can be obtained without a cost, therefore could be employed as inexpensive sorbents. Therefore the present investigation reports the adsorptive capacity of an industrial residue for the removal of azo dyes. Batch experiments were carried out for the sorption of the dye onto the adsorbent. The influence of contact time, adsorbent dose, pH and initial dye concentration on the adsorption capacity of the material was studied. Kinetics and adsorption isotherms were also studied to evaluate the rate of dye removal and the capacity of the adsorbent. The equilibrium data best fits freundlich isotherm equation. Adsorption capacity (K_f) and intensity of adsorption (n) as determined by fitting the equilibrium data to freundlich isotherm equation are calculated to be 0.26 and 0.82, respectively. The adsorption process was found to undergo via a pseudo-second-order adsorption kinetics with a rate constant of 3.81×10^{-3}(g /mg / min). The removal of dye was not affected for the initial dye concentration range of 15 to 256 mg/L. An adsorption process; requiring an equilibrium time of 30 h with optimum adsorbent dose of 19 g/L for 77.4% dye removal efficiency was observed at near neutral pH. However, as the pH of water is adjusted from 7 to 9, the dye removal efficiency was greater than 90%. The overall result shows that the industrial by product investigated in this study exhibited a high potential for the removal of dye from aqueous solution.

Key words: Dye, adsorbent, adsorption isotherms, batch adsorption, removal.

INTRODUCTION

It is estimated that 10,000 different types of dyes and pigments are produced worldwide annually (Wallace, 2001) out of which a large number of dyes are azo compounds (-N=N-), which are linked by an azo bridge.

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Table 1. Percentage composition of the chemical constituents in waste residue.

Chemical composition	Percent (wt. %)	Chemical composition	Percent (wt. %)
Quartz (SiO_2)	40	K_2SO_4	0.005
Kaolin	8.883	$Al_2(SO_4)_3$	1.778
$Al(OH)_3$	0.878	$CaSO_4$	0.194
$Fe_2(SO_4)_3$	0.023	Fe_2O_3	0.001
$MgSO_4$	0.008	Na_2SO_4	0.007

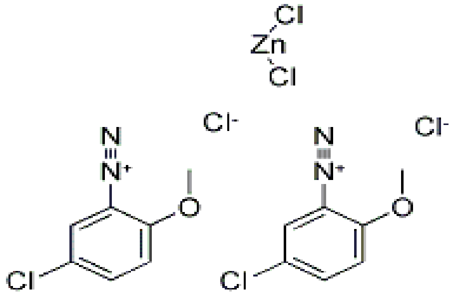

Figure 1. The molecular structure of the dye.

It is estimated that 10,000 different types of dyes and pigments are produced worldwide annually (Wallace, 2001) out of which a large number of dyes are azo compounds (-N=N-), which are linked by an azo bridge. Azo dyes are used by a wide number of industries. While textile mills predominantly use them, azo dyes can also be found in the food, pharmaceutical, paper and printing, leather, and cosmetics industries (Asamudo et al., 2005). Many of these dyes find their way into the environment via effluent discharges. These compounds retain their color and structural integrity under exposure to sunlight, soil and bacteria; they also exhibit a high resistance to microbial degradation in wastewater treatment systems.

Therefore these compounds have become a major environmental concern (Asamudo et al., 2005). In current dyeing processes, as much as 50% of the dye is lost in the wastewater. This can lead to acute effects on exposed organisms due to the toxicity of the dyes, abnormal coloration and reduction in photosynthesis because of the absorbance of light that enters the water (Slokar and Marechal, 1998).

“Currently there are many dye removal methods, out of these methods ion exchange and adsorptions using natural clays are preferable because of cost effectiveness and ease of operation”. Activated carbon is the preferred adsorbent widely employed to treat wastewater containing different classes of dyes. Activated carbon adsorption has been cited by the US Environmental Protection Agency as one of the best available control technologies (Bhattacharyya and Sarma, 2003). However, the disadvantage associated with is its high cost (Babel and Kurniawan, 2003). The regeneration of saturated carbon is also expensive, not straightforward, and results in loss of the adsorbent. The use of carbons based on relatively inexpensive starting materials is also unjustified for most pollution control applications (Street et al., 1995). Due to the problems mentioned above, research interest into the production of alternative sorbents to replace the costly activated carbon has been intensified in recent years. Cost is actually an important parameter for comparing the adsorbent materials. A sorbent can be considered low-cost if it requires little processing, is abundant in nature or is a by-product or waste material from another industry. In this paper laboratory investigations were carried out to evaluate the efficiency of the waste residue of aluminum sulfate and sulfuric acid factory to adsorb azo dyes from water.

MATERIALS AND METHODS

The waste residue, generated during the manufacture of aluminum sulfate using kaolin and sulfuric acid, was collected from Awash Melkasa Aluminum Sulfate and Sulfuric Acid Factory, which is located at the central part of the Ethiopian Rift Valley Region. Samples were taken from more than 30 batches of aluminum sulfate production residues and then mixed to maintain homogeneity. The waste directly discarded contains about 52% of solid. The chemical compositions of this industrial by product are given in Table 1. The collected waste residues were sundried for one day and ground to fine powder using mortar and the resulting material is considered as untreated media. The chemical composition of the waste material indicates the absence of any hazardous and carcinogenic substances in the material and hence it is suitable to use as a decolorization agent. The dye used for the investigation of the adsorptive capacity of the waste residue was obtained from Akaki textile industry located in Addis Ababa, Ethiopia. The molecular structure of the dye is shown in Figure 1.

Analytical methods and instrumentation

Uv-vis spectrophotometer is selected as an analytical tool to

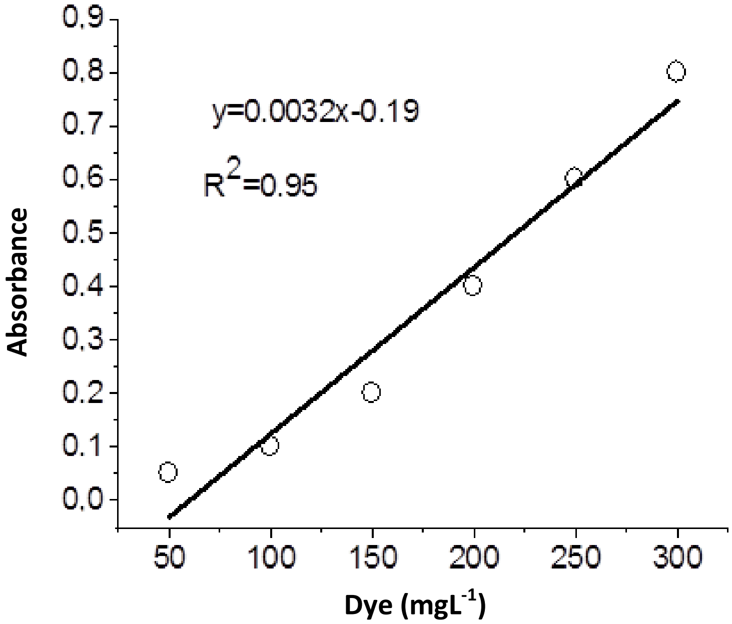

Figure 2. Calibration curve of the dye at its λmax.

determine the concentration of dye solutions. This selection is made based on the fact that most dyes absorb electromagnetic radiation in the Uv-vis region. Concentration of dye solution was calculated from the absorbance measurements using Lambert Beer's law Equation (1)

$$A = \varepsilon cl \tag{1}$$

Where A is absorbance, ε is the molar absorptivity, C is the concentration, and l is the path length.

The dye removal capacity of the adsorbent is expressed as follows using Equation 2:

$$\frac{C_i - C_e}{m} \times V \tag{2}$$

Where C_i and C_e are the initial and final dye concentration (mg/L) in the liquid phase respectively, m is the mass of adsorbent (g) , and V is the volume of experimental solution (mL).

The percentage of dye removal was calculated using Equation 3:

$$\%\text{ dye adsorption} = \frac{C_i - C_e}{C_i} \times 100\% \tag{3}$$

Batch adsorption studies

After the wavelengths of maximum absorbance (λ_{max}= 373 nm) of the solutions is determined calibration curve is constructed by dissolving an amount of dye to make 300 mg/L of dye solution. Then the other series of solutions to make the calibration curve are made by taking the corresponding volume of the previously concentrated dye solutions, diluting using distilled water and measuring their absorbance at their respective λ_{max}. Experimental solutions were prepared by pipetting a known amount of dye into a 1 L conical flask and diluting it with a known amount of distilled water. Batch experiments for decolorization were conducted in 500 mL conical flask containing 300 mL of dye solution at room temperature (22 ± 2°C), to evaluate dye removal efficiency and capacity of the media. The media (waste residue) was placed in the flask and then stirred continuously at a constant slow mixing rate with magnetic stirrer during the experiment. The initial dye concentration selected for batch experiments is within the range recommended in the actual textile effluent (Galster and Hansen, 1998). The effect of dose of the media, pH of water and initial concentration of the dye were investigated by varying any one of the process parameters and keeping the other parameters constant. Investigation of the effect of dose experiments was conducted by varying adsorbent doses (1 to 25 g/L) at constant initial dye concentration of 100 mg/L.

The effect of pH was studied by varying the pH from 7−9 either with 0.1 M NaOH or 0.1 M HCl. To investigate the effect of initial dye concentration, experiments were conducted by varying dye concentrations from 50 to 258 mg/L at constant adsorbent dose of 19 g/L. The kinetic analysis of the adsorption data is based on reaction kinetics of pseudo-first order and pseudo-second-order mechanisms. Adsorption kinetics was determined using constant adsorbent dose of 19 g/L corresponding to the initial dye concentration of 100 mg/L. Isotherm experiments were conducted by changing the adsorbent dose from 1 to 43.3 g/L at initial dye concentration of 100 mg/L. For all experiments, the remaining concentration was determined spectrophotometrically at its corresponding λ_{max} when the equilibrium contact time is reached.

RESULTS AND DISCUSSION

Wave length of maximum absorbance and Calibration curves

The calibration curve (Figure 2) is obtained by preparing dye solution for which the concentration is within the effective concentration range of the dye. The correlation coefficient from the curve shows strong linear relationship between the concentration of the dye solutions and the

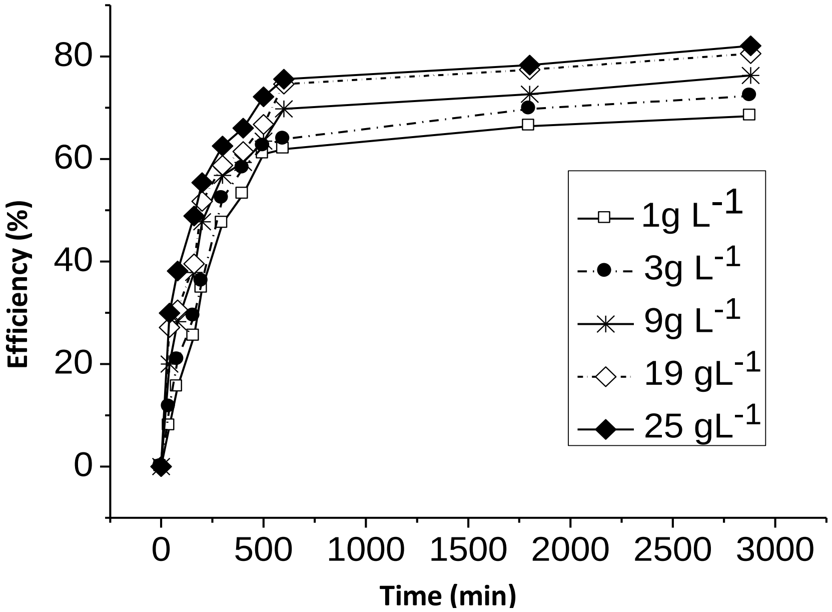

Figure 3. Efficiency of dye removal as a function of time for different doses of untreated media (initial dye concentration = 100 mg /L, pH = 3-4).

absorbance at the dye's wavelength of maximum absorbance.

Effect of dose and contact time

To investigate the effect of dose and contact time, experiments were conducted by varying adsorbent doses (1 to 25 g/L) at constant initial dye concentration of 100 mg/L. Further addition of adsorbent does not provide more increment in the adsorption amount (Figure 3). The results show that the adsorption reached equilibrium after about 30 h. Further increase in contact time did not increase the uptake. In general the decolorization efficiency was increased with dose as reflected by the measured residual dye concentration. The increase in the dye adsorption was due to the increased in availability of dye binding sites resulting from an increase in adsorbent dosage. Higher dose of the media (greater than 19 g/L) will increase the amount of sludge without causing a significant change on the amount of dye removed. On the other hand, the adsorption capacity decreases with increasing dose (Figure 4). To maintain maximum capacity and high removal efficiency, the surface loading (that is the mass ratio of the dye to adsorbent dose) should be lower than the optimum value. A dose of 19 g/L corresponds to the capacity of about 4.74 mg dye /g of adsorbent if there is 90% removal. The surface loading obtained for the dose of 19 g/L in this experiment was 4.1 mg dye /g of adsorbent. Lower capacity of the material is due to the presence of H^+ ions which may cause the surface to be positively charged and hence reduce its interaction with the cationic dye. These experimental results suggest that modification of the surface chemistry of the adsorbent may enhance its capacity.

Effect of pH

About 80% of the dried waste residue is quartz. In quartz [SiO_2], Si and O are structural elements; the Si-O bond has about 50% covalent character (Huang and Ostovic, 1978). The siloxane groups, -SiOSi-, interact with water forming -SiOH (Fan et al., 2003). Any oxide surface attains (positive or negative) charge on its surface. The hydroxyl groups can gain or lose proton, resulting in a surface charge that varies with changing pHs. At lower pH, surface sites are protonated and the surface become positively charged. Maximum removal efficiency at pH 7 to 9 and the removal rate increases with an increase in pH in general. At higher pH, the surface hydroxides lose their protons and the surface becomes anionic. This can be the reason for the higher efficiency of the adsorbent for the cationic dye at higher pH value (Figure 5). The other main constituent of the adsorbent mixture is kaolinite (kaolin), a class of natural clay minerals. Here the adsorption capabilities result from a net negative charge on the surface, which gives clay the capability to adsorb positively charged species. Their sorption properties are also due to their high surface area and high porosity (Alkan et al., 2004). Clay mineral exhibits a strong affinity for both heteroatomic cationic and anionic dyes however; the sorption capacity for basic dyes is much higher than for acid dyes because of the ionic

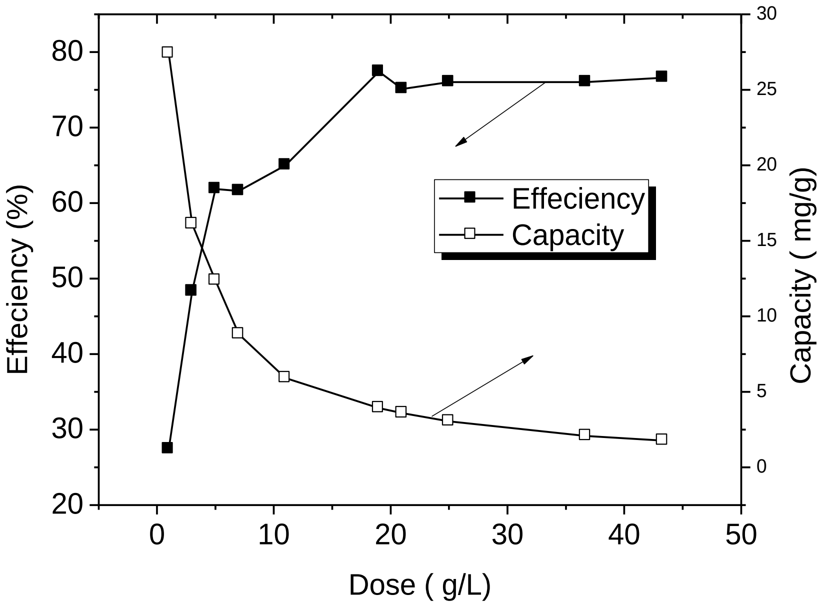

Figure 4. The relationship between adsorbent dose versus percentage of dye removal and adsorbent dose versus removal capacity at fixed dye concentration.

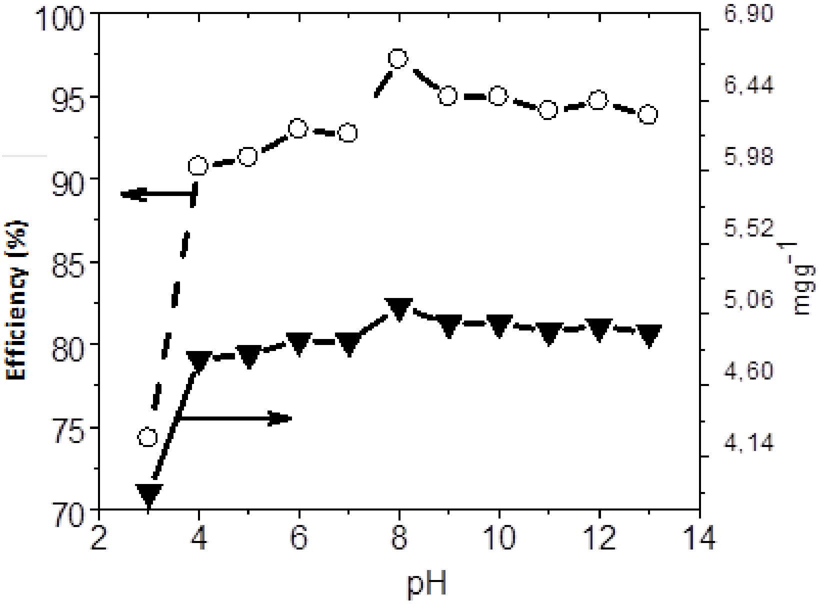

Figure 5. Effect of pH on efficiency and capacity of dye removal at fixed dye concentration and adsorbent dose.

charges on the dyes and character of the clay. Some researchers show that the adsorption of dyes on kaolinite was about 20 times greater than alumina (Harris, 2001).

The possible mechanism for the adsorption of the dye for this experimental condition can also be explained based on the theoretical meaning of *pHzpc* (pH of zero point charge). Silica adsorbents have a low pHzpc nearly 2 (Rao and Sridharan, 1984). The measured pH for the dye-adsorbent system is 3 to 4 in this particular experiment, that means the surface of the material will have a slight negative charge even at this lower pH; there is a columbic attraction towards the cationic dye. The other possible mechanism for the adsorption of the dyes by quartz can be attributed to the formation of surface

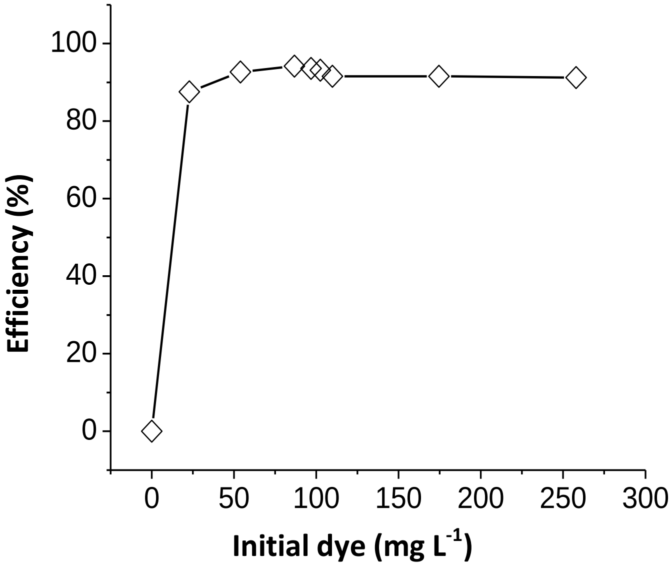

Figure 6. Effect of initial dye concentration on percentage of dye removal at fixed adsorbent dose. (PH = 7 to 9).

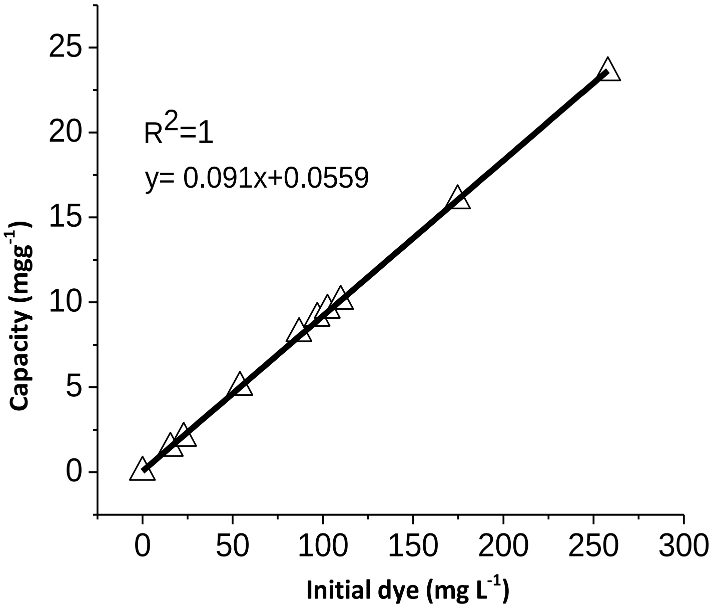

Figure 7. Effect of initial dye concentration on capacity of dye removal at fixed adsorbent dose for (pH = 7 to 9).

hydrogen bonds between the surface hydroxyl groups on the surface of the silica adsorbent and the nitrogen atoms of the dye.

Effect of initial dye concentration

The effect of initial dye concentration at a fixed quantity of the adsorbent dosage is shown in the following figures. The percentage of dye removal at fixed adsorbent dose increased with increasing initial dye concentration (Figure 6). This is expected because in surface adsorption reactions the equilibrium concentration of a given solute in the solid phase is proportional to the equilibrium concentration in the liquid phase. From Figure 7, it is observed that increasing the initial dye concentration

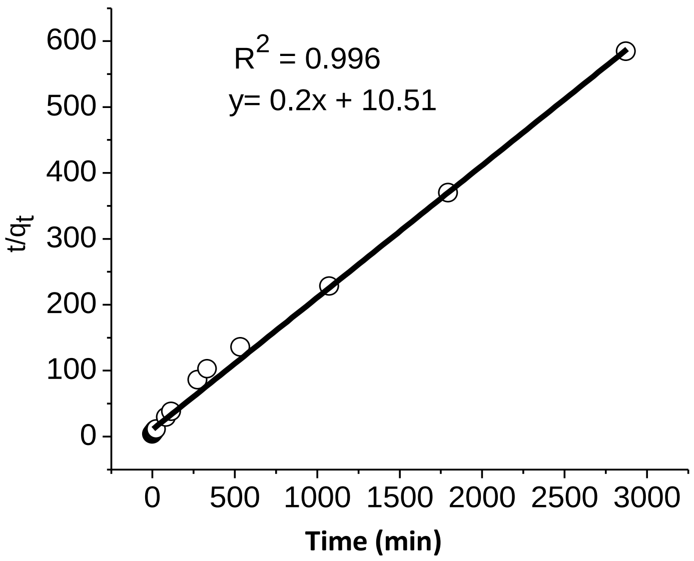

Figure 8. Pseudo-second-order plot of the dye adsorption kinetics on untreated media (pH = 7-9, dose = 10 g/L and an initial dye concentration of 100 mg/L).

increases the removal capacity of the adsorbent. The correlation coefficients of the experiments show that there is a strong linear relationship between the initial concentration of the dye and the removal capacity of the adsorbent. This result indicates that the method is suitable for the treatment of high-strength textile effluent in terms of dye concentration.

Reaction rates

The adsorption kinetics was studied at constant dye and adsorbent concentrations. The kinetic analysis of the adsorption data is based on reaction kinetics of pseudo-first-order and pseudo-second-order mechanisms. The uptake of the dye on untreated adsorbent reached equilibrium in 30 h. The kinetics of adsorption was analyzed by using the Lagergren equation as shown below(Yeheyes et al., 2005):

$$\frac{dqt}{dt} = K_2(qe - qt)^2$$

$$\frac{d(q_e - q_t)}{(q_e - q_t)^2} = -k_2 dt \qquad (4)$$

For the boundary conditions t = 0 to t = t and q_t = 0 to q_t = q_t, the integrated form of Equation (5) becomes:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \qquad (5)$$

This is the integrated rate law for a pseudo second-order reaction. Equation (5) can be rearranged to obtain Equation (6), which has a linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}(t) \qquad (6)$$

Where, k2 (g /mg /min) is the equilibrium rate constant of second-order sorption. The untreated materials can be described very well by the pseudo-second-order rate equation as shown in Figure 8. The correlation coefficient was found as near to unity. The values of q_e and K_2 are 5 (mg/g) and 3.81 (g /mg /min) respectively which are determined by plotting t/qt against t of Equation (7), and using the slope and y-intercept of the plot. The equilibrium between the adsorbed layer and the solution slightly delayed and this is due to (1) the solute molecules do not diffuse immediately from the bulk of the solution to the interface and (2) the solute molecules do not cross immediately the energy barrier which exists near the interface, and moreover a flow of solute molecules leaving the interface-desorbing-slackens the adsorption.

Adsorption isotherm

The adsorption isotherm of the dye is shown in Figure 9 at a constant temperature (22 ± 2°C). Langmuir (data not shown) and Freundlich isotherms were used to describe the equilibrium nature of dye adsorption by the adsorbent. The values of n and log k_f were calculated

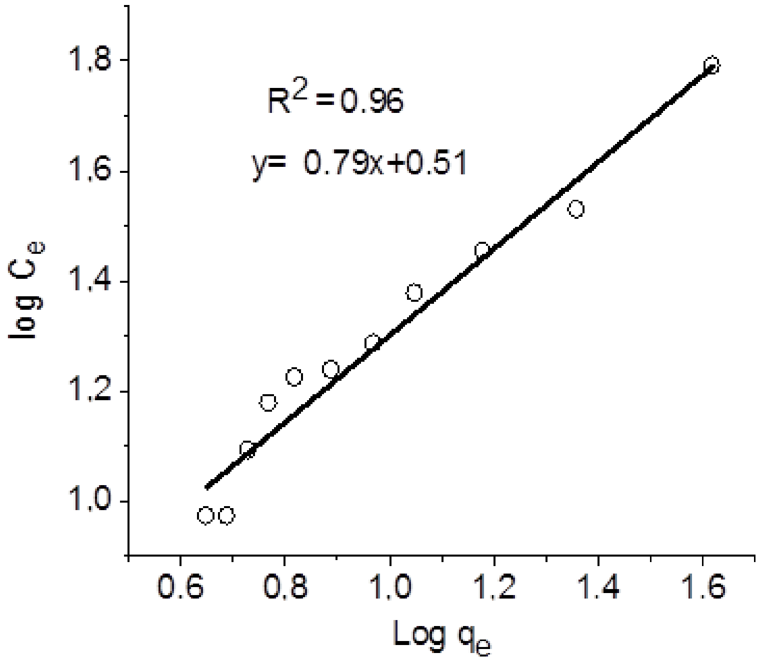

Figure 9. Linearized Freundlich isotherm (initial dye concentration = 103 mg/ L, pH = 7-9, temperature = 24°C).

Table 2. Important adsorption parameters to plot an isotherm for untreated material.

Dose (g/L)	C_e (mg/L)	q_e (mg/g)	1/q_e	1/C_e	Log q_e	Log C_e
1	61.58	41.53	0.02	0.02	1.62	1.789
3	33.62	23.16	0.04	0.03	1.36	1.527
5	28.25	14.97	0.07	0.04	1.18	1.451
7	23.73	11.34	0.09	0.04	1.05	1.375
9	19.21	9.32	0.11	0.05	0.97	1.284
11	17.23	7.81	0.13	0.06	0.89	1.236
13	16.67	6.65	0.15	0.06	0.82	1.222
15	14.97	5.88	0.17	0.07	0.77	1.175
17	12.43	5.33	0.19	0.08	0.73	1.09
19	9.32	4.94	0.20	0.11	0.69	0.97
25	9.32	3.75	0.27	0.11	0.65	0.97

from the slope and interception of Freundlich plots as listed in Table 2. The adsorption data were analyzed with the help of linear form of Freundlich isotherm. Freundlich model attempts to account for surface heterogeneity (Gupta et al., 1988).

Freundlich isotherm:

$$\text{Log}\, q_e = \log k_f + \frac{1}{n}\text{log}C_e \qquad (7)$$

Where, k_f is roughly a measure of adsorption capacity and 1/n is an indicator of adsorption effectiveness; q_e is the amount of dye adsorbed per unit mass of adsorbent (in mg g^{-1}) and C_e is the equilibrium concentration of dye (in mg l^{-1}). Figure 9 shows a plot of log q_e vs. logC_e. The constants $1/\text{n}$ as the slope and k_f as the intercept. The values of Freundlich isotherm parameters along with the kf and n were found as 0.26 and 0.82, respectively. It is found that the related correlation coefficient R_2 value for the Freundlich model is near to unity (0.962) and hence the process of decolorization using untreated material is well fitted to the Freundlich isotherm. The Freundlich coefficient, n should have values in the range of 0 < n <1 for favorable adsorption (Pola et al., 2003). The data did not fit well to the Langmuir isotherm model (data not shown). The condition for the validity of a Freundlich type adsorption model is adsorption on heterogeneous surfaces (Gupta et al., 1988). The increase in equilibrium dye removal capacity with residual dye concentration observed during the investigation of effect of initial dye concentration on capacity of dye removal can support the condition of heterogeneous adsorption.

Conclusions

The ability of locally available industrial by product to remove textile dyes from aqueous solutions was investigated employing an adsorption process. The media could remove about 77.4% of the dye from water at 19 g/L dose in pH range of less than 3-4 in the first 30 h. However, the media has an efficiency of 90% when the pH of the adsorbent and adrobate mixture is between 7 to 9. The removal of dye was not affected by the initial dye concentration range of 15 to 256 mg/L that suggests the industrial by product has high efficiency for high strength textile dye removal. The kinetics of dye adsorption by the industrial by product in the batch study was satisfactorily described by a pseudo second order rate kinetics model, and the experimental data correlated reasonably well with that of the Freundlich adsorption isotherm. The results of these studies indicate that the waste residue is an efficient and low cost adsorbent for dye removal from the aqueous phase.

Conflict of Interests

The author(s) have not declared any conflict of interests.

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