

**ADDIS ABABA UNIVERSITY
SCHOOL OF GRADUATE
STUDIES**



**REMOVAL OF AZO DYES FROM WATER BY
ADSORPTION USING WASTE RESIDUE FROM
ALUM MANUFACTURING PROCESS**

BY

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ENVIRONMENTAL SCIENCE**

July 2007

Declaration

I the undersigned declare that this Thesis is my original work and has not been presented for any degree in any university and all the resource of materials used for the Thesis have been duly acknowledged.

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Addis Ababa University

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**ADDIS ABABA UNIVERSITY
SCHOOL OF GRADUATE STUDIES
ENVIRONMENTAL SCIENCE PROGRAM**

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USING USING WASTE RESIDUE FROM ALUM MANUFACTURIN
PROCESS**

***A Thesis Submitted to The School of Graduate
Studies of Addis Ababa University in Partial
Fulfillment Of the Requirement for the Degree of
Master of Science in Environmental Science***

By

Haimanot Habte Lemji

July 2007

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**FACULTY OF SCIENCE
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REMOVAL OF AZO DYES FROM WATER BY ADSORPTION

USING AN INDUSTRIAL BY PRODUCT

BY HAIMANOT HABTE

Advisors: Dr. Feleke Zewge and Dr. Mesfin Redi

ABSTRACT

Huge consumption of water and low biodegradability of textile dye wastes calls for a combination of biological, chemical, physico-chemical and physical processes along with a complementary treatment process to remove more of the dyes. Persistent aromatic structure and recalcitrant nature of various dyes and textile chemicals makes the biological treatment not always successful in the treatment of cotton textile wastewater. Chemical methods also have limitations. No universally accepted and efficient method is yet developed for dye removal.

In the present study water-soluble reactive azo dyes, fast red RC salt and solar yellow BG were removed from water using locally available industrial by product, a waste residue generated from the manufacture of alum from kaolin by the sulfuric acid process. Batch experiments are carried out for the sorption of fast red salt RC and solar yellow BG onto the adsorbent. The operating variables studied for that of FR-RC salt are adsorbent dose, contact time, system pH, initial dye concentration, and kinetics and adsorption isotherms. And for SY-BG the operating variables studied are adsorbent dose and contact time. The mechanism of dye adsorption for FR-RC salt onto the media is investigated by using the experimental results. The adsorption process is slow for FR-RC salt; requiring 30 hours to reach equilibrium and an adsorbent dose of 19g/L is optimum for this equilibrium contact time for 77.4 % removal efficiency. For SY-BG the

equilibrium contact time and optimum dose are 12 minutes and 0.3g/L respectively for 99.3 removal efficiency. When the pH of the system is 7to9 the dye removal efficiency for FR-RC salt is greater than 90%. For the given concentration range the removal of dye from water was not depend on initial dye concentration for FR-RC salt. The adsorption process was found to undergo via a pseudo-second-order adsorption kinetics with a rate constant of $3.81 \times 10^{-3} (\text{g mg}^{-1} \text{min}^{-1})$. The equilibrium data are fitted to Freundlich isotherm equations for that of FR-RC salt. From these the adsorption efficiency, adsorption capacity and intensity of adsorption are calculated. The overall result shows the adsorbent is efficient decolorizing material.

Key Words: Textile dye, Batch decolorization, an industrial by product; Dye removal efficiency, Adsorption capacity, equilibrium time.

Introduction

1.1 Back ground

The world's ever increasing population and the progressive adoption of an industrial-based life style has inevitably led to an increased anthropogenic impact on the biosphere. Textile industries are found in most countries and their numbers have increased. These industries have shown a significant increase in the use of synthetic complex organic dyes as the coloring material. The global consumption of textiles is currently around 30 million tones with expected growth at 3% per annum [1]. The coloration of this total needs approximately 8×10^5 tons of dyes [1].

Synthetic textile dyes used each year are lost during manufacture and processing operation and 20% of these dyes enter the environment through effluents that result from the treatment of residual industrial waters [2]. It is estimated that 10,000 different types of dyes and pigments are produced worldwide annually [3]. 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 [4]. Many of these dyes find their way into the environment via effluent discharges. Because 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. So it is not surprising that these compounds have become a major environmental concern. [4]. Textile effluents can be leached into the aquifer and pollute the underground water, or if it is discharged without proper treatment into rivers, the pollutants cannot be confined within specific boundaries.

They can therefore affect aquatic life in enormous ways [5]. Moreover it is recognized that public perception of water quality is greatly influenced by the color. Color is the first contaminant to be recognized in wastewater [6]. Among the various classes of dyes, basic dyes are found to be the brightest class of soluble dyes used by the textile industry as their tinctorial value is very high. The presence of very small amounts of dyes in water (less than 1 ppm for some dyes) is highly visible and undesirable [6, 7]

Colored wastewater is a consequence of batch processes both in the dye manufacturing industries and in the dye-consuming industries. Two per cent of dyes that are produced are discharged directly in aqueous effluent, and 10% are subsequently lost during the textile coloration process [8]. The main reason for dye loss is the incomplete exhaustion of dyes on to the fiber. The amount of dye lost is dependent upon dyestuff type, the application of reactive azo dyes, with its chromophore, containing azo/keto-hydrazone groups, the reactive centers and its solubilising components.

Residual color, which is the amount of dyes that remains in the wastewater after a dyeing process is a problem with reactive dyes. 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 [9, 10].

Although Ethiopia does not have the industries that flourished in the developed countries, textile and leather industries are given more attention due to the availability of raw materials and further expansion of such industries is expected. However, almost all of the available industries (textile, paper, plastic, leather, food, cosmetic, etc) release their

untreated or partially treated wastewaters into municipal sewers, or directly into nearby drains, rivers, stagnants, ponds, lagoons, or lakes. Such wastewater disposal may cause damage to the quality of the receiving water bodies, the aquatic ecosystem and the environment at large. [11]

1.2 Dyes and their properties;

Chemical requirements for dyes, Electronic transition and Chemical structure:

Dyes are organic compounds. Like all organic compounds, their atomic orbitals combine to form molecular orbitals. When a group with π orbitals (e.g. NO_2 or COOH) is attached to an aromatic compound, overlapping of the two π orbitals normally occurs, leading to new bonding and antibonding states. Orbital overlapping and combination also occurs when aromatic carbons carry substituents that have lone pairs of electrons (e.g. OH , NR_2 , etc.) [12].

Color is produced when light is absorbed. The absorbed energy promotes one of the electrons inhabiting the molecular orbital to a level of higher energy [12]. The spacing between available bonding orbitals determines the amount of energy that can be accepted and thus the wavelength of light absorbed. The degree of conjugation (number of π orbitals and electrons) determines whether the electromagnetic radiation absorbed is within the range of visible wavelengths [13]. The additional carbon-carbon double bonds increase the number of delocalized π electrons and decrease the energy required for excitation. The shifting of absorption from the ultraviolet range to the range of visible wavelengths is described as a bathochromic shift [12].

All dyes are organic aromatic compounds with a conjugated double bond system, to which chromophores and auxochromes are attached. These functional groups reduce the number of conjugated double bonds needed for light absorption and result in molecules that are small enough to diffuse into fibers. Chromophores [13, 14] are unsaturated functional groups. Alone, they absorb visible or near ultraviolet radiation. In a dye molecule, they function as electron acceptors. Auxochromes [15] are saturated functional groups. Auxochromes act as electron donors because the atom attached to the conjugated system has nonbonding electrons. Dye chromogens can be described as electron acceptor(s) (chromophores) interacting with electron donor(s) (auxochromes) through a conjugated double bond system.

The color of a compound depends on the wavelength of light which it absorbs. If a compound does not absorb any visible light it will be colorless. If a compound absorbs light we will perceive the complementary color, because the light which reaches our eyes is missing the wavelengths which have been absorbed. The ability of a dye to absorb light depends on the presence of certain kinds of structural features called chromophores. "Chromophore" is one of those useful but sloppy words whose meaning depends somewhat on the context. If we are talking about color, then a chromophore will be an extended conjugated system, particularly the one's in which different resonance contributing forms differing in charge distribution are there to give a colored system. Many natural pigments are based on the quinone chromophore; the parent quinone, benzoquinone, is yellow; with larger conjugated systems, and especially with hydroxyl groups to modify the chromophore, they can be bright red [16]. The depth of color is

related to the molecular structure of the dyes, which is related to the chromophores ($-N=N-$ or $>C=O$) involved within the structure.

Two different approaches are used to classify dyes, the first one is based on the nature of the chromophore (the aromatic group absorbing visible light to impart color) while the second follows the mode of application. According to the former criteria, twelve dye classes are usually defined among which the most important group are azo dyes, because of the great extent in number and tonnage of their application (17). Azo dyes can be used on natural fibers (cotton, silk, wool) and synthetic fibers (polyesters, polyacrylic, rayon, etc.); their molecules include one or more azo groups ($-N=N-$). The latter classification of dyes includes seven classes: acid, basic, direct, disperse, reactive, sulphur and vat. Overlaps of the two classifications are possible e.g. azo dyes may belong to one of the above classes. Numerous structures of dyes exist. All are assigned a Color Index classification number. Most of the dyes and pigments in the Color Index are placed in one of the 25 structural classes according to their chemical type [18]. Azo dyes, the largest class, depending on the number of azo groups within the dye molecule are subdivided into four sections:

Azo dyes with one azo group are called mono azo dyes, with two azo groups, diazo dyes, followed by triazo and polyazo dyes. Azo dyes with more than three azo linkages are designated polyazo dyes. The most commercial important are mono and diazo dyes, triazo dyes, whereas poly azo is much less important [19]. Significant differences in the degree of fixation are reported for the various dye classes. It is therefore obvious that the lower the fixation, the higher the residual color and COD discharged.

Dyeing is an operation used to add color to textiles by applying a wide range of dyestuffs which are largely synthetic, typically derived from coal tar and petroleum-based intermediates. Dyes are always used in combination with other chemicals (acids, alkali, salts, fixing agents, carriers, dispersing agents, surfactants, etc.) that are partly or almost completely discharged into effluents together with the numerous additives and impurities present in commercial dye products.

In addition, visible and the Uv irradiation electron transfer effects at varying wavelengths on the dye structures have been observed, supporting tautomeric capabilities of the dye molecules [20]. An oscillation between the double and single bonds occurs along the conjugated molecular chain; therefore, as the chain becomes longer, the vibration rate becomes slower resulting in a slower kinetic degradation rate [20]. Reactive dye structures are 95 percent azo dyes, except for some bright blues and greens [20]. Reactive dyes react with a substrate to form a covalent dye-substrate bond, where a substance such as cellulose acts as the substrate [20]. Dye fixation onto fibers depends on the dye property known as fastness, which describes its ability to bond to the material. Any additional chemicals that are added during the dye application, such as salts or detergents, will affect the wastewater and subsequently the treatment process.

Table 1. General description of some classes of dyes

| Class | General description | Mode of application | Applied on |
|-------|---------------------|---------------------|------------|
|-------|---------------------|---------------------|------------|

| | | | |
|----------|---|--|----------------------------|
| Direct | They are always azo dyes & sodium salts. | Do not require any form of fixing. They are applied from water solution. | Cotton-wool or cotton-silk |
| Vat | They often contain multi-ring systems and carbonyl groups. They are sparingly insoluble in water. The solvent used is NaSO ₃ | They are impregnated into the fiber under reducing condition which is then air oxidized on the fabric to an insoluble color. | Cotton. |
| Reactive | They are capable of forming covalent bond with the appropriate textile functionalities. Functional group is Cl, fixed by urea dissolving agent, developed by soda Ash (Na ₂ CO ₃) (fixing agent) | Once attached to the fiber they are very difficult to remove from the fiber. | Cotton, silk,& wool |
| Sulfur | They contain sulfur or are precipitated from sodium sulfide bath, furnish dull shades with good fastness to light, washing and acids, but susceptible to chlorine. | Applied to fibers from aqueous sodium sulfide solutions because they are insoluble in water. | Cotton |
| Azo | Contain -N=N- group which links two sp ² hybridized carbon atoms that are often part of an aromatic moiety | Fabric is first soaked in a solution of coupling component followed by soaking in a solution of azo dye. | Cotton, wool, silk, |

1.3 Review of available decolorization methods

Wastewaters from dyeing industries are released in to near by land or rivers without any treatment because the available treatment methods are not cost effective and /or inefficient. There are different reported methods for the removal of pollutants from effluents [Table 2]. The technology can be divided into three categories: biological,

chemical and physical [6]. All of them have advantages and drawbacks. Because of the high cost and disposal problems, many of these conventional methods for treating dyes wastewater have not been widely applied on a large scale in the textile and paper industries [5]

Discharge standards will undoubtedly restrict color to a maximum value of 100 mg Pt. Co/L. [21]. But the results of the conventional treatments are far from being in compliance with this level. The Provisional Environmental Standard for Ethiopia, proposed by the Environmental Protection Authority (EPA) sets emission limits of 5 mg/L of adsorbable organic halogenated compounds [22]. It is therefore indispensable to become more familiar with the behavior of organic dyes in order to determine the dye removal technology that best meets the needs and economy of each user company.

1.3.1 Biological methods

Dyestuffs and polymers are generally difficult to biodegrade and many substances are totally unsuitable for conventional biological treatment. For textiles in particular the emphasis is on physical, chemical and biological treatment systems. All biological systems require a continuous input of effluent. Therefore, where the aqueous process discharge is relatively small or likely to be discontinuous, then physical and or chemical treatments are more appropriate. [23]

Biological treatment requires a large land area and is constrained by sensitivity toward diurnal variation as well as toxicity of some chemicals, and less flexibility in design and operation [24]. Biological treatment is incapable of obtaining satisfactory color

elimination with current conventional biodegradation processes [25]. Moreover, although many organic molecules are degraded, many others are recalcitrant due to their complex chemical structure and synthetic organic origin [25]. In particular, due to their xenobiotic nature, the biodegradability of azo dyes is very limited.

1.3.2 Chemical methods

Chemical methods include coagulation or flocculation combined with floatation and filtration, precipitation-flocculation with $\text{Fe}^{2+}/\text{Ca}(\text{OH})_2$, electro floatation, electro kinetic coagulation, conventional oxidation methods by oxidizing agents (ozone), irradiation or electrochemical processes. These chemical techniques are often expensive, and there is the possibility that a secondary pollution problems will arise because of excessive chemical use.

1.3.3 Physical methods

Adsorption is the other alternative which is a physicochemical technique. It is the process by which ions or molecules present in one phase tend to accumulate and concentrate on the surface of another phase [22]. Physical adsorption occurs when weak interparticle bonds exist between the adsorbate and adsorbent. Examples of such bonds are Van der Waals interactions, hydrogen bonding and dipole-dipole interactions. In the majority of cases physical adsorption is easily reversible [27].

Chemical adsorption occurs when strong interspecies bonds are present between the adsorbate and adsorbent due to an exchange of electrons. Examples of such bonds are covalent and ionic bonds. Chemisorption is deemed to be irreversible in the majority of

cases [27]. Suzuki [28] discussed the role of adsorption in water environmental processes and also evaluated the development of newer adsorbents to modernize the treatment systems and the role modeling of the findings plays in their development. Most adsorbents are highly porous materials. As the pores are generally very small, the internal surface area is in the order of magnitude greater than the external area.

Amongst the numerous techniques of dye removal, this technique gives the best results as it can be used to remove different types of coloring materials [29, 30]. Adsorption techniques for wastewater treatment have become more popular in recent years owing to their efficiency in the removal of pollutants that are not easily biodegradable. Adsorption can produce high quality water while also being a process that is economically feasible [31]. Decolorization is a result of two mechanisms - adsorption and ion exchange [32] and is influenced by many factors including dye/sorbent interaction, sorbent surface area, particle size, temperature, pH and contact time. If the adsorption system is designed correctly it will produce a high-quality treated effluent.

Table 2. Principal existing and emerging processes for dye removal [33]

| | Technologies | Advantages | Disadvantages |
|-----------------------------------|---|--|---|
| Conventional treatments processes | Coagulation Flocculation Biodegradation | Simple, economically feasible. Economically attractive, publicly acceptable treatment | High sludge production, handling and disposal problems Slow process , necessary to create an optimal favorable environment |

| | | | |
|--------------------------------|--------------------------------|--|--|
| | Adsorption on activated carbon | The most effective adsorbent , great capacity , produces high – quality treated effluent | Ineffective against disperse and vat dyes , the regeneration is expensive and results in loss of the adsorbent , non destructive process |
| Established recovery processes | Membrane separations | Removes all dye types, produce a high- quality treated effluent. | High pressure ,expensive ,incapable of treating large volumes |
| | Ion-exchange | No loss of sorbent on regeneration, effective. | Economic constraints, not effective for disperse dyes. |
| | Oxidation | Rapid and efficient process | High energy cost, Chemicals required. |
| Emerging removal processes | Advanced oxidation processes | No sludge production .Little or no consumption of chemicals efficiency for recalcitrant dyes | Economically unfeasible , formation of by-product ,technical constraints |
| | Selective bioadsorbents | Economically attractive , regeneration is not necessary , high selectivity | Requires chemical modification , non destructive process |
| | Biomass | Low operating cost , good efficiency and selectivity ,no toxic effects on microorganisms | Slow process performance requires some external factors (pH) |

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 [30]. However, the disadvantage associated with is its high cost [33]. 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 [34].

Various carbonaceous materials, such as coal, lignite, coconut shells, wood and peat are used in the production of commercial activated carbons [35, 36]. However, the

abundance and availability of agricultural by-products make them good sources of raw materials for activated carbons. Agricultural by products [37] are renewable sources of raw materials for activated carbon production because the development of methods to reuse waste materials is greatly desired. Residues from agriculture and agro-industries are the non-product outputs from the growing and processing of raw agricultural products such as rice, corn, beans and peanuts [38]. Disposal of agricultural by-products is currently a major economic and ecological issue, and the conversion of by-products to adsorbents, such as activated carbon, represents a possible outlet.

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 have been carried out to evaluate the efficiency of the waste residue of Awash Melkasa Aluminum Sulfate And Sulfuric Acid Factory to adsorb azo dyes from wastewater.

1.4 Objectives

The general objective of the research is to assess the dye adsorption capacity of the waste residue, produced during the production of aluminum sulfate from kaolin and sulfuric acid, and its potential application in Ethiopia.

The specific objectives of the study will be as follows:

1. To investigate the effectiveness of this waste residue material in the removal of dye under varying experimental conditions: adsorbent dose, contact time, and system pH on adsorption of dye onto the material.
2. To show the efficiency of the material on another different type of dye.
3. To examine effect of initial dye concentrations; on adsorption of the dyes onto the material.
4. To investigate reaction mechanisms.
5. To investigate adsorption kinetics.
6. To establish adsorption isotherms or equilibria.

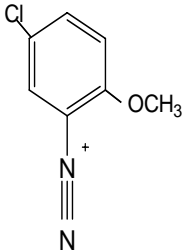
2. Experimental

2.1 Dyes

Water soluble dyes fast red salt RC and solar yellow BG that is obtained from Akaki textile factory were used in this study. The characteristics of the dyes are shown in Table 3.

Table 3. General characteristic of the dyes selected

NA: Not Available

| Dyes | λ_{max} (nm) | Class | Color | Form | Mol.wt. (g/mol) | Structural formula |
|--------|-------------------------|--------|--------|--------|--------------------|--|
| FRS-RC | 373 | Azo | Yellow | Powder | 169.6 |  <p>[40]</p> |
| SY | 394 | Direct | Yellow | Powder | NA | NA |

SY: Solar Yellow BG

FRS-RC: Fast Red salt RC

2.2 Adsorbent

The waste residue used in this study was collected from Awash Melkasa Aluminum Sulfate and Sulfuric Acid Factory (15 km from Nazareth on the way to Assella). Samples were taken from more than 30 batches of aluminum sulfate production residues and then mixed to maintain homogeneity. The waste discarded contains 50 % of solid. The chemical compositions of this industrial by product are given in Table 4 [41].

Table 4. Chemical composition of the waste residue with their percentage.

| Chemical composition | Percent (% wt.) |
|---|-----------------|
| Quartz (SiO ₂) | 39.991 |
| 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 ₂ O ₃ | 0.001 |
| MgSO ₄ | 0.008 |
| Na ₂ SO ₄ | 0.007 |
| K ₂ SO ₄ | 0.005 |
| H ₂ SO ₄ | 0.001 |
| H ₂ O | 48.178 |
| Others | 0.059 |

In the production of aluminum sulfate no significant variation in the chemical composition of the raw materials kaolin and sulfuric acid were recorded since 1989 till October 2005. Since the reactor and the filter press also work efficiently, there is no

considerable variation in the composition of the waste residue from the different batches of alum production till the date of this sampling. The collected waste residues were sun-dried for one day and grinded to fine powder using mortar. This material is considered as untreated media.

2.3 Analytical methods and instrument

Uv-vis spectrophotometer is selected as an analytical tool to 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. Uv-vis spectrophotometer that operates in the Uv-vis range was used to determine the wave length of maximum absorbance (λ_{max}) and to measure all the samples. Concentration of dye solution was calculated from the absorbance measurements using Lambert Beer's law. [Eq.1]

$$A = \epsilon_0 C l \dots\dots\dots [1]$$

Where: **A** is absorbance,

ϵ_0 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:

$$\text{Amount of dye adsorbed} = \frac{(C_i - C_e) V_{\text{solution}}}{m_{\text{sorbent}} \dots\dots\dots [2]}$$

Where, C_i is the initial dye con. in the liquid phase

C_e is the final dye conc. in the liquid phase
 m is the mass of adsorbent, and
 V is the volume of experimental solution.

The percentage of dye removal was calculated using:

$$\% \text{ adsorption} = \frac{[C_i - C_e]}{C_i} \times 100 \dots\dots\dots [3]$$

2.4 Wavelength of maximum absorbance (λ_{max}) and calibration curves

To determine the wavelength of maximum absorbance for the two dyes different concentrations of dye solutions were prepared depending on the characteristic intensity of the dye color and sensitivity of the instrument for the dye type. The wavelengths of maximum absorbance (λ_{max}) of the solutions were determined for the dyes and calibration curves are constructed to determine the initial and final concentration. To this end a calibration curve was prepared by dissolving an amount of the dye to make 300 mg/L of dye solution for FRS-RC and 100mg/L for SY-BG. Then the other series of solutions are made by taking the corresponding volume of the previously concentrated dye solutions using distilled water and measuring their absorbance at their respective λ_{max} . The concentration and measured absorbance for each dye solution is used to construct the calibration curve.

2.5 Batch adsorption studies

Experimental solutions were prepared by pipetting a known amount of dye into a 1 liter (L) Erlenmeyer 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. To ensure that dye does not adsorb on the inner walls of the adsorption vessels, blank runs were performed. In this procedure a 100 mg/L dye solution was added to a glass vessel and the concentration measured after 4 h, 12 h, 24 h and 30hr. No significant reduction in dye concentration was found. The initial dye concentration selected for batch experiments is within the range recommended in the actual textile effluent [19].

The effect of dose of the media, contact time, system pH and initial concentration of the dye were investigated by varying any one of the process parameters and keeping the other parameters constant. All the experiments were performed in triplicate and the mean values were reported.

2.5.1 Effect of dose and contact time

To investigate the effect of dose and contact time experiments were conducted by varying adsorbent doses (1 to 25g/L) for FR-RC and (0.03 to 0.33) for SY-BG at constant initial dye concentration of 100 mg/L. The residual dye concentrations were measured by taking samples at different contact time. The effects of adsorbent dose at the optimum contact time were also studied on the same initial dye concentration with adsorbent doses varied between 1.0 and 43.3.00 g/L for FRS-RC and 0.03 to 3 for SY-BG and stirring slowly in aqueous solution at the ambient pH values. The remaining concentration was determined spectrophotometrically at its corresponding λ_{max} when the equilibrium contact time is reached.

2.5.2 Effect of system pH

The effect of system pH on the adsorption of the dye on to the media was studied by varying the adsorbate-adsorbent system pH for FRS-RC. The pH was adjusted to the desired level either with 0.1 M NaOH or 0.1 M HCl. The initial dye concentrations (100 mg/L), adsorbent dose (19 g/L), and temperature were all kept constant during the experiment. The residual dye concentration was determined after 30 hours of contact time.

2.5.3 Effect of initial dye concentration

To investigate the effect of initial dye concentration, experiments were conducted by varying dye concentrations of 15.54, 22.88, 53.95, 86.72, 96.89, 102.5, 109.9, 174.6, 257.9 and at constant untreated adsorbent dose of 19 g/L , system pH = 7-9 and equilibrium time = 18 hrs The final dye concentration was analyzed from the absorbance of the supernatant.

2.5.4 Kinetics of adsorption

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 19g/L corresponding to the initial dye concentration of 100 mg/L. Residual dye concentrations were measured at different time intervals by taking samples periodically.

2.5.5 Isotherm studies

All adsorption measurements carried out through batch technique at room temperature and desired pH. In each measurement, 300 mL of the dye solution of desired concentration and appropriate amount of the media were taken in a 500 mL graduated airtight conical flask and mechanically agitated for about 18 hours to achieve equilibrium. The adsorbent were now removed from the solution after carefully filtering by Whatman filter paper No. 42 and the concentration of the dye was determined spectrophotometrically by recording the absorbance at $\lambda_{\text{max}} = 373\text{nm}$.

3. Results and Discussions

3.1 Wave length of maximum absorbance and Calibration curves

Fig. 1 and 2 show, the wave length of maximum absorbance for the tow dyes. The curves are obtained by preparing dye solutions for which the concentration is with in the effective concentration range of the dyes.

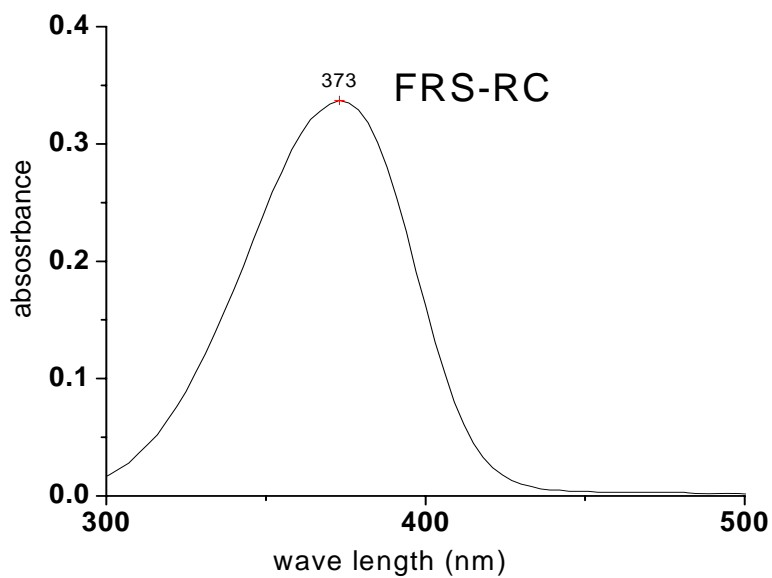


Fig. 1 Uv-vis spectrum of wavelength of maximum absorbance for FRS-RC.

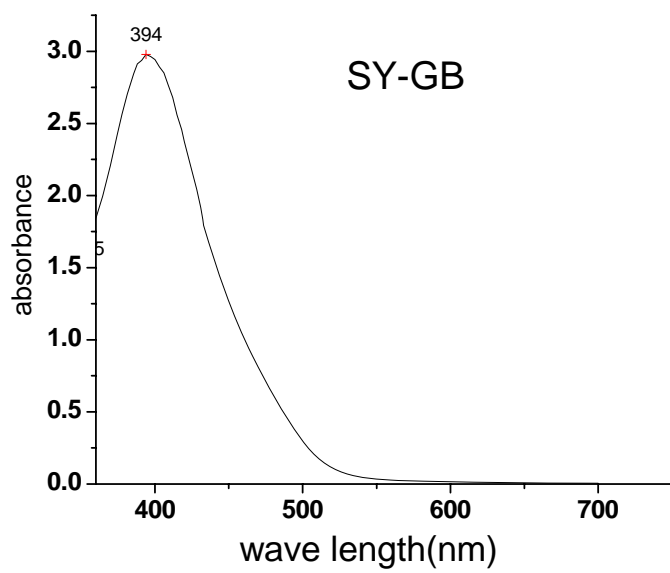


Fig. 2 Uv-vis spectrum indicating wave length of maximum absorbance for SY-BG.

Uv-vis spectrum obtained during calibration of the instrument for FRS-RC and SY-BG is shown in Fig. 3 (a) and (b) below, respectively. In both of the dyes the spectrum shows that the absorbance of the dyes decreases proportionally with a decrease in dye concentration.

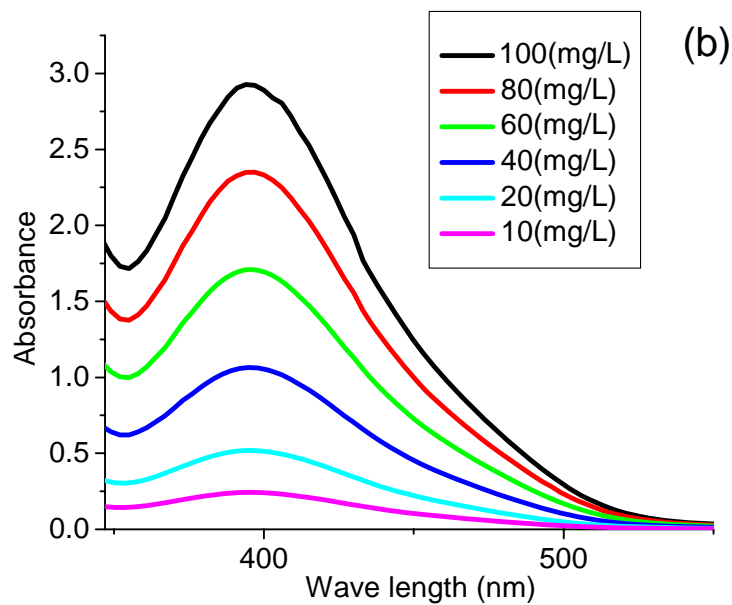
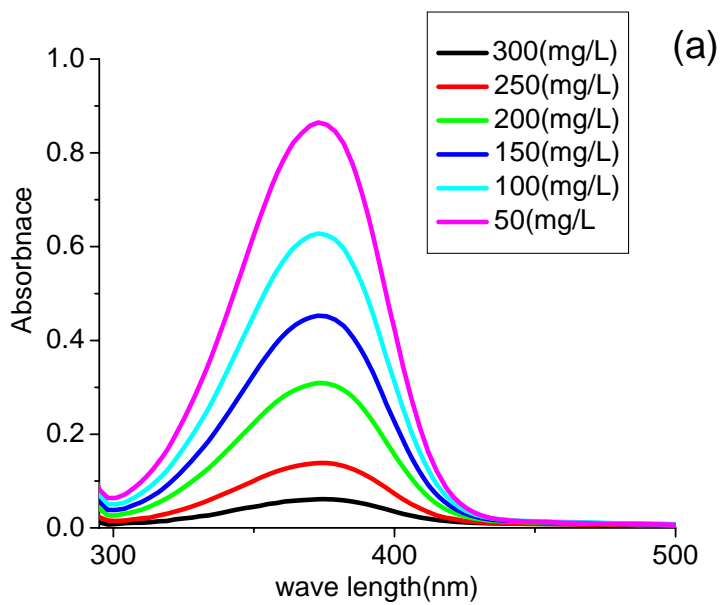


Fig. 3 Uv-vis spectrum of the calibration curve; (a) for SY-BG and (b) for FRS-RC.

Absorbance versus concentration relationship studied for FRS-RC and SY-BG is shown in Fig. 4 (a) and (b) below, respectively. The correlation coefficients for both of the dyes show strong linear relationship between the concentration of the dye solutions and the absorbance at the dye's wavelength of maximum absorbance.

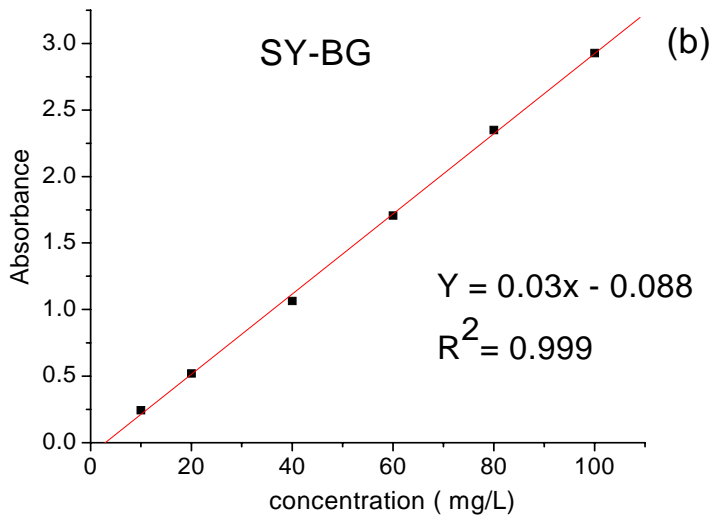
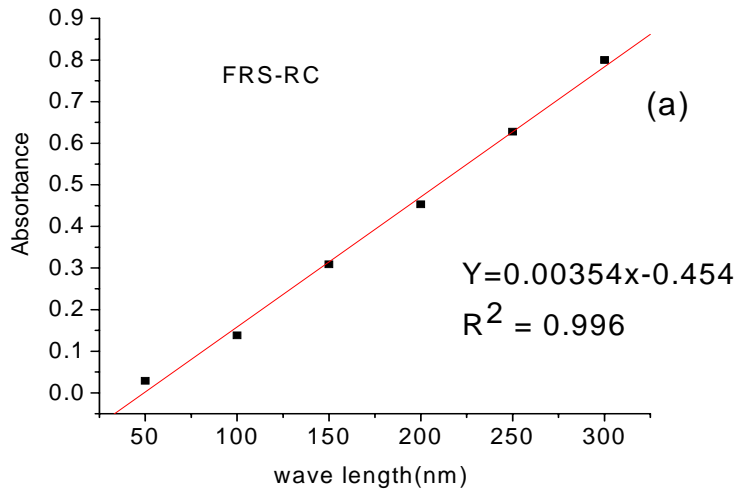


Fig. 4 Calibration curve for FRS-RC (a) and SY-BG (b) at their respective λ_{max} .

3.2 Effect of dose and contact time

To investigate the effect of dose and contact time experiments were conducted by varying adsorbent doses (1 to 25g/L) for FRS-RC and (0.03 to 0.33 g/L) for SY-BG at constant initial dye concentration of 100 mg/L. Further addition of adsorbent does not provide more increment in the adsorption amount (Fig. 5 and Table 5 for FRS-RS and Fig 6 and Table 6 for SY-BG).

The results show that the adsorption of FRS-RC on to the media is relatively slow and reached equilibrium after about 30 hours where as the adsorption of SY-BG is very fast and reached equilibrium within 12 minutes. Further increase in contact time did not increase the uptake . It may be due to the nature of the pores in the sorbent and the nature of the dyes that the contact time required to attain equilibrium is long for FRS-RC and very short for SY-BG. The other possible reason for the slow nature of the adsorption process for FRS- RC (about 30 hours) could be the hydrophilic nature of the dye. Reactive dyes are very soluble in water and, therefore, are poorly adsorbed [42].

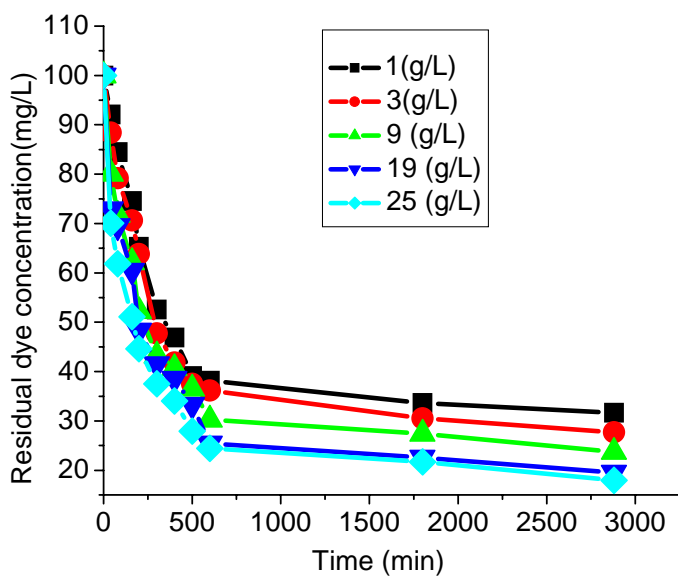


Fig. 5 Residual dye concentration as a function of time for different doses of untreated media for FRS-RC (initial concentration = 100 mg/L, pH = 3-4).

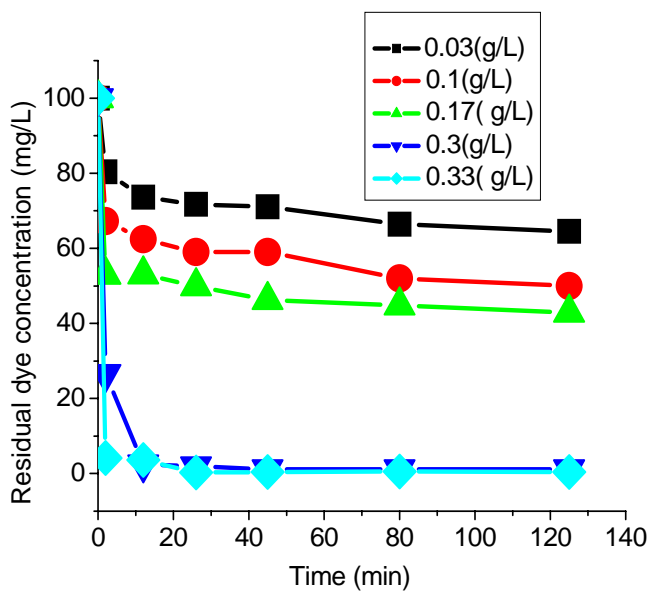


Fig. 6 Residual dye concentration as a function of time for different doses of the untreated media for SY-BG (initial concentration = 100 mg/L).

In general the decolorization efficiency was increased with dose as reflected by the measured residual dye concentration. Furthermore it was found that by increasing the amount of the adsorbent the adsorption increases. 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) for FRS-RC and (greater than 0.3g/L) for SY-BG will increase the amount of sludge without causing a significant change on the amount of dye removed. The decrease in residual dye concentration was most significant when the amount of media is increased from 0.3 to 5.7 g for FRS-RC (Table 7) and from 0.01 to 0.09 g for SY-BG (Table 8). Therefore 5.7 g of the media was used in all the studies for FRS-RC.

Table. 5 Residual dye concentrations as a function of dose and time at constant pH and temperature for FRS-RC.

| Time (min) | Residual dye concentration as a function of dose (g/L) and time. | | | | |
|------------|--|-------|-------|-------|-------|
| | 1 | 3 | 9 | 19 | 25 |
| 0 | 100 | 100 | 100 | 100 | 100 |
| 40 | 92.09 | 88.42 | 80.05 | 72.88 | 70.07 |
| 80 | 84.46 | 79.19 | 71.75 | 69.49 | 61.86 |
| 160 | 74.58 | 70.62 | 62.15 | 60.45 | 51.13 |
| 200 | 65.25 | 63.84 | 52.26 | 48.31 | 44.63 |
| 300 | 52.54 | 47.74 | 43.22 | 41.53 | 37.52 |
| 400 | 46.89 | 41.81 | 40.68 | 38.55 | 34.03 |
| 500 | 39.09 | 37.52 | 36.55 | 33.27 | 27.92 |
| 600 | 38.14 | 36.16 | 30.25 | 25.42 | 24.45 |
| 1800 | 33.62 | 30.53 | 27.4 | 22.6 | 21.7 |
| 2880 | 31.64 | 27.71 | 23.73 | 19.49 | 17.97 |

Table.6 Residual dye concentrations as a function of dose and time at constant pH and temperature for SY-BG.

| Time (min) | Residual dye concentration as a function of dose (g/L) and time | | | | |
|---------------|---|------|-------|------|------|
| | 0.03 | 0.1 | 0.17 | 0.3 | 0.33 |
| 0 | 100 | 100 | 100 | 100 | 100 |
| 2 | 80.4 | 67.3 | 53 | 26.5 | 4.13 |
| 12 | 73.6 | 62.4 | 53.03 | 2.47 | 3.6 |
| 26 | 71.6 | 59 | 49.9 | 1.93 | 0.3 |
| 45 | 71.1 | 59 | 46.2 | 1.13 | 1.13 |
| 80 | 66.4 | 52 | 44.8 | 1.13 | 0.53 |
| 125 | 64.5 | 50 | 42.9 | 1.13 | 0.4 |

On the other hand, the adsorption capacity decreases with increasing dose for FRS-RC (Fig.9). The adsorption capacity shows similar trend also for SY-BG (Fig.10) .To maintain maximum capacity and high removal efficiency, the surface loading (i.e. the mass ratio of the dye to adsorbent dose) should be lower than the optimum value.

A dose of 19 g/L corresponding to the capacity of about 4.74 mg dye /g of adsorbent if there is 90% removal but this is not attained by the adsorbent under the given experimental condition for FRS-RC. The surface loading obtained for the dose of 19 g/L in this experiment is only 4.1mg dye /g of adsorbent as can be seen from table 7.

Lower capacity of the material for FRS-RC at this low pH is probably 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.

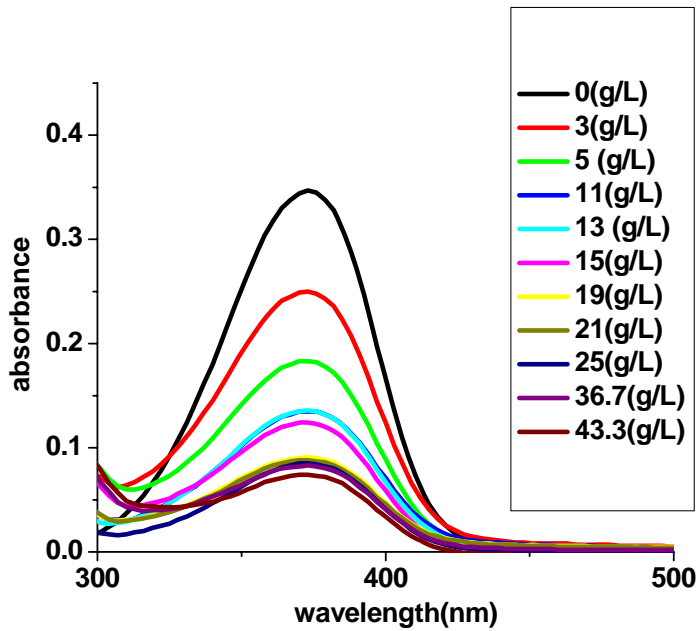


Fig .7 Uv-vis spectrum of FRS-RC at different adsorbent dose at equilibrium (Initial dye concentration = 100mg/L)

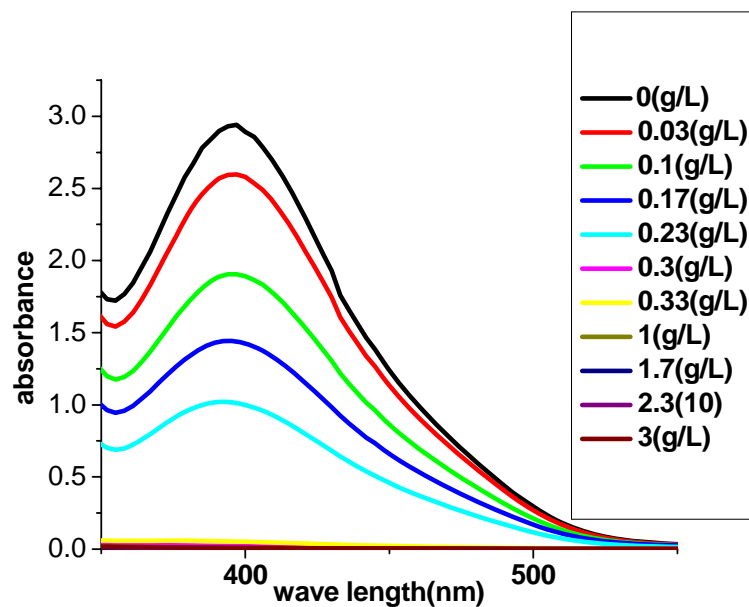


Fig .8 Uv-vis spectrum of SY-BG at different adsorbent dose at equilibrium (Initial dye concentration = 100mg/L)

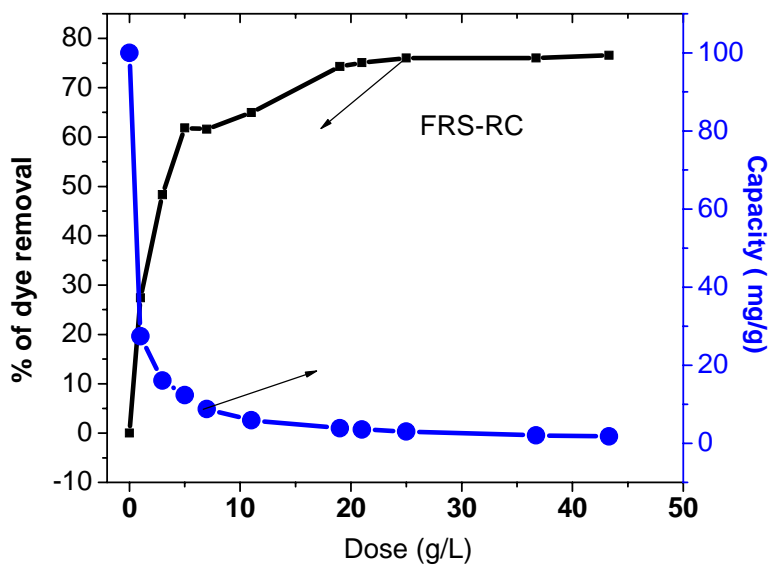


Fig .9 The relationship between adsorbent dose versus percentage of dye removal and adsorbent dose versus removal capacity at fixed dye concentration for FRS-RC (system pH = 3 to 4)

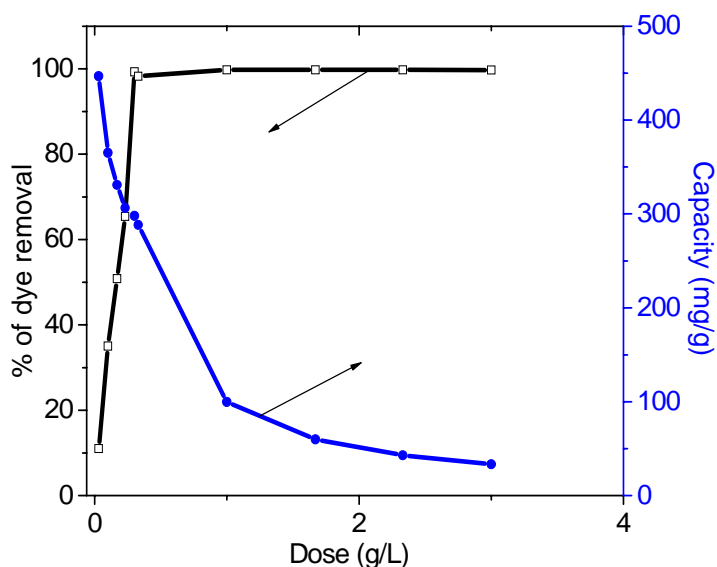


Fig .10 The relationship between adsorbent dose verses percentage of dye removal and adsorbent dose verses removal capacity at fixed dye concentration for SY-BG (system pH = 3 to 4).

As the adsorbent doses were increased from (1-19 g/L), the percent adsorption increased from 27.4% to 77.4 % for FRS-RC and as the adsorbent doses were increased from (0.03-0.3 g/L), the percent adsorption increased from 11% to 99.3% for SY-BG (Table.7 and Table.8). It is considered that the number of available adsorption sites and the surface area increase by increasing the adsorbent dose and, therefore, results in increase of amount of dye adsorbed.

Although percent adsorption increases with increase in adsorbent dose, amount adsorbed per unit mass decreases .Thus, increase in adsorption is there with respect to increase in dose, but the trend of amount adsorbed per unit mass is decreasing with increasing dose. The decrease in adsorption capacity with increase in adsorbent dose is mainly because of unsaturation of adsorption sites through the adsorption process [43

Table .7 Effect of dose of the untreated media on the removal of FRS-RC (Initial dye concentration = 100 mg/L, equilibrium contact time = 30 hr, system pH = 3-4 to 4)

| Dose (g/L) | Residual dye concentration (mg/L) | Capacity (mg/g) | % of dye removal |
|------------|-----------------------------------|-----------------|------------------|
| 0 | 100 | 0 | 0 |
| 1 | 72.6 | 27.4 | 27.4 |
| 3 | 51.7 | 16.1 | 48.3 |
| 5 | 38.14 | 12.37 | 61.86 |
| 7 | 38.4 | 8.8 | 61.6 |
| 11 | 35.03 | 5.91 | 64.97 |
| 19 | 25.7 | 3.91 | 77.4 |
| 21 | 24.9 | 3.58 | 75.1 |
| 25 | 24.01 | 3.04 | 76.00 |
| 36.7 | 24.01 | 2.07 | 76.00 |
| 43.3 | 23.4 | 1.77 | 76.6 |

Table .8 Effect of dose of the untreated media on the removal of SY-BG (Initial dye concentration = 100mg/L, equilibrium contact time = 12 minutes)

| Dose (g/L) | Residual dye concentration(mg/L) | Capacity (mg/g) | % of dye removal |
|-------------|----------------------------------|-----------------|------------------|
| 0 | 100 | 0 | 0 |
| 0.03 | 86.6 | 446.7 | 11 |
| 0.1 | 63.5 | 365 | 35 |
| 0.17 | 47.9 | 331 | 50.8 |
| 0.23 | 33.7 | 306.5 | 65.4 |
| 0.3 | 0.7 | 297.9 | 99.3 |
| 0.33 | 1.7 | 288.26 | 98.3 |
| 1 | 0.2 | 99.8 | 99.8 |
| 1.67 | 0.2 | 59.8 | 99.8 |
| 2.33 | 0.2 | 42.8 | 99.8 |
| 3 | 0.3 | 33.2 | 99.7 |

3.3 Effect of system pH

In any adsorbate-adsorbent system, the pH of the system affects the nature of the surface charge of the adsorbent. Generally, a positive charge develops on the surface of oxides of adsorbent in an acid medium, resulting in a higher adsorption of anionic dyes than in a basic solution, [44, 45]. Conversely a negative charge will be developed on the surface so that there will be a higher adsorption of the cationic dyes.

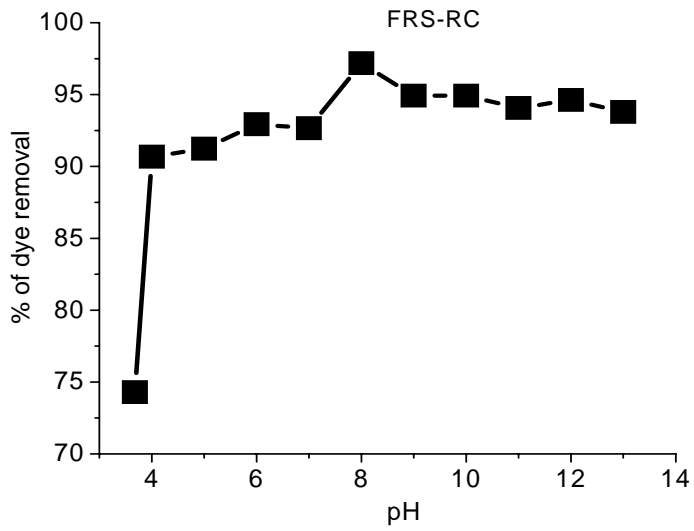


Fig.11 Effect of system pH on percentage of dye removal at fixed dye concentration and adsorbent dose.

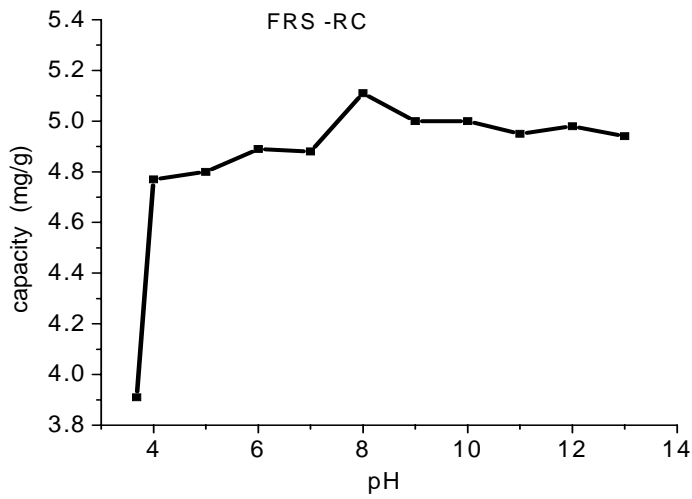


Fig .12 Effect of system pH on capacity of dye removal at affixed dye concentration and adsorbent dose.

Table. 9 Effect of system pH on residual dye concentration and absorbance at fixed dye concentration and adsorbent dose for FRS-RC.

| pH | Residual dye absorbance | Residual dye concentration (mg/L) |
|------|-------------------------|-----------------------------------|
| 3.68 | 0.09 | 25.71 |
| 4 | 0.033 | 9.32 |
| 5 | 0.031 | 8.76 |
| 6 | 0.025 | 7.06 |
| 7 | 0.026 | 7.34 |
| 8 | 0.010 | 2.82 |
| 9 | 0.018 | 5.08 |
| 10 | 0.018 | 5.08 |
| 11 | 0.021 | 5.93 |
| 12 | 0.019 | 5.37 |
| 13 | 0.022 | 6.21 |

Table. 10 Effect of system pH on efficiency and capacity at fixed dye concentration and adsorbent dose for FRS-RC.

| pH | Dye adsorbed (mg/L) | % of dye removal | Capacity (mg/g) |
|------|---------------------|------------------|-----------------|
| 3.68 | 74.29 | 74.29 | 3.91 |
| 4 | 90.68 | 90.68 | 4.77 |
| 5 | 91.24 | 91.24 | 4.80 |
| 6 | 92.94 | 92.94 | 4.89 |
| 7 | 92.66 | 92.66 | 4.88 |
| 8 | 97.18 | 97.18 | 5.11 |
| 9 | 94.92 | 94.92 | 5.00 |
| 10 | 94.92 | 94.92 | 5.00 |
| 11 | 94.07 | 94.07 | 4.95 |
| 12 | 94.63 | 94.63 | 4.98 |
| 13 | 93.79 | 93.79 | 4.94 |

About 80 % of the dried waste residue is quartz. In quartz [SiO₂], Si and O are structural elements; the Si-O bond has about 50 % covalent character [46]. The siloxane groups, -SiOSi-, interact with water forming -SiOH [47].

Undoubtedly the pH value of the system (dye-adsorbent system) plays an important role in the whole adsorption capacity. Experimental results showed that the adsorbent has maximum efficiency and capacity in the pH range between 7 and 9. Any oxide surface attains (positive or negative) charge on its surface. This charge is proportional to the pH of the solution which surrounds the oxide particles. A convenient index of the propensity of a surface to become either positively or negatively charged as a function of the pH value is called point of zero charge (pH zpc) [48, 49]. pHzpc is the critical value for determining quantitatively the net charge (positive or negative) carried on the adsorbent surface during adsorption of reactive dyes.

The hydroxyl groups formed when the siloxane groups, -SiOSi- interact with water, -SiOH- can gain or lose proton, resulting in a surface charge that varies with changing pH. At lower pH, surface sites are protonated and the surface become positively charged. At higher pH, the surface hydroxides lose their protons and the surface becomes anionic. Maximum removal efficiency for FRS-RC took place at pH 7 to 9, (Table 10 and Figures 11 and 12) and the removal rate increases with an increase in system pH in general.

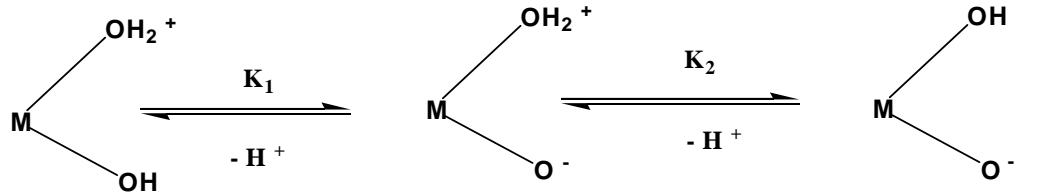
At higher pH the percentage of color removal was relatively high, which may be attributed to the presence of negative charge of the adsorbent. So it can be proposed that higher efficiency of the untreated material for any cationic dyes is achieved by the conversion of the surface of the material from a positive to a negative charge. It can therefore be said that coulomb interaction plays an important role on the adsorption of such dyes onto the media [49].

As the surface charge density decrease with an increase in the system pH , the electrostatic repulsion between the positively charged dye (FRS-RC) and the surface of the adsorbent is lowered, which may result in an increase in the rate of adsorption [50, 51]. And this is found to be the most probable reason to bring the equilibrium contact time from 30 hours to 18 hours (Annex1, Annex 2) after the pH of the system is adjusted between 7 and 9.

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 [52]. 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 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 [53].

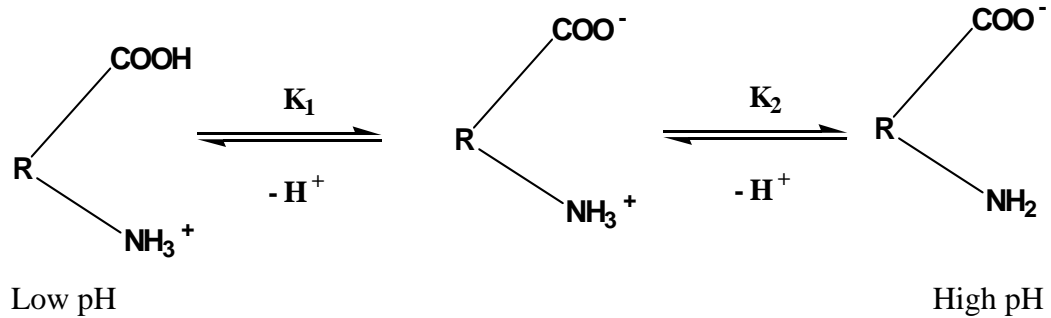
A) Inorganic matter

Low pH



High pH

B) Organic matter



Low pH

High pH

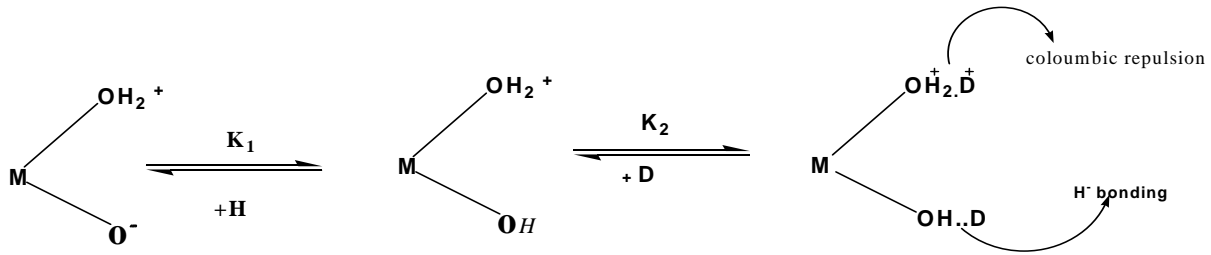
Protonated

deprotonated

Fig. 13 Response of organic and inorganic matter at various pH values.

And also many researchers have found that anion adsorption sites on clay mineral are aquo groups ($-M-OH_2^+$) and hydroxo groups ($-M-OH$) [55]. Therefore, the most probable mechanism for the adsorption of the dye by the inorganic matter kaolin (kaolinite mineral) may probably be as shown in Fig.13 (A) at low pH and (B) at high pH depending up on the surface chemistry of the mineral.

A) At low pH



B) At high pH

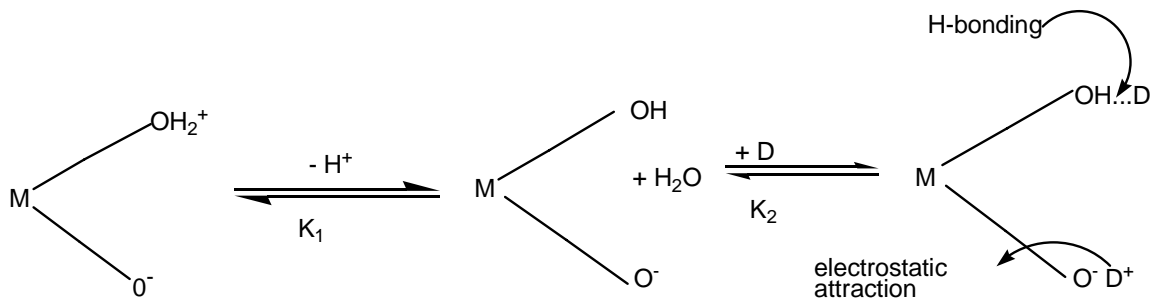


Fig.14 Possible mechanism for the adsorption of the dye (FRS-RC) by kaolin in, inorganic matter at low and high pH values.

N.B: Where D is the reactive dye structure

The adsorption process is a function of the dye structure and the adsorbent structure. Different dyes will experience different physical and electrical attractive and repulsive forces according to their structure, molecular size and functional groups. The process may involve combination of ionic attraction/repulsion, hydrogen bonding, ion-dipole forces, covalent bonds and van der waals forces. The possible mechanism for the

adsorption of the dye for this experimental condition can be explained based on the theoretical meaning of pH_{zpc} . Silica adsorbents have a low $pH_{zpc} \sim 2$ [54]. 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 (FRS-RC).

The other possible mechanism for the adsorption of the dyes by quartz can be attributed to the formation of surface hydrogen bonds between the surface hydroxyl groups on the surface of the silica adsorbent and the nitrogen atoms of the dye (FRS-RC). However the removal efficiency of the material is not as needed and this can be improved by increasing the pH of the system further in order to have greater columbic attraction towards the dye.

As we can see from the above proposed mechanism in fig.14, at low pH the forces responsible for the adsorption of the dye can be H-bonding, Vander walls force, and dipole-dipole interaction. But at high pH in addition to these forces there is a strong electrostatic attraction between the positively charged dye and the negatively charged surface. This is the most probable reason for the greater efficiency and rate of adsorption of FRS-RC at higher pH values.

3.4 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 (Fig.15 and Fig.16) and data (Table 11). The percentage of dye removal at fixed adsorbent dose increased with increasing initial dye concentration. 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 Fig.16 it is observed that increasing the initial dye concentration 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.

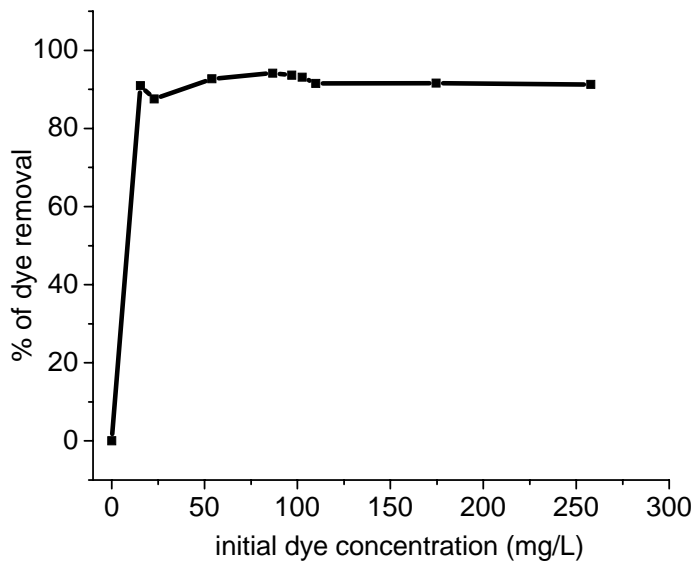


Fig .15 Effect of initial dye concentration on percentage of dye removal at fixed adsorbent dose for FRS-RC. (System pH = 7 to 9)

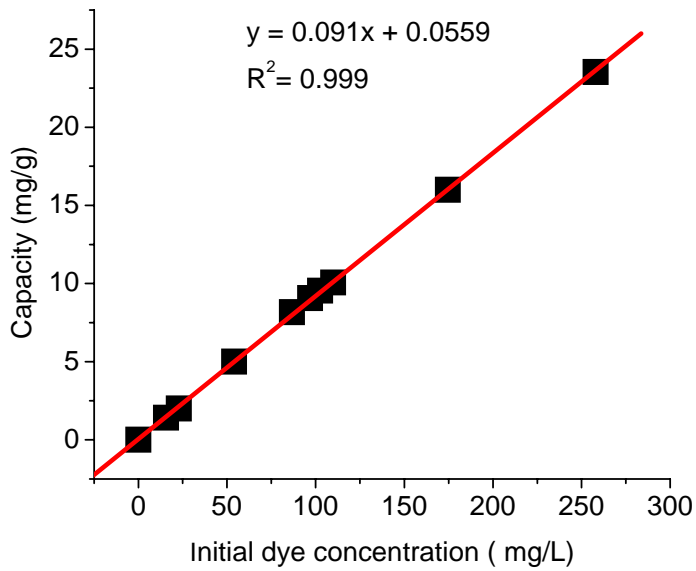


Fig .16 Effect of initial dye concentration on capacity of dye removal at fixed adsorbent dose for FRS-RC (System pH = 7 to 9)

Table 11. Effect of initial dye concentration on percentage and capacity of dye removal at fixed adsorbent dose for FRS-RC (system pH = 7-9)

| Initial dye concentration (mg/L) | Efficiency (%) | Capacity (mg/g) |
|-------------------------------------|----------------|-----------------|
| 15.54 | 90.93 | 1.41 |
| 22.88 | 87.54 | 2.00 |
| 53.95 | 92.68 | 5.00 |
| 86.72 | 94.14 | 8.16 |
| 96.89 | 93.59 | 9.07 |
| 102.5 | 93.11 | 9.54 |
| 109.9 | 91.52 | 10.06 |
| 174.6 | 91.57 | 15.99 |
| 257.9 | 91.24 | 23.53 |

3.5 Reaction Rates

The kinetics of sorption describes the solute uptake rate, which in turn governs the residence time of sorption reaction. It is one of the important characteristics in defining the efficiency of sorption. In the present study, the adsorption kinetics of the dye (FRS-RC) was studied to understand the behavior of this locally available industrial by-product.

To investigate the rate of adsorption of the dye, we focused only on the kinetics of the dye, regarding constant dye concentration and adsorbent dose. In order to determine which integrated law (model) correctly fits the measured data. Typically this is done by ascertaining which type of plot gives a straight line. Once the correct straight line plot is found the correct integrated rate model can be chosen and the values of the rate constant ‘‘k’’ will be obtained from the slope.

A comparison of the rate constants and calculated by the pseudo- first (Annex 3 and Annex 5) and pseudo-second order kinetic models using the equation of Lagergren [17] proves the applicability of the pseudo-second order equation [Eq.4]. The table {Table 13} and figure 17 below show the time course change of the concentration for FRS-RC for kinetic study.

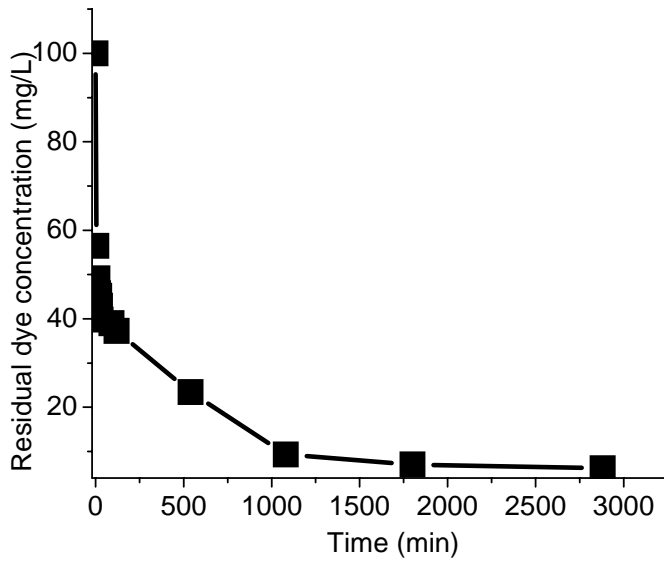


Fig .17 Change in dye concentration as a function of time.

The kinetics of adsorption was analyzed by using the Lagergren equation as shown below

[17]:

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \quad [4]$$

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

For the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the integrated form of Eq.

[5] becomes:

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

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

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

Where k_2 ($\text{g mg}^{-1}\text{min}^{-1}$) is the equilibrium rate constant of second-order sorption.

The concentration decay profile for the adsorption of the dye is correlated by pseudo first order (annex 3, annex 5) and pseudo second order (Table 11). The untreated materials can be described very well by the pseudo-second-order rate equation as shown in Fig.18 below. The correlation coefficient was found as near to unity. The values of q_e and K_2 are 5 (mg/g) and $3.81(\text{g mg}^{-1}\text{min}^{-1})$ respectively which are determined by plotting t/q_t against t of Eq. (6). , and using the slope and y-intercept of the plot. The larger the k_2 value, the slower the adsorption rate.

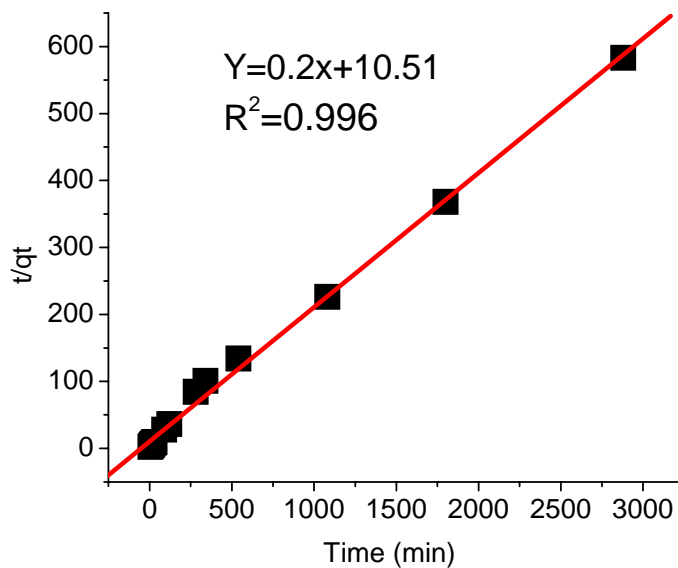


Fig .18 Pseudo-second-order plot of the dye (FRS-RC) adsorption kinetics on untreated media (pH = 7-9, dose = 10 g/L and an initial dye concentration of 100 mg/L).

Table12.change in dye concentration as a function of time.

| Time (min) | Residual dye concentration (mg/L) | q_t (mg/g) | t/q_t (min(mg/l ⁻¹)) |
|------------|-----------------------------------|--------------|------------------------------------|
| 5 | 56.50 | 2.29 | 2.22 |
| 10 | 49.15 | 2.68 | 3.73 |
| 15 | 45.76 | 2.85 | 5.26 |
| 20 | 45.20 | 2.88 | 6.94 |
| 25 | 42.94 | 3.00 | 8.33 |
| 30 | 39.83 | 3.17 | 9.46 |
| 90 | 38.98 | 3.21 | 28.03 |
| 120 | 37.29 | 3.3 | 36.36 |
| 280 | 37.00 | 3.31 | 84.59 |
| 340 | 35.88 | 3.37 | 100.89 |
| 540 | 23.45 | 4.03 | 134 |
| 1080 | 9.32 | 4.77 | 226.42 |
| 1800 | 7.06 | 4.89 | 368.10 |
| 2880 | 6.21 | 4.94 | 583.00 |

3.6 Adsorption Isotherm

The adsorption isotherms for FRS-RC and SY on the adsorbent are shown in Fig .19 and Fig.20, respectively at a constant temperature (22 ± 2 °C). The normal shape of the isotherm for SY represents the formation of a monolayer on the adsorbent meaning that the adsorption is favorable at low concentration range [55, 57]. The isotherm curve for FRS-RC is rather less favorable and seems to have increased at high relative concentrations. 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 K_f were calculated from the slope and interception of Freundlich plots (Fig.21) as listed in Table 13

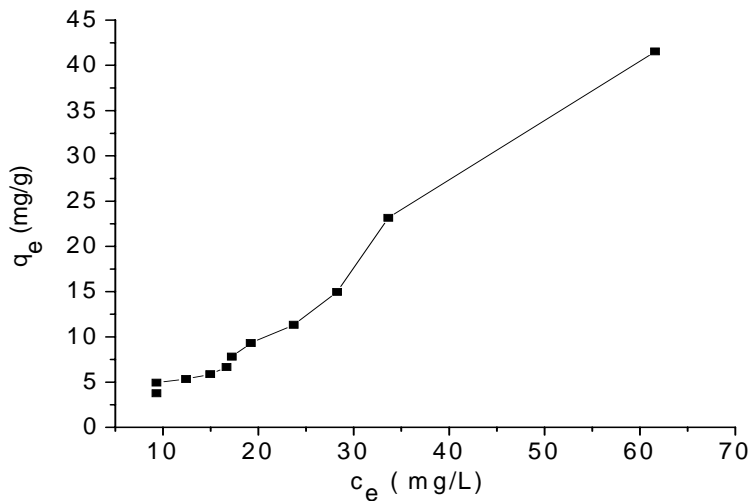


Fig.19 Adsorption isotherm of different doses of the media for FRS -RC (dose = 1-43.3g/L, initial dye concentration = 103.11 mg/L, contact time = 18 h, system pH = 7-9).

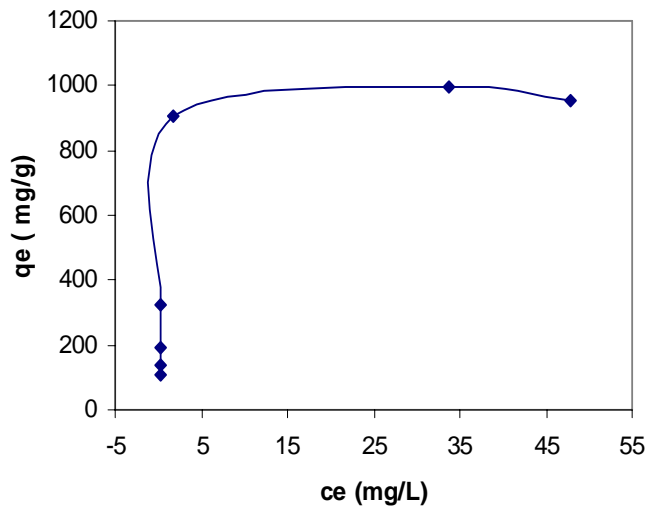


Fig. 20 Adsorption isotherm of different doses of the media for SY-BG (dose = 0.03-3g/L, initial dye concentration = 100 mg/L, contact time = 12 minutes).

The shape of the curve for the plot of amount of dye adsorbed per unit weight of the adsorbent (capacity) of the material for the tow dyes indicate that the adsorbent has high affinity for that of SY-BG than that of FRS-RC. So in case of SY-BG the system reaches equilibrium point at very small adsorbent dose (0.3g/L) and sufficient contact time of only about 12 minutes.

Table 13. Important adsorption parameters to plot an isotherm for untreated material (Contact time = 18h, pH = 7-9, initial dye concentration, =103.11 mg/L).

| 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 |

The adsorption data were analyzed with the help of linear form of Freundlich isotherm.

Freundlich model attempts to account for surface heterogeneity [59].

Freundlich isotherm: $\text{Log } q_e = \text{log } k_f + (1/n) \text{ log } C_e$ (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}).

Fig . 21 below shows a plot of $\log q_e$ vs. $\log c_e$. The constants $1/n$ as the slope and k_f as the intercept. The values of Freundlich isotherm parameters along with the k_f 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 (0.9624) 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 [11]

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 [59]. The increase in equilibrium dye removal capacity with residual dye concentration observed in Fig. 16 can support the condition of heterogeneous adsorption.

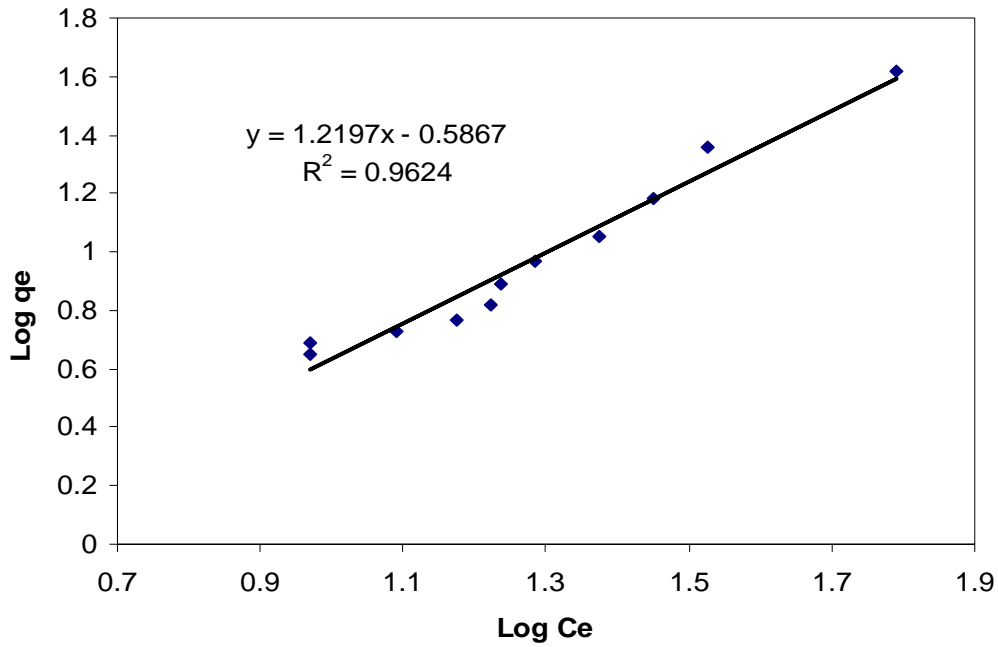


Fig. 21 Linearized Freundlich isotherm (initial dye concentration = 103.11 mg/L, Equilibrium contact time = 18 h, system pH = 7-9, temperature = 24 °C).

4. Concussions and Recommendations

The ability of locally available industrial by product to remove textile dyes from aqueous solutions was investigated. The results reveal that the low cost locally available industrial waste material generated from aluminum sulfate manufacturing process have important practical implications for removal of dyes from textile wastewater. The waste residue contains different oxides, hydroxides and sulfates with a heterogeneous surface.

The media removes about 77.4 % of the dye, (FRS-RC) from water at 19 g/L dose in pH range of less than 4 in the first 30 hours and about 99% of the dye SY-BG at 0.1g/L dose within 12 minutes. Longer contact time has no effect in improving decolorization efficiency. The amount of dyes adsorbed increases with the increase in pH of the medium for FRS-RC. The adsorption followed pseudo second order rate kinetics, and data fit in to linear form of Freundlich adsorption isotherm model for FRS-RC. Adsorption tests conducted on the adsorbent indicated that adsorption capacity decreases with increasing adsorbent dose, and the curve slows down at an adsorbent dose of 19g/L. The experimental data correlated reasonably well with that of the Freundlich adsorption isotherms and the respective isotherm parameters are calculated.

Since most of the textile and garment industry in Ethiopia is with out treatment plant which is economically feasible and efficient and which is specially designed for the removal of textile dyes this study on the dye removal capacity of the locally available waste residue with its promising result can be taken as a good option.

Hence to put this in practice further studies should be considered on:

- Capacity of the material in continuous mode adsorption
- Factors which might have an effect on efficiency:
 - ✓ Stirring time and order of chemical addition
 - ✓ pH , turbidity and alkalinity of the water to be used
- The effect of other organic substances
- The BOD and the COD level of the treated water

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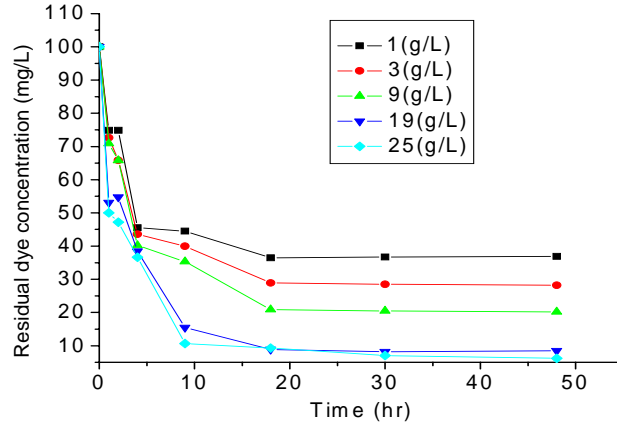
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Annex



Annex .1 Change in residual dye cocentartion as a function of dose and time (system PH= 7-9)

Annex 2. Residual dye concentraration as a function of dose (g/L) and Time (system pH = 7-9)

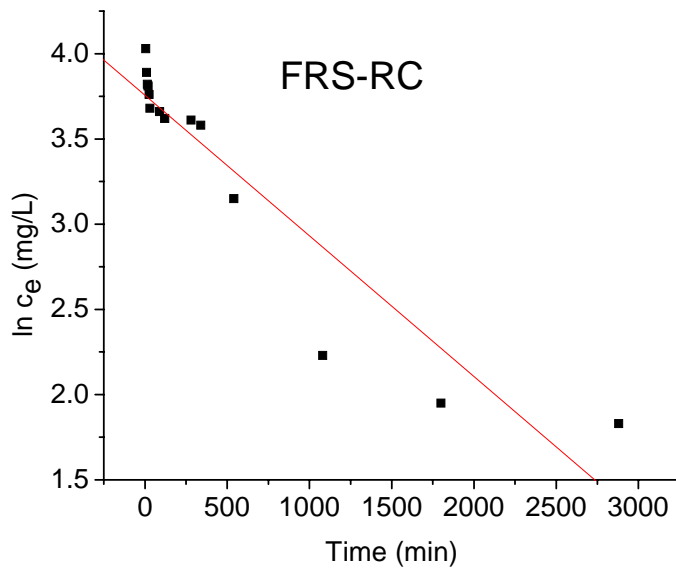
| Time (hours) | Residual dye absorbance as a function of dose and time | | | | |
|------------------|--|--------|---------|---------|---------|
| | 1(g/L) | 3(g/L) | 9 (g/L) | 19(g/L) | 25(g/L) |
| 0 | 100 | 100 | 100 | 100 | 100 |
| 1 | 74.86 | 72.6 | 70.9 | 53.11 | 50 |
| 2 | 72.86 | 65.85 | 65.81 | 54.8 | 47.18 |
| 4 | 45.52 | 43.6 | 40.2 | 38.5 | 36.68 |
| 9 | 44.5 | 40 | 35.31 | 15.5 | 10.66 |
| 18 | 36.5 | 28.9 | 20.9 | 8.9 | 9.32 |
| 30 | 36.7 | 28.5 | 20.5 | 8.2 | 7.06 |
| 48 | 36.9 | 28.2 | 20.2 | 8.5 | 6.21 |

Annex 3. Pseudo- first-order data for FRS-RC

| Time (min) | Residual dye absorbance | Residual dye concentration (mg/L) | lnC (mg/L) |
|------------|-------------------------|-----------------------------------|------------|
| 5 | 0.20 | 56.50 | 4.03 |
| 10 | 0.174 | 49.15 | 3.89 |
| 15 | 0.162 | 45.76 | 3.82 |
| 20 | 0.160 | 45.20 | 3.81 |
| 25 | 0.152 | 42.94 | 3.76 |
| 30 | 0.141 | 39.83 | 3.68 |
| 90 | 0.138 | 38.98 | 3.66 |
| 120 | 0.132 | 37.29 | 3.62 |
| 280 | 0.131 | 37.00 | 3.61 |
| 340 | 0.127 | 35.88 | 3.58 |
| 540 | 0.083 | 23.45 | 3.15 |
| 1080 | 0.033 | 9.32 | 2.23 |
| 1800 | 0.025 | 7.06 | 1.95 |
| 2880 | 0.022 | 6.21 | 1.83 |

Annex 4. Pseudo-firsts-order data for SY-BG

| Time(min) | C (mg/L) | Ln c |
|-----------|-----------|------|
| 0 | 100 | 4.61 |
| 2 | 26.5 | 3.3 |
| 12 | 2.47 | 0.9 |
| 26 | 1.93 | 0.66 |
| 45 | 1.13 | 0.26 |
| 80 | 1.13 | 0.26 |
| 125 | 1.13 | 0.26 |



Annex 5. Pseudo-first-order plot for FRS-RC

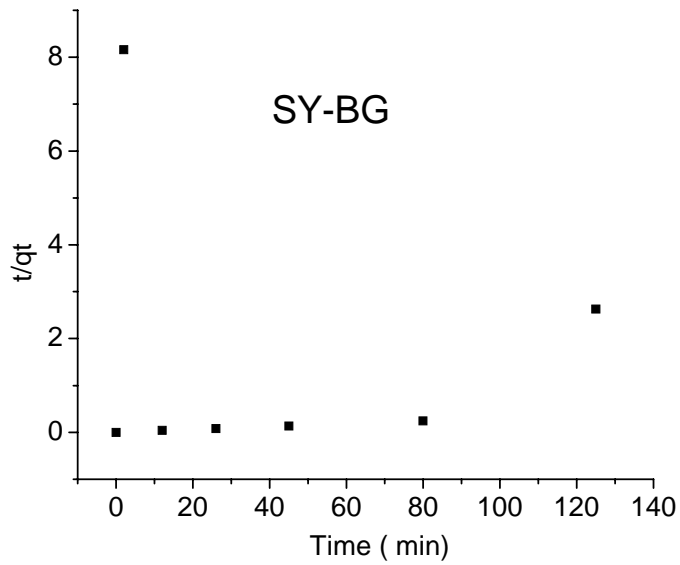
[8/16/2007 01:25 "/Graph1" (2454328)]

Linear Regression for Data1_B:

$$Y = A + B * X$$

| Parameter | Value | Error |
|-----------|-------------|------------|
| A | 3.75632 | 0.0848 |
| B | -8.24938E-4 | 8.72924E-5 |

| R | SD | N | P |
|----------|---------|----|---------|
| -0.93891 | 0.26866 | 14 | <0.0001 |



Annex 6. Pseudo-second- order plot for SY-BG.

[8/16/2007 01:25 "/Graph1" (2454328)]

Linear Regression for Data1_B:

$$Y = A + B * X$$

| Parameter | Value | Error | | |
|-----------|-------------|------------|---------|--|
| A | 3.75632 | 0.0848 | | |
| B | -8.24938E-4 | 8.72924E-5 | | |
| ----- | | | | |
| R | SD | N | P | |
| -0.93891 | 0.26866 | 14 | <0.0001 | |

[8/16/2007 02:18 "/Graph2" (2454328)]

Linear Regression for Data1_B:

$$Y = A + B * X$$

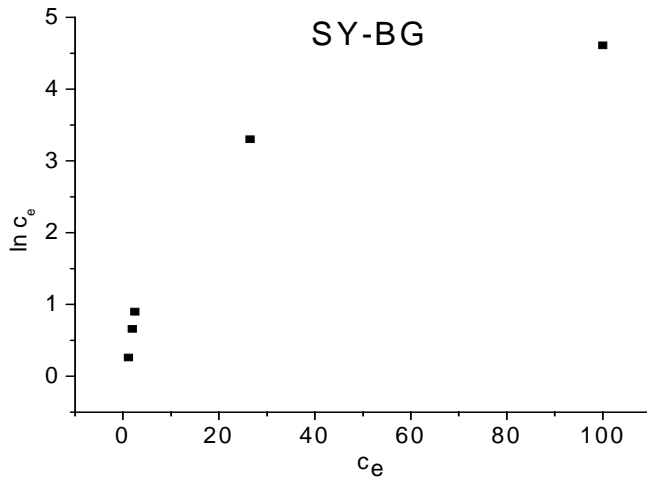
| Parameter | Value | Error | | |
|-----------|----------|---------|--------|--|
| A | 1.91728 | 1.73843 | | |
| B | -0.00735 | 0.02916 | | |
| ----- | | | | |
| R | SD | N | P | |
| -0.11197 | 3.30711 | 7 | 0.8111 | |

Annex 7. Pseudo second order data for SY_BG

| Time(min) | qt | t/qt |
|-----------|-------|-------|
| 0 | 0 | 0 |
| 2 | 245 | 8.16 |
| 12 | 325.1 | 0.04 |
| 26 | 326.9 | 0.08 |
| 45 | 329.6 | 0.137 |
| 80 | 329.6 | 0.243 |
| 125 | 329.0 | 2.63 |

Annex 9. Pseudo-first-order data for SY-BG

| Time(min) | c | Ln c |
|-----------|------|------|
| 0 | 100 | 4.61 |
| 2 | 26.5 | 3.3 |
| 12 | 2.47 | 0.9 |
| 26 | 1.93 | 0.66 |
| 45 | 1.13 | 0.26 |
| 80 | 1.13 | 0.26 |
| 125 | 1.13 | 0.26 |



Annex 10. Pseudo-second-order plot for SY-BG

[8/16/2007 01:25 "/Graph1" (2454328)]

Linear Regression for Data1_B:

$$Y = A + B * X$$

| Parameter | Value | Error |
|-----------|-------------|------------|
| A | 3.75632 | 0.0848 |
| B | -8.24938E-4 | 8.72924E-5 |

| R | SD | N | P |
|----------|---------|----|---------|
| -0.93891 | 0.26866 | 14 | <0.0001 |

[8/16/2007 02:18 "/Graph2" (2454328)]

Linear Regression for Data1_B:

$$Y = A + B * X$$

| Parameter | Value | Error |
|-----------|----------|---------|
| A | 1.91728 | 1.73843 |
| B | -0.00735 | 0.02916 |

| R | SD | N | P |
|----------|---------|---|--------|
| -0.11197 | 3.30711 | 7 | 0.8111 |
