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ADSORPTION STUDIES OF METHYLENE BLUE ON MARINE SOURCE AS ADSORBENT AND ITS KINETIC STUDY

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ABSTRACT

Methylene blue contamination in wastewater causes problems in several ways. The presence of dyes in water, even in very low quantities, retards photosynthesis; inhibits the growth of aquatic biota and interferes with gas solubility in water bodies. They cannot be decomposed easily. Therefore, it is highly necessary to reduce dye concentration in the wastewater. The conventional methods for treating dye containing wastewaters are electrochemical treatment, coagulation and flocculation, chemical oxidation, liquid–liquid extraction and adsorption. Adsorption has been shown to be an effective way for removing organic matter from aqueous solutions in terms of initial cost, simplicity of design, ease of operation and insensitivity to toxic substances. From literature survey, it was inferred that there is lesser work on the biosorbents derived from marine bio waste. Hence, an attempt has been made in the present study to remove Methylene blue dye using marine biowaste shells [**Crab Shells**] entitled. The present study deals with Marine bio-waste shells converted in to biosorbent powder for polluted waste water treatment studies. The effects of pH, contact time, initial dye concentration and dosage on adsorption capacity were investigated.

Keywords: Methylene blue dye, Marine bio-waste shells

INTRODUCTION

SYNTHETIC DYE'S IMPACT ON THE ENVIRONMENT

During the coloration process, a large percentage of the dye does not bind to the fabric and is lost to the waste water stream. Approximately 10-15%dyes are released into the environment during dyeing process making the effluent highly colored and aesthetically unpleasant. Public perception of water quality is greatly influenced by the colour. So, the removal of colour from waste water is often viewed as more important than the removal of the soluble colourless organic substances.

A great environmental concern with dyes is the absorption and reflection of sun light entering the water. Light absorption diminishes photosynthetic activity of algae and seriously influence on the food chain as the algae are the base of the food chain, thus affecting every organism above it. The lack of algae is one of the main reasons that the aquatic life suffers in areas that dyes are discharged, but another is because of the toxicity of the dyes themselves.

DYING FOR FASHION

Clothing comes into prolonged contact with one's skin, the largest organ, and so toxic chemicals are often absorbed into the skin, especially when one's body is warm and skin pores have opened to allow perspiration. This absorption has been shown to cause significant health effects, such as an increase in tumours. They have been shown to have carcinogens, as they are made with many chemicals. Textile dyes can also cause allergies such as contact dermatitis and respiratory diseases, allergic reaction in eyes, skin irritation, and irritation to mucous membrane and the upper respiratory tract. These diseases are most prevalent in the workers who are dyeing the clothes as they are around the chemicals all day. These workers are literally disinformation.

SOME METHODS OF DYE REMOVAL FROM WASTEWATER

The textile organic dyes must be separated and eliminated from water but especially from industrial wastewaters by effective and viable treatments methods. Two different treatment concepts are (1) separation of organic pollutants from water environment, or (2) the partial or complete mineralization or decomposition of organic pollutants. Separation processes are based on fluid mechanics (sedimentation, centrifugation, filtration and flotation) or synthetic membranes (micro-,ultra – and nanofiltration, reverse osmosis). Additionally, physico-chemical processes (i.e.adsorption, chemical precipitation, coagulation-flocculation, and ionic exchange)can be used to separate dissolved, emulsified and solid-separating compounds from water environment.

Methods for treating textile dye wastewaters consist of various chemical, physical and biological processes. These include: adsorption(Sanghietal 2002), nanofiltration(koyuncu 2003), colloidal gas aphrons (Roy et al 1992), ultrasonic decomposition (Ge and Qu 2003) ,electro coagulation(VanderBruggenetal2001), coagulation(Patriciaetal2005) and precipitation(Liu et al 2003), advanced chemical oxidation(Arslan et al 2000), electro chemical oxidation (Lopez-GrimauandGutierrez2006), photooxidation, predispersed solvent extraction(Lee et al 2000), ozonization (Sniderand Porter (1994), Beszedits (1980), Green and Sokol (1985) and Gould and Groff (1987)), supported liquid membrane(Murphy et al (2001) and Venkateswaran and Palanivelu 2006), liquid- liquid extraction (Kasuga et al 1998) and aerobic and anaerobic biological processes(Liakou et al 2003). The advantages and disadvantages of some methods of dye removal from wastewater are given in Table 3. The liquid membrane technique known as ‘‘Supported Liquid Membrane’’ (SLM) has the advantage of achieving selective removal and concentration in single stage, thus having great potential for reducing cost significantly. SLM system has several advantages including: (a) low capital investment and operating cost, (b) low energy consumption, (c) minimum loss of extractant, (d) low liquid membrane requirement and thus less amount of expensive extractants which offer good selectivity and (e) simple to operate and easy to scale up. There have been a number of studies dealing with organic compound transport through SLM in synthetic solutions (Kasuga et al1998). No work has been carried out in the use of liquid membrane technology to recover textile dye. However, these methods are not widely used due to their high cost and economic disadvantage. Chemical and electrochemical oxidations, coagulation are generally not feasible on large scale industries The major advantages of an adsorption system for water pollution are less investment in terms of initial cost, simple design, easy operation, lessenergyintensiveness,non-toxic,andsuperiorremovaloforganicwasteconstituents as compared with the conventional biological treatment processes (Noroozietal 2007).The most common adsorbent materials are alumina, silica, metal hydroxides and activated carbon. As proved by many researchers, removal of dyes by activated carbon is economically favorable and technically easier. Activated carbon is widely used as an adsorbent due to its high adsorption capacity, microporous structure and high surface area.

ADSORPTION ON ACTIVATED CARBON

Each activated carbon has a unique set of physical and chemical characteristics that are dependent on the type of raw material and the processing methods (physical, chemical or a combination) employed in its manufacture (Allen et al 1998). Adsorption is defined as a process where the adsorbate is attached to the surface of the adsorbent. The kinetics of adsorption onto the activated carbon is controlled by the process of diffusion. The transfer of the impurities from the bulk solution to the surface of the carbon proceeds through three stages.

Molecules can bind to the surface by two types of binding forces namely, physical and chemical forces. Physisorption or physical adsorption is the result of intermolecular Van derWaals forces or hydrogen bonds of attraction between molecules of the solid and the substance adsorbed. The physical adsorption is relatively weak and the adsorbed particles are assumed to be free to move on the surface of the adsorbent. There is no significant redistribution of electron density in either the molecule or at the substrate surface. Chemisorption or activated adsorption is associated with the transfer and sharing of electrons between adsorbate and adsorbent resulting in a chemisorptive bond, a chemical bond stronger than Van der Waals forces. The process is irreversible and on desorption the original substance will often be found to have undergone a chemical change. In general, the adsorption of a compound on activated carbon increases with increasing molecular mass, a higher number of functional groups such as double bonds or halogen compounds, increasing polarizability of the molecule. This is related to electron clouds of the molecule.

MARINE BIOWASTE SHELLS COLLECTION

a) Sampling

Generally, the dead marine biowaste shells, **AbyloniaSpirata Shells, CerastodermaeduleShells and Crab Shells** shown in figure:1 to 3 were collected by hand picking from fish landing centers from Sholinganallur to Kalpakkam beach. After the collection, the marine bio waste is placed in properly labelled plastic bags subsequently were separate based on size, shape, colour etc. The experimental procedure is divided into three parts which deals with preparation of CaO from waste shells.

Synthesis of n-HAP powder from CaO by wet precipitation hydro thermal method and chromium adsorption experiments.

b) Pre-Treatment of Marine waste Shells

The collected dead Marine biowaste ($CaCO_3$, 95–99%) was washed with warm water, rinsed with distilled water, dried at 105˚C for overnight and then allowed to cool in desiccators.

c)Drying

The dried Biowaste shells were grounded by using agate mortar and pestle and converted into powder, followed by the heat treatment at 900°C for the period of 3 h to convert calciumcarbonate ($CaCO_3$) to calcium oxide (CaO). The CaO was transformed to calcium hydroxide [$Ca(OH)_2$] due to its high hygroscopic property which easily absorbs atmospheric moisture whenitis exposed to the atmosphere.

d) Synthesis of CaO from marine biowaste

The major constituent exists in the marine biowaste is $CaCO_3$, which accounts nearby94% of the overall weight. Thus, in this method biowaste shells were used to synthesis CaO.. The biowaste shell evolves carbon dioxide beyond 850˚C and converted intocalciumoxide. The micrographs are given in below figure nos (1, 2& 3).

Fig1 AbyloniaSpirataShells

Fig 2 CerastodermaeduleShells (BIVALVE)

Fig 3 CrabShell

GENUS CHARACTERS

The dextral shell has up to about nine whorls and a more or less slender typical buccinoide shape with an acuminate apex. When the shell is held in upright position, the lowest point of the last whorl and the columellar base are situated at about the same horizontal line. Apart from the growth-lines and more delicate spiral lines, the surface is smooth. The height of adult shells varies from ca. 20 to 93 mm; the breadth comes to 50-70% of the height. A sutural canal is always present in some species itis very conspicuous and developed along all the whorls, whereas it can be seen only on the third or fourth whorl and with the help of a hand-lens in others. The aperture has a small groove for the anus above and a large notch for the sipho below. The umbilicus varies from wide open to completely closed and is surrounded by a more or less raised fasciole which ends at one side in the callus on the last whorl and at the other side in the notch for the sipho. A sinistral specimen is known of only one species (B. japonica). The shell colour is white to orange-yellowish, with orange to brown spots; sometimes the colour-pattern is vaguely seen inside the aperture. In nearly all species the dark spots are principally arranged in four spiral rows. As the spots of a single or of different rows may be connected in various ways, horizontally or vertically, the arrangement in four rows may be obscured. In B. kirana the colour-pattern is nearly invisible. B. areolata is the only species with three rows of spots. The fossil species B. gracilis has an upper row of large spots and, on the remaining part of the shell, very many small spots, distributed regularly, without an arrangement in rows. The colour pattern of the fossil species B.pangkaensi is similar, although not in all specimens studied. Sexual dimorphism in shell structures could not be demonstrated so far. The periostracum is brown to yellowish and very variable in thickness. The brownish operculum (pl.1) has an eccentric nucleus and many growth lines, which are more or less accentuated by raised ridges. . Sometimes a centric nucleus occurs Having studied many opercula of Babylonia species, we can say that a concentric operculum is formed when the region of the nucleus has been damaged during the life of the animal. In a sample of 36 specimens of B. spirataspirata, collectednearJakarta,7specimens have a more or less centricoperculum, demonstrating that this phenomenon is not very rare. A monstrosity with a combination of two small centric opercula is figured by Lan. The radula consists of about 40 rows of three teeth. The Single rows of radulae of adult Babylonia(X25).

Crab Shell

Crustaceans constitute a wide spread class of organisms of both marine and land-dwelling species. They possess an exoskeleton that stabilizes the whole body of the animal and also serves for protection against predators. In the case of crabs, the claws are part of the exoskeleton optimized to serve as a cutting tool. The exoskeleton of crustaceans is a biomineralized structure which consists of an organic matrix α-chitin together with an inorganic mineral, calcium carbonate. This composite has a distinct microstructure which gives it an optimal performance with respect to mechanical strength (for protection) and flexibility (for movement). The contents of the main components in the crab shells (chitin, protein, and calcium carbonate) were estimated by the ninhydrin-hydrindantin protein test and gravimetric analysis.

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The present study deals with Marine bio-waste shells converted in to biosorbent powder for polluted wastewater treatment studies. The effects of pH, contact time, initial dye concentration and dosage on adsorption capacity were investigated.

EXPERIMENTAL

PREPARATION OF ADSORBATES TO STOCK SOLUTION WORKING SOLUTION

All working solutions of the desired concentrations were prepared by diluting the stock solution with distilled water.

PREPARATIONOFADSORBENT

Shells were collected by hand picking from fish landing centers from Besant nagar beach, Chennai and a specimen was kept in their laboratory. After the collection, the marine bio waste is placed in properly labelled plastic bags, subsequently were separated based on size, shape, colour etc. The collected material was allowed to dry in sunshade for a week and after that it was crushed, powdered and then screened for homogenizing. The homogenized powder issued as adsorbent in our study.

EXPERIMENTALPROCEDURE

BATCH ADSORPTION METHOD

ORBITALSHAKER

❖ Orbital shakers are widely used in cell culture applications for evenly mixing cell suspensions, media, and nutrients in culture flasks or plates. This ensures uniform distribution of cell sand nutrients, promoting optimal cell growth and viability.

❖ In microbiology, orbital shakers are employed for culturing microorganisms in liquid media. By gently shaking the culture vessels, microbial growth can be enhanced, and oxygen and nutrients can be evenly distributed throughout the medium.

❖ Orbitalshakersfacilitatechemicalreactionsbyprovidingcontinuousmixingoragitationof reaction mixtures. This is particularly useful for reactions requiring homogeneous mixing of reagents or for maintaining consistent conditions throughout the reaction.

❖ In molecular biology and biochemistry, orbital shakers are used for protein expression in bacterial or yeast cultures. They can also aid in protein purification processes by gently mixing protein samples with affinity resins or chromatography matrices.

ADSORPTION EQUILIBRIUM EXPERIMENT

The batch adsorption experiment was carried out the to determine the equilibrium time.100 ml of sample solution was added to one gram of adsorbent and allowed to agitate in a shaker at 200 rpm. and 27^{o}C. After 10 minutes of agitation, the content of the flask was filtered and from the filtrate10 ml was taken in a cuvette and its OD at 560 nm was recorded. Theremaining90ml of the sample was again added to one gram and the procedure was repeated. This step was continued until same OD was obtained. The values are recorded in table 1. The concurrency of OD shows the time required for the attainment of equilibrium. To study the various factors influencing the adsorption process, the following experiments were carried out and the readings are tabulated.

EFFECT OF ADSORBENT DOSE

The effective removal of dye from the sample solution may vary with respect to the amount of the adsorbent used. To study this,50ml of sample solution was added to 4 flasks which contains 5,10,15 and 20g of adsorbent in the ratio1:10 respectively. The optical density data at different adsorbent concentrations are tabulated inTable2.

EFFECT OF CONCENTRATION OF ADSORBENT

To study the effect of concentration on adsorption the experiment was carried out at different concentrations of adsorbent and the optical density measurements are tabulated in table 3.

EFFECT OF CONTACT TIME

Adsorption is a surface phenomenon and the quantity of adsorbate adsorbed on the adsorbent depends on the contact time. To evaluate the effect of contact time on adsorption,10gof adsorbent and 50ml of sample were studied at various contact times. The optical density data at different contact time are presented in Table 4.

EFFECT OF pH

The pH of the solution plays an important role in the whole adsorption process, particularly on the adsorption capacity. To study the effect of pH , 50ml of solution at different pH were studied at fixed adsorbent dosage and a contact time of40 minutes. The optical density data at different pH are tabulated in Table 5.

EFFECT OF SURFACTANT

Presenceofsurfactantmayinterferetheadsorptionprocess.Thereforestudyonadsorption in presence of surfactant was carried out. Sodium dodecyl sulfonate was used as surfactant. The change in optical density in the presence of surfactant for the adsorption process at various concentration of surfactant was found out and listed in table 6.

RESULTS AND DISCUSSION

ADSORPTION EQUILIBRIUM EXPERIMENTS

The batch adsorption experiments were conducted in 250mL. conical flask containing adsorbent and 50 ml of 50mg/L methylene blue solution at a pH of 7. The flasks were agitated ina shaker at 200 rpm. and 27^{o}C until the equilibrium is reached. After decantation and filtration, the equilibrium concentrations of dye in the solution were measured at 660nm using colorimeter. The agitation was carried out at time interval of 20,30,40,50,60 minutes. Each time after decantation and filtration OD was found out. The constant at 50min and 60min shows the attainment of equilibrium.

Table–1 ADSORPTION EQUILIBRIUM EXPERIMENTS

S.NO	Time (mts)	Optical density (unit)
1	10	0.25
2	20	0.36
3	30	0.45
4	40	0.50
5	50	0.52
6	60	0.52

EFFECT OF ADSORBENT DOSE

In order to study the effect of adsorbent mass on the adsorption of methylene blue, a series of adsorption experiments was carried out with different adsorbent dosages at initial dye concentration of 1g. Table 2 shows the effect of adsorbent dose on the removal of methylene blue. Along with the increase of adsorbent dosage from 1 - 4g , the percentage of dye adsorbed increased from 20.8-98.91%. Above 1-4g of adsorbent dose, the adsorption equilibrium of dyes were reached and there molar ratios of dyes kept almost in variable. The increase in adsorption may be due to the availability of more adsorbent sites as well as greater availability of specific surfaces of the adsorbent. However, no significant changes in removal efficiency were observed beyond1g/50ml adsorbent dose. Due to conglomeration of adsorbent particles, there is no increase in effective surface area of adsorbent OD before Adsorption.

Table–2 EFFECT OF ADSORBENT DOSE ON ADSORPTION

S.No	Weight of Adsorbent(gm)	Optical Density (Unit)	% Dye removal= $\frac{A_0-A_1}{A_0}\times 100$
1	1	1.45	29.46
2	2	1.35	20.53
3	3	1.29	15.17
4	4	1.15	2.67

EFFECT OF CONCENTRATION OF ADSORBATE

Exactly one gram of adsorbent was weighed and adsorbate of various volume is added to it and allowed to be shaken for 60 mts in orbital shaker with 200 rpm . The optical density of the adsorbate at 660 nm after one hour was observed and recorded in the following table 3. The percentage removal of methylene blue was calculated using the following equation. Similar experiments were conducted with different weights of adsorbent.

Table 3 EFFECT OF CONCENTRATION OF ADSORBENT ON ADSORPTION

S.No	Concentration of adsorbate(ml)	OD After Adsorption	% Dye removal= $\frac{A_0-A_1}{A_0}\times 100$
1	10	0.33	70.53
2	20	0.68	39.28
3	30	0.96	14.28
4	40	1.02	8.92

EFFECT OF CONCENTRATION OF ADSORBATE ON ADSORPTION

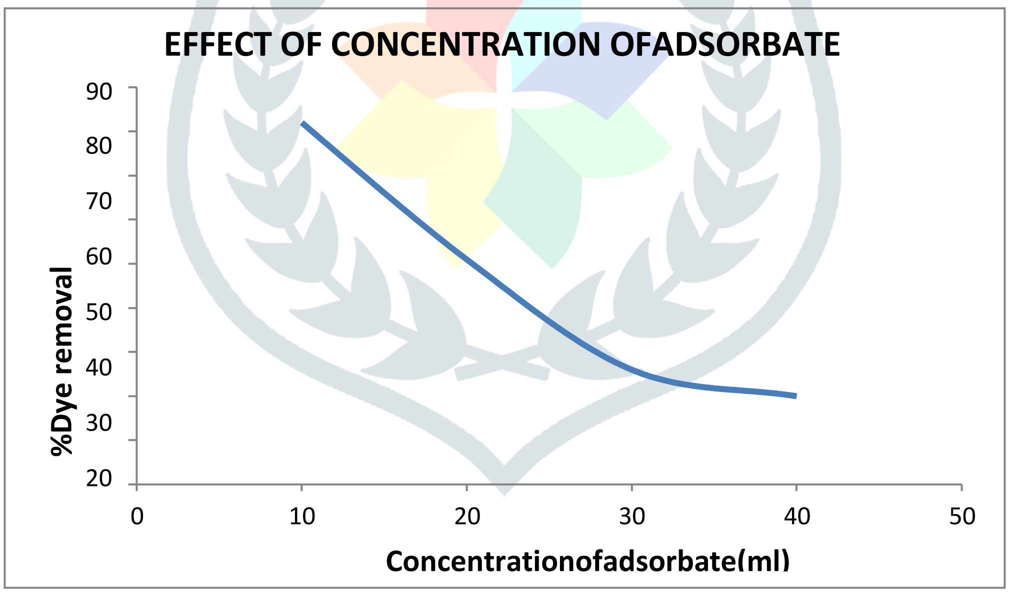

Fig .4

The above graph reveals that when the concentration of adsorbate increases adsorption of dye removal decreases.

EFFECT OF CONTACT TIME

Exactly one gram of adsorbent was weighed and 50 ml adsorbate was added to it and allowed to be shaken for 60 mts in orbital shaker with 200 rpm. The optical density of the adsorbate at 660 nm after different contact time was observed and recorded in table 4. The dye removal increased with the increase of contact time. Initially, there is no much change observed after the equilibrium was reached as shown in Fig 5. The change in the rate of adsorption might be due to the fact that initially all the adsorbent sites would have been vacant and solute concentration gradient is very high. Later, the lower adsorption rate is due to a decrease in number of vacant sites of adsorbent and dye concentrations.

Table– 4 EFFECT OF CONTACT TIME ON ADSORPTION

S.No	Contact time(minutes)	Optical density	%Dye removal= $\frac{A_0-A_1}{A_0}\times 100$
1	30	0.52	53.57
2	60	0.30	73.21
3	90	0.25	77.67
4	120	0.915	86.60

EFFECT OF CONTACT TIME ON ADSORPTION

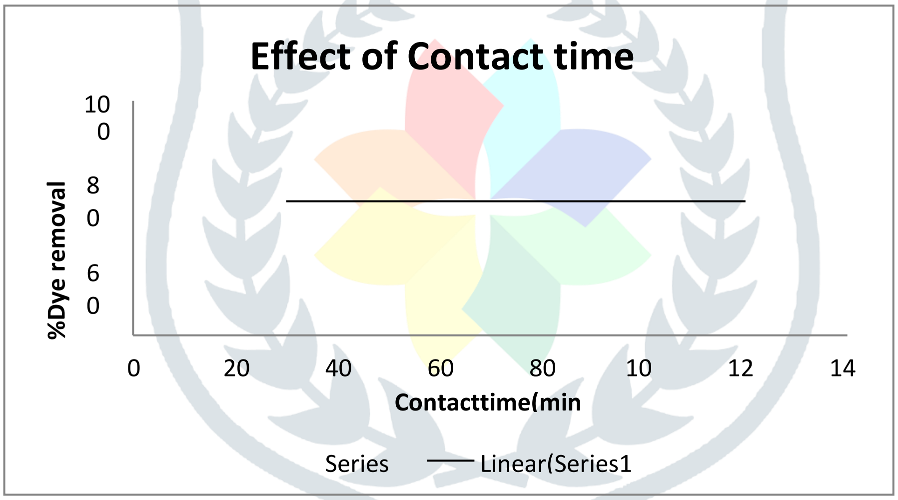

Fig.5

The above graph shows that the percentage of dye removal increases with increases in contact time and this confirms that the rate of adsorption process is very low at the beginning.

EFFECT OF pH

Exactly one gram of adsorbent was weighed and 50ml of adsorbate added to it and, various volume of HCl are allowed to be shaken for 30mtsin orbital shaker with 200 rpm. The optical density of the adsorbate at 660nm after one hour was observed and recorded in table-5.

Table-5 EFFECT OF pH ON ADSORPTION

S.NO	Volume of HCl(ml)	pH	Optical Density	% Dye removal= $\frac{A_0-A_1}{A_0}\times 100$
1	0.5	0.301	0.85	24.10
2	0.1	1.00	0.72	35.71
3	0.05	1.301	0.35	68.75
4	0.01	2.00	1.05	6.25
5	0.001	3.00	1.08	3.571

EFFECT OF pH ON ADSORPTION

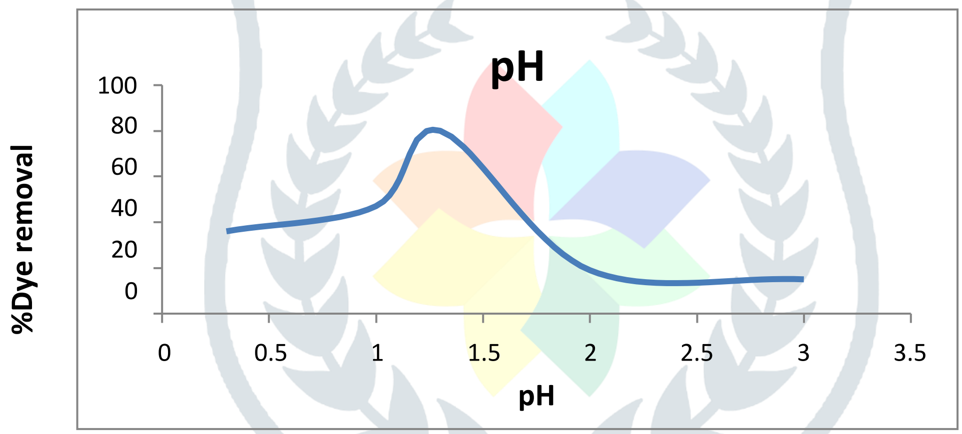

Fig-6

The above graph shows that at low pH, the% of dye removal is very low. At particular pH , the % of dye removal is maximum and this shows that adsorption is effective at pH more than 0.5.As shown in Figure-5.5 a consistent increase in adsorption capacity was noticed as the pH increased from 0.3 – 1.3, whereas in the range 1.5 – 3.0, the adsorption amount was only slightly affected by pH. As pH of the system increased, the number of negativelychargedadsorbentsitesdecreasedandthenumberofpositivelychargedsurfacesitesincreasedwhichdidnotfavort headsorptionofpositivelychargeddyecationsduetoelectrostaticrepulsion. In addition, lower adsorption of methylene blue at acidic pH might be due to the presence of excess H+ ions competing with dye cations for the available adsorption sites.

EFFECT OF SURFACTANTS

Exactly one gram of adsorbent was weighted, 50 ml of adsorbate and various volumes surfactant sodium dodecyl sulphate (SDS) are added to it and allowed to be shaken for 60 mts in orbital shaker with 200 rpm. The optical density of the adsorbate at 660 nm after one-hour was observed and recorded in table 6.

Table.6 EFFECT OF SURFACTANTS ON ADSORPTION

S.NO	Surfactant (ml)	Optical Density	%Dye removal= $\frac{A_0-A_1}{A_0}\times 100$
1	10	0.95	15.17
2	20	0.4	64.28
3	30	0.35	69.64
4	40	0.21	81.25

EFFECT OF SURFACTANTS ON ADSORPTION

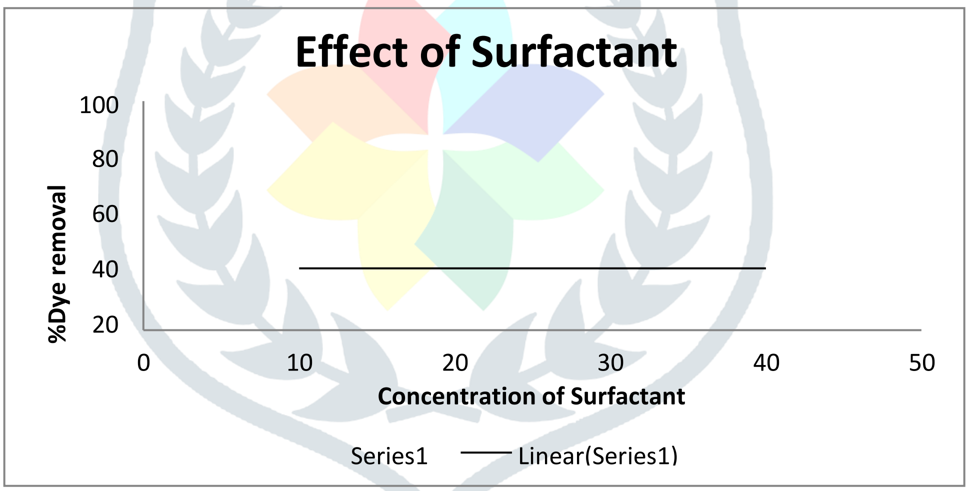

Fig.7

The above graph shows that the % of dye removal increases with the increase of concentration of surfactant sodium dodecyl sulfate (SDS).This may be attributed due to tendency of surfactant to increase surface tension between the dye layer and the solid layer of adsorbent. From this it is clear that increase of surfactant increases the efficiency of adsorption.

SUMMARY AND CONCLUSION

Methylene blue is a common dye which is used in many dye industries in the modern world. The dye present in the industrial effluent enters in to the surface water, ground water and also sewage water. Higher concentration in water can alter the aesthetic quality of water. Hence its presence in aquatic environment must be checked regularly. The dye removal process which is outlined in this work can be utilized well in any water treatment process.. Based on the results, the following conclusions can be drawn.

The efficiency of the adsorption is excellent. The handling of materials is very easy and harmless. The adsorption on the adsorbent used is effective at high concentration of adsorbate. The percentage of adsorption increases with increases in contact time. and increases with less pH in the range of 3-4. The efficiency of adsorption increases with increases of concentration of surfactant sodium dodecyl sulfate.

From the above work we draw the conclusion that the experimental conditions are very simple and operational cost is low. The proposed technology is economically feasible and eco-friendly in nature. The adsorption in aqueous solution is 95% with the effective dose of 2g of adsorbent.

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