BATCH ADSORPTION STUDIES ON REMOVAL OF DYES FROM WASTE WATER USING MODIFIED SEASHELLS AS ADSORBENTS

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ABSTRACT

Environmental pollution has become a major concern amongst all the pollution for the sustainability of life. Contamination of soil, groundwater and surface water with textile effluents is causing health related problems to both human being and marine life. Removal of such effluents before releasing to atmosphere is primary concern. To reduce the concentration of these in the water body's methods like precipitation, ion exchange, adsorption, membrane processes, and electrolytic methods are used. In the present investigation an effort has been made to remove the contaminants using adsorption method by using seashells as the source of biopolymers as adsorbents as they have the capacity to lower the transition metal ion concentrations to sub part per billion levels and also they are environmentally safe. Indigo carmine is chosen as the model dye for our study by varying the metrics like Concentration of IC dye, Contact time, Adsorbent dosage and pH. All the metrics were optimized and kinetic study was carried out. The optimized conditions were obtained, Concentration 10ppm, Contact time 120 min, Adsorbent dosage 20g/L and pH 5. The removal percent was found to be 88%. Kinetic studies was done to determine the reaction rate constant and it was found to be 0.006min^{-1} and the it follows first order kinetics.

Keyword: *Adsorption, Biopolymers, Indigo Carmine, Seashells*

1. INTRODUCTION

Water pollution has become a major concern amongst all the pollution for the sustainability of life. Contamination of soil, groundwater and surface water with toxic heavy metals and dyes released from textile industries are causing health related problems to both human being and marine life [1, 2]. Heavy metal ions such as copper, nickel, zinc, chromium, cadmium and lead which are dangerous pollutants are being constantly discharged into the environment/water bodies by various industries such as surface finishing industry, fertilizer, pesticide, metallurgy and leather industries etc. [3]. Methods such as precipitation, ion exchange, adsorption, membrane processes, and electrolytic methods have been used in order to reduce concentration of these toxic metal ions in water bodies which are quite expensive in nature [4]. Amongst the available methods adsorption method is found to be cost effective and less expensive process to remove the contaminants from waste water. Biopolymers are industrially attractive because they are, capable of lowering transition metal ion concentrations to sub-part per billion concentrations, widely available, and environmentally safe. Another attractive feature of biopolymers is that they possess a number of different functional groups, such as hydroxyls and amines, which increase the efficiency of metal ion uptake and

the maximum chemical loading possibility to which the metal ions can bind either by chemisorption or by physisorption. New polysaccharide-based-materials were described as modified biopolymer adsorbents (derived from chitin, chitosan, and starch) for the removal of heavy metals from the wastewater [5, 6]. Biopolymeric materials include cellulose, alginates, carrageenan, lignins, proteins, chitosan and chitin derivatives. Among the biopolymers worked with for adsorption of metal ions, chitin and the derivates of chitin have played significant role in their capacity as adsorbent and complexing agent by virtue of their hydroxyl, acetate, amido and amino groups. Research and development work on chitin and chitosan has reached a status of intense activities in many parts of the world [7-9]. Chitin has been reported to be the second most abundant natural polysaccharide in nature [10] and is commonly found in crab and shrimp shells containing 10-15% of chitin [11]. Chitin and chitosan are of commercial interest due to their high percentage of nitrogen (7.21%) compared to synthetically substituted cellulose (1.25%) [12]. The naturally abundant materials also exhibit a limitation in their reactivity and process ability [13-14]. In this respect, chitin and chitosan are recommended as suitable functional materials, because these natural polymers have excellent properties such as biocompatibility, biodegradability, non toxicity, chelating properties, etc. The present investigation shows the feasibility of using Seashells (Source of biopolymers) as adsorbents to degrade indigo carmine as model dye with metrics like pH, adsorbent dosage and concentration of dye solution which is the main constituent of the effluents coming from many textile industries.

2. MATERIALS AND METHODS

2.1 Reagents and Apparatus
Indigo Carmine, Caustic Soda, Hydrochloric Acid, Distilled water and other necessary chemicals were obtained from department laboratory. Sea shells were obtained from Kundapur Beach.
Obtained sea shells were washed with distilled water and then dried in a tray drier and then they were grinded to fine powder. Thus obtained powder was sieved using a sieve shaker. The powder obtained in the pan size was used for the further studies.
A standard solution of 1000 ppm of Indigo Carmine dye solution was prepared as the stock solution. This was further diluted to certain concentrations ranging from 10ppm to 50ppm. Biopolymers (Seashells) were used as adsorbents and were modified using HCl. Conical flasks were used for the preparation and storage of different concentration solutions. Appropriate amount of adsorbents were weighed and added to each conical flask for shaking in a rotary shaker for a given contact time. Spectroscopic analysis was then conducted to get the final concentrations of the solutions. The percentage removal of IC dye was thus obtained

2.2. Experimental Setup
The equipments used were rotary shaker, pH meter, UV visible spectrophotometer. HACH-DR-4000 UV Visible spectrophotometer was used for determination of Indigo Carmine in standard and treated solutions. The pH of the solution was measured with a EUTECH make digital microprocessor based pH meter previously calibrated with standard buffer solutions. The chemical analysis was carried out by standard methods of chemical analysis.

UV spectrophotometer:
The solutions were analysed for absorbance at a wavelength of 610 nm.

Fig 1: UV Vis Spectrophotometer

Rotary Shaker:
Rotary shaker was applied for shaking to all the solutions in conical flasks for a constant time. The contents of the flask were shaken at a constant value of 100 rotations per min.

Fig 2: Rotary Shaker

2.3 Procedure
Preparation of Standard Stock Solution
The stock solution containing 1000 ppm of Indigo Carmine dye was prepared by dissolving a known quantity of Indigo Carmine in 1000 ml of distilled water.

Sea Shells
Sea shells were obtained from shores of Kundapur District and they were washed and sun dried for two days and then they were grinded using mortar and pestle. The grinded powder was then subjected to sieve shaker for the particle size distribution. The particles obtained from the pan size (Pass through 8 mesh) was used for further analysis. Thus obtained adsorbents were further treated with 0.5N HCl and it was soaked for 2 hours and then it was sundried for 24hours. The dried powder was further washed with distilled water to remove the acid content and it was ven dried at $105^{o}C$ and used for the analysis.

2.4 Batch Adsorption Studies
All the laboratory scale experiments were carried out at room temperature, i.e., $30 \pm 5^{o}C$. A stoppered conical flask containing 100ml of test solution was used to carry out batch adsorption studies. Desired pH value, contact time and adsorbent dosage level was maintained, pH of the solution was monitored by adding 0.1N HCl and 0.1N NaOH solution as required. Calculated amount of adsorbent material was then added and contents in the flask were shaken by varying the contact time in a rotary shaker working at 100 rotations per minute. The time required for reaching the equilibrium condition estimated by drawing samples at regular intervals of time till equilibrium was reached. The contents of the flask were filtered using Whatmann filter paper no 41 and the filtrate was analysed for the concentration of the sample using the UV Visible Spectrophotometer by following the standard methods to evaluate water and waste water.

The amount of IC dye adsorbed per unit mass of the adsorbent was evaluated by using the following mass balance equation,
$q = (C_o - C_f)(v/w)$
The percent removal of Indigo Carmine dye was calculated as follows:

$$\text{Percentage removal (\% removal)} = \frac{(C_o - C_f)}{C_o} \times 100$$

Where,
C_o and C_f are initial and final concentrations of the dye
q→Adsorption capacity (mg/g)
C_o →initial concentration (ppm)
C_f →final concentration (ppm)
v→ volume of the solution (L)
w→ weight of the adsorbent (g)

Effect on variation of initial concentrations was studied with the variation of Indigo Carmine dye solution from 10ppm to 50ppm with an adsorbent dosage of 4g/L and contact time of 60 minutes. Further metrics were varied to know the best percentage removal of IC dye under the given conditions.

The effect of contact time was studied on the percent removal of IC dye concentration of 10 ppm with pH adjusted to 5. The contact time was varied from 30 minutes to 120 minutes.

The effect of adsorbent dosage level on percent removal of IC dye was studied using IC dye concentration of 10ppm with pH adjusted to 5. The adsorbent load was varied from 4g/L to 20g/L.

Adsorption experiments for the effect of pH were conducted by using a solution having concentration 10ppm of IC dye with an adsorbent dosage of 4g/L and contact time of 120 minutes.

2.5 Metrics Study

2.5.1 IC dye concentration:

100 ml solutions were prepared of different concentrations by appropriate dilution of the standard solution. The concentrations taken were ranging from 10ppm to 50ppm. The five different concentration solutions were prepared in 250 ml conical flasks. The adsorbent was used for different contact times to be shaken with the solution samples and the final concentration readings were taken to determine the percentage removal of IC dye.

2.5.2 Adsorbent Dosage:

100 ml of different concentration solutions were taken in 250ml conical flasks and adsorbent was used for the adsorption process .The adsorbent amount was varied ranging from 4g/L to 20g/L. Experiments were carried at room temperature at a constant pH determined experimentally. The results were obtained showing that with increase in the amount of adsorbents used, the adsorption increased initially. After a certain point the graph was getting constant meaning no further increase in adsorbent dosage had no effect on the removal of IC dye.

2.5.3 Contact Time:

The concentration of IC dye was maintained constant of 10ppm and the contact time was varied from 30 min to 180 mins keeping the pH value and adsorbent dosage constant. The results were obtained and it was seen that with the increase in contact time, i.e., the shaking time of the samples with the adsorbent, the adsorption also increases, till a certain time, after which the graph became constant meaning the equilibrium has attained.

2.5.4 pH:

The concentration of IC dye solution chosen for this experiment was 10ppm. The pH was varied from 3 to 11 and the contact time was taken to be 120 minutes. The results were thus obtained and it was found that maximum removal took place at a pH of 5.

3. RESULTS AND DISCUSSION

This chapter mainly deals with the results obtained by varying different metrics and the inference drawn from each of them. Graphical plots are included to show the effect on the percent removal of IC dye. Different metrics such as contact time, pH, and adsorbent dosage are varied to determine the optimized condition.

3.1 Effect of IC dye concentration:

The efficiency of the % removal of IC dye was affected with the variation of the initial concentration of the dye solution. The %removal decreased with increase in the concentration of the solution from 10 to 50 ppm. As the concentration increases the amount of adsorbent required to adsorb decreases and thus it reaches equilibrium.
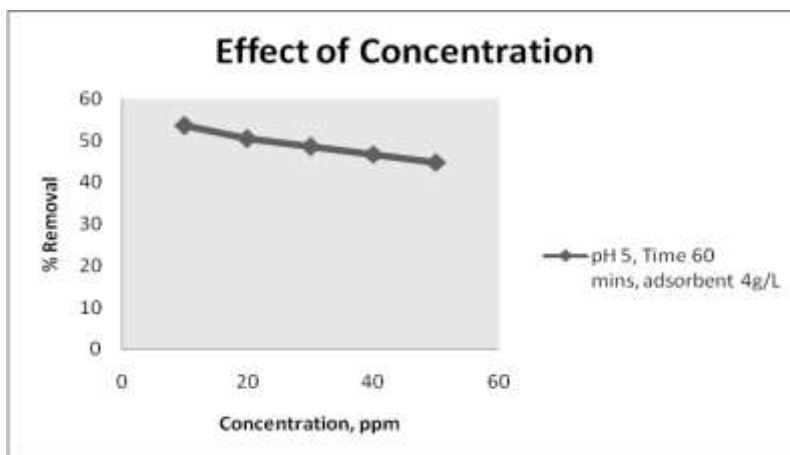
Fig 3: % Removal vs Concentration

3.2 Effect of Adsorbent dosage:

The efficiency of the % removal of IC dye was affected with the variation of the adsorbent dosage. The % removal increased as the amount of adsorbent dosage increased from 4 to 20 g/L. Increase in the active sites of the adsorbent increased the % removal and the variation was found to saturate at 20g/L.
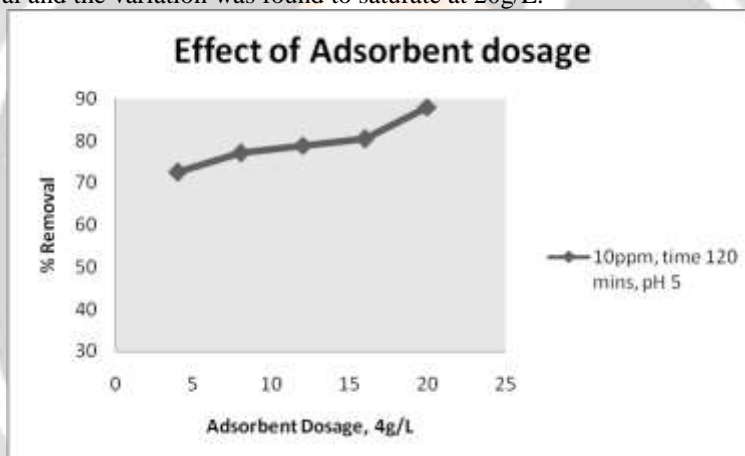

Fig 4: % Removal vs Adsorbent dosage

3.3 Effect of Contact time:

The experimental runs measuring the effects of contact time on the batch adsorption of Indigo Carmine was carried out at pH maintained at 5 for 10 ppm concentration and 4g/L adsorbent dosage. In the first 30 mins the % removal was increased to 50% and was increasing with time. At 120th min % removal became constant and no change in removal % with increase in time.
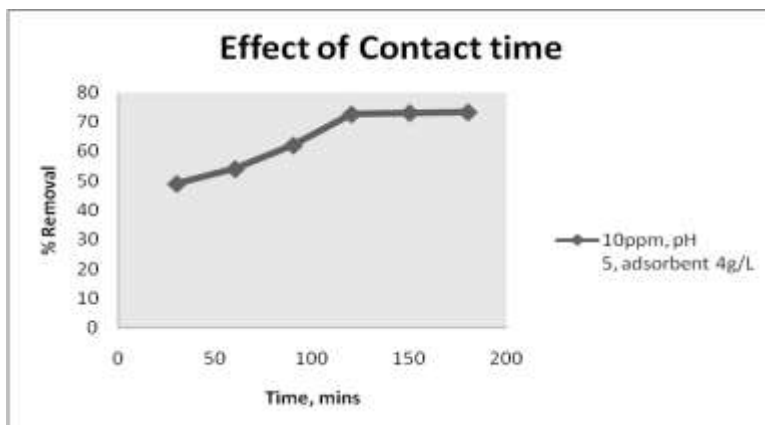
Fig 5: % Removal vs Contact time

3.4 Effect of pH:

The experimental runs measuring the effects of contact time on the batch adsorption of Indigo Carmine was carried out for 10ppm concentration, 120 min contact time and 4g/L adsorbent dosage. The percent removal was found in range of pH between up 3 to 5, and there after it decreases with further decrease in pH upto 11.
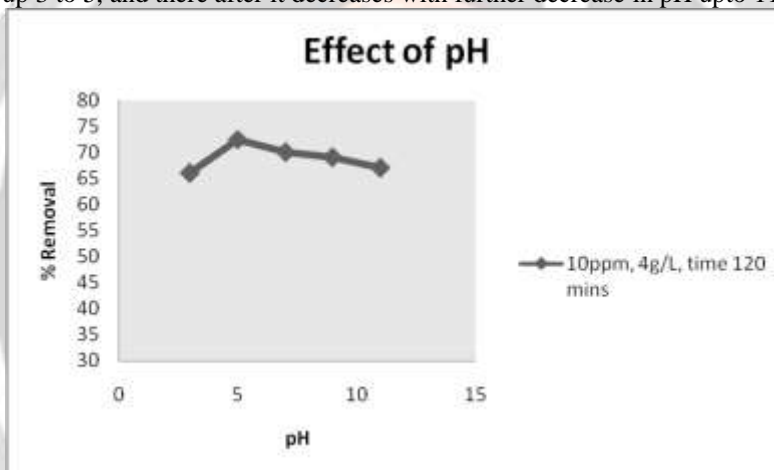

Fig 6: % Removal vs pH

3.5 Kinetic Studies:

Kinetic studies were carried out for the samples obtained and checked for the reaction rate constant. A plot of $-\ln(C_f/C_o)$ vs time yielded a slope of 0.006 min^{-1} which indicates the rate constant. Thus the values obtained follows first order kinetics.
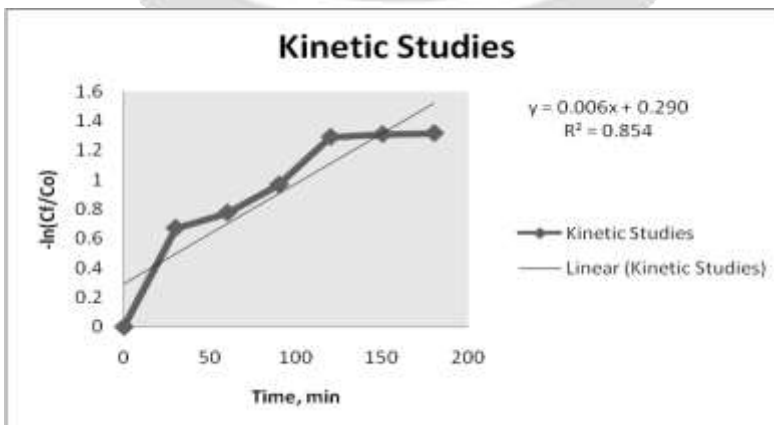

Fig 7: Kinetic parameter evaluation

4. CONCLUSIONS

Batch adsorption studies for the removal of IC dye from aqueous solutions have been carried out by using modified biopolymer (Seashells) as adsorbent. The study indicated the suitability of the seashells as adsorbent for removal of IC dye. Thus the selected biopolymer is suitable for the removal IC dyes from the prepared synthetic waste water. The obtained results are summarized as follows. The concentration variation studies showed that at lower concentrations the removal efficiency was maximum and it increases further with the increase in the adsorbent dosage and contact time. The pH of the solution was found to be optimum at 5. The following are the optimized conditions Concentration 10ppm, Contact time 120 min, Adsorbent dosage 20g/L and pH 5. The removal percent was found to be 88%. Kinetic studies was done to determine the reaction rate constant and it was found to be 0.006min^{-1} and the it follows first order kinetics.

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