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Removal of methylene red from aqueous solution by adsorption on treated and untreated red Kotta powder

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ABSTRACT

In the present work, the building waste material Red Kotta was treated with sulphuric acid and formaldehyde and used as an adsorbent for the removal of Methylene red from aqueous solution. The adsorption characteristics of Methylene red dye on untreated and treated Red Kotta powder was evaluated as a function of pH, adsorbent dose, initial concentration of adsorbate, contact time and temperature. The effective adsorption was found to be in pH range 2 to7, adsorbent dose 1gm to 5 gm, initial concentration (100ppm to 500ppm) and temperature range (283K to 313K). The results show that Red Kotta powder holds a great potential in removal of Methylene red dye from industrial wastewater.

Introduction

Dyestuffs play an important role in the textile, food and cosmetic industries[1]. Due to their good solubility, synthetic dyes are common water pollutants and they may frequently be found in trace quantities in industrial wastewater. However, the discharge of dye bearing wastewater into natural streams and rivers possess a several problem, as dye impart toxicity to aquatic life and are damaging the asthetic nature of the environment however, wastewater containing dyes is difficult to treat since the dyes are recalcitrant organic molecules resistant to aerobic digestion, and are stable to light, heat and oxidizing agents due to light, heat and oxidizing agents due to their structure and molecular size[2,3].

There are various conventional methods of removing dyes including coagulation and flocculation[4], oxidation or ozonation[5] and membrane separation[6], However, these methods are not widely used due to their high cost and economic disadvantages chemical and electrochemical oxidations, coagulation are generally not feasible on large scale industries. In contrast, an adsorption technique is by far the most versatile and widely used to remove dyes in waste water because of its excellent adsorption ability. Adsorption techniques have gained favor in recent years because of their proven efficiency in the removal of pollutants from effluents too stable for conventional treatment methods .The most common adsorbent materials are alumina silica[7] and activated carbon[8]. As proved by many researchers[9,10], removal of dyes by activated carbon is economically favorable and technically easier.

Material and methods

Preparation of adsorbents:

The waste red kotta stone were collected from a local stone cutting shop. Red kotta powder were grinded into powder and were boiled in distilled to remove any dust from it and filter the residue of red kotta (untreated) and then it was treated with formaldehyde and finally with very dilute solution of sulphuric acid. It was then stirred for half an hour vigorously using mechanical stirrer at room temperature then it was filtered and washed with distilled water repeatedly to remove free acid.

After chemical treatment the residue (treated Red kotta) was dried first in air and finally in oven at 90-100^{0}c for 8-10 hours and powdered electric grinder.

The adsorbent once prepared were used throughout the experimental work. The particle size of the adsorbent was of the same mesh (micron).

Dye solution preparation:

Methylene red (sigma–Aldrich chemic Gmbn, Germany) was used to prepare the simulated waste water.

An accurately weighed quantity of methylene red (0.5635 g) was dissolved in distilled water to prepare the stock solution was then properly wrapped with aluminum foil and stored in dark place to prevent direct sunlight, which may cause decolourisation experimental solutions of the desired concentration were obtained by successive dilutions.

Experimental methods and measurements:

In each adsorption experiment, 100ml of dye solution of known concentration and pH was added to 1gm of adsorbent in 250 round bottom flask.

This was done at a room temperature (27 $\pm$ 1^{0}c) and the mixtures were stirred on a rotator orbital shaker at 160 rpm. The initial pH of the mixtures was varied between 2-7 this was controlled by addition of dilute HCl or NaOH solutions.

Kinetic of adsorption was determined by analyzing adsorptive uptake of the dye from aqueous solution therefore, samples were withdrawn from the shaker every 15 to 30 minutes and adsorbent was separated from the solution by centrifugation at 4500 rpm for 5 minutes. In order to determine the residual dye concentration the absorbance value of the supernatant solution was measured before and after the treatment, at 617 nm with shimadzu spectrophotometer.

The experiment was done by varying the amount of adsorbents(1gm to 5gm 100ml^{-1}) concentration of dye solution (100-500 mg L^{-1}) and pH (2-7) at different time interval.

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Results and discussion

Effect of initial dye concentration:

In the present study, it has been observed that for the activated Red Kotta powder, the percentage of dye removal was very high as compared with untreated Red Kotta. The experiments were carried out at fixed adsorbent dose (0.9 gm 100ml) at constant temperature.

The variation in the concentration of the dye solution (0.5to5.0/10^{-5}M) does not show any measurable change in the equilibrium time though the variation in uptake is observed at intermediate stages is in the range of (0.5 to 5.0/10^{-5}M). These concentration ranges follows the Lambert's Beer's law[15] generally adsorption consists of diffusion of the dye molecule from the bulk solution to the surface of the adsorbent mostly the adsorbed dye content gradually increases constantly upto certain time limit and finally attains the equilibrium indicating a saturated adsorption[16-17]. The lower uptake at higher concentration resulted from an increased ratio of initial adsorption number of moles of the dye to the available surface area; hence fractional becomes dependent on initial concentration. For a given adsorbent dose the total number of available adsorption sites is fixed thereby adsorbing almost the same amount of adsorbate, thus resulting in a decrease in the removal of adsorbate corresponding to an increase in initial adsorbate concentration (figure 1). Similar results were also reported by other researchers [18].

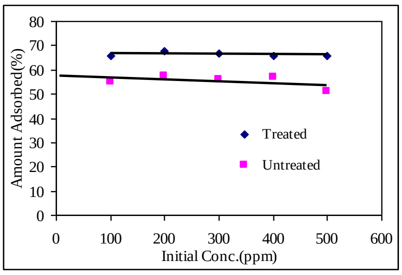

Fig. 1 Effect of Initial Concentration on adsorption of Methylene Red

Effect of adsorbent dose:

The adsorption of methylene red on sulphuric acid treated by changing the quantity of adsorbent (1gm to 5gm/100ml) in the test solution while keeping the initial dye concentration (250mg/L) temperature (27 ± 1^0c) at pH 7.0 constant. Experiments were carried out at different contact time for 30 minutes. It followed the predicted pattern of increasing percentage sorption as the dosage was increased. This is probably because of the resistance to mass transfer of dye from bulk liquid to the surface of the solid, which becomes important at high adsorbent loading in which the experiment was conducted.

The percent adsorption increased and equilibrium time decreased with increasing adsorbent doses. The adsorption increased from 66.88 to 71.98 % as the sulphuric acid treated dose was increased from 1gm to 5gm/100ml at equilibrium time maximum dye removal was achieved within 90-120min after which methyl red concentration in the rest solutions was almost constant (figure 2). Increase in the adsorption with adsorbent dose can be attributed to the increase in the adsorbent surface area and availability of more adsorption sites[19]. The present study reveals that with increase in the amount adsorbent dose i.e. from 1gm to 5gm there is an increase in the adsorption of dyes onto the surface of untreated and treated red kotta powder, which may be attributed to the increase adsorbent dose which provides a greater surface area and larger number of adsorption sites and hence enhancement of dye uptake[20].The primary factor explaining this characteristic is that adsorption sites remain unsaturated during the adsorption reaction whereas the number of sites available for adsorption site increases by increasing the adsorbent dose[21].

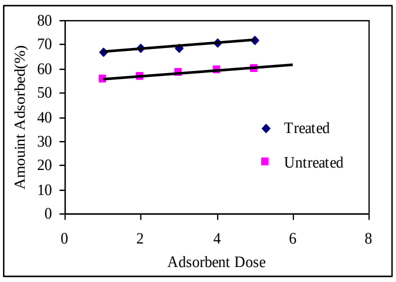

Fig. 2 Effect of adsorbent dose on adsorption of Methylene Red.

Effect of pH:

In order to study the effect of pH on methylene red adsorption on red kotta powder and sulphuric acid treated red kotta powder. Experiments were carried out at 250mg/L initial dye concentration with 0.9gm/100ml adsorbent mass at room temperature of 27 ± 1^0c for one hour. In the case of untreated red kotta powder, maximum dye removal of 46.67% and 75.78% was recorded at pH 7 between pH range of 2-7, the percentage of dye removal was nearly equal 20% although dye adsorption efficiency for sulphuric acid treated red kotta powder is having higher adsorption.

The adsorption at lower pH may be attributed to the increase in concentration of hydrogen ion in dye solution which neutralizes hydroxyl group in the vicinity of adsorbent surface and facilitated the diffusion of dye molecule toward the surface of adsorbent similarly diminished adsorption were reported by Bahadur et al[22]. At higher pH due to the availability of large number of OH^- ion and consequently the diffusion barrier is increased which results into poor adsorption. In present findings at higher pH there is change in order of reaction with change in pH(figure 3), which suggests the role of adsorbent as it may be leaching out at higher pH as adsorbent is building waste material consisting mainly various organic components, therefore our studies restricted to the higher pH level upto 7.20.

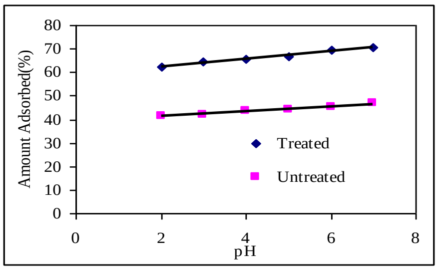

Fig. 3 Effect of pH on adsorption of Methylene Red

Effect of contact time:

Equilibrium time is an important parameter for an economical wastewater treatment system. For a given substance to be effective as an adsorbent of organic dyes, its adsorption rate must be fast and quantitative. The effect of contact time on the amount of dye adsorbed on the untreated and treated red kotta was investigated at 100 ml of dye solution of initial concentration of 10^{-5}M at room temperature. In case untreated red kotta removal of Methylene red was maximum (figure 4). Such uptake indicates a high degree of affinity towards dye molecules via chemisorptions[23]. After the rapid uptake, the capacity of the adsorbent became exhausted and the adsorption would be replaced by the transportation of dye from the external sites to the internal sites of the adsorbent particles. The uptake rate began to drop down in case of treated red kotta, which may be attributed to intra-particle diffusion model[24].

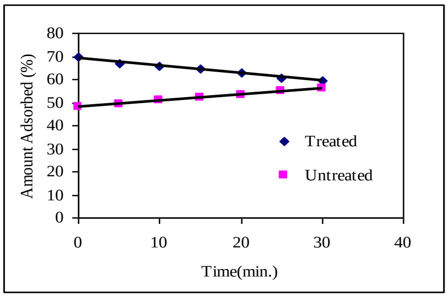

Fig 4. Effect of Contact time on Adsorption of Methylene Red

Effect of temperature:

Temperature is one of the most important factors, which determines the extent of adsorption of given system. Its influence in deciding the actual alternation is both positive and negative, and depends on the nature of interaction involved. In general, the level of adsorption at any particular concentration usually decreases with increase in temperature, i.e., the overall process is exothermic[25-26]. A lowering of temperature is favorable for large adsorption in the case where physical adsorption is predominant. On the other hand in chemisorptions or in activated adsorption, an elevated temperature is preferred. In present investigation removal of Methylene red on both treated and untreated red kotta decrease in temperature (figure 5). Our finding is well supported by the earlier reported work[27].

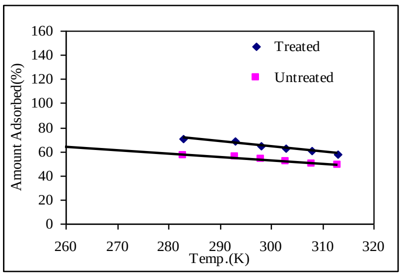

Fig. 5 Effect of Temperature on adsorption of Methylene Red

Conclusion

Building waste material red kotta powder is easily available at a negligible price. The removal of methylene red from simulated wastewater using untreated and chemically treated red kotta powder with sulphuric acid has been investigated under different experimental conditions in batch mode. The adsorption of methylene red was dependent on the adsorbent dose and the methylene red concentration in wastewater. The results show that as amount of the adsorbent was increased, the percentage of dye removal increased accordingly as the concentrations of methylene red increases, percentage of adsorption also increases. Higher adsorption percentages were observed at 2-7 pH. Sulphuric acid treated red kotta powder showed a better performance compared to untreated red kotta powder. This study proved that red kotta powder is an attractive option for dye removal from dilute industrial effluents.

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