



STUDIES ON THE REMOVAL OF CATIONIC DYES FROM AQUEOUS SOLUTION BY MIXED ADSORBENTS

AMITA SHARMA*

Chemistry Department, Dhanauri College, Dhanauri, HARIDWAR – 247667 (Uttarakhand) INDIA

ABSTRACT

Studies on the (FA) removal of cationic dyes from aqueous solution by adsorption on low cost mixed adsorbents, namely flyash, bagasse (BG) and rice husk (RH) as an adsorbent and blending (mixing) them with bentonite. The modifications and combinations of sorbents to form bentonite blended decolourizers enhanced sorption capacity of sorbents by 10 to 20%. The effect of various parameters affecting the adsorption such as initial dye concentration, adsorbent dose and pH were determined. Adsorption decreases with rise in dye concentration but increases with increases in adsorbent dose. The maximum removal was with FA: 69.0% CV, 64.1% MB and 63.6% MG at dye concentration 10 mg/L, sorbent dose 10 g/L, at pH 7.5, temperature 25°C, contact time 5 h and rpm 150. Under the same conditions RH.: was found to remove 62.2% CV, 53.9% MB and 49.3% MG. The order of dye removal capacities for these chemical (mixed) adsorbents was found FA > BG > RH. The order of removal/sorption of dyes was CV > MB > MG. The optimum pH was 7.5 for all the dyes under investigation. Thus, alkaline medium favours the dye removal.

Key words: Cationic dye, Crystal violet, Malachite green, Methylene blue, Adsorbent, Fly ash, Bagasse, Rice husk.

INTRODUCTION

Textile industry plays an important role in the industrial development of India and is the second largest sector of India economy, next to agriculture. Textile dyeing industries are a part of textile industry, which involves the dyeing process for making coloured garment by means of large consumption of dyestuffs. During the dyeing process, a large quantity of water (100 to 200 L/Kg of fabric) is used and the wastewater is highly coloured due to the presence of unfixed dye. In India, the textile dyeing industries are placed under the category of highly polluting industries and the removal of colour from the textile dyeing wastewater has been brought under the preview of legal and regulatory requirements¹.

* Author for correspondence; E-mail: pk80sharma@gmail.com

The adsorption process plays an important role in different fields, like industrial, chemical, metallurgical, engineering, wastewater engineering and analytical chemistry. It is widely employed for wastewater treatment^{2,3}. Adsorption methods using activated carbon are not economical either, because the raw materials for the preparation of activated carbons are not cheap. Hence, there is a need to produce low cost adsorbents for the economic treatments for industrial effluents. Effective and economical removal of dyes from industrial wastewater has resulted in a search for low cost nonconventional methods and materials⁵. This paper reports the preliminary findings of the applications of the carbon prepared from flyash, bagasse and rice husk as an adsorbent and blending (mixing) them with 1, 5, 10, 15, 20% bentonite for maximum removal of cationic dyes from aqueous solutions by batch processes. The composition of different blends were investigated and optimized to enhance decolourization. The blends may behave similar to AC, resins and chelating agents that are very expensive in comparison with clay based materials. Bentonite is a natural clay containing mainly mineral montmorillonite as an important constituent, getting its name from Montmorillon, France where montmorillonite was discovered in 1847. From this constituent, bentonite derives its specific properties such as its capacity for suspending, supporting, stabilizing and swelling. The study includes the effect of nature and concentration of dye, contact time, sorbent dose and pH.

EXPERIMENTAL

Material and method

Dye solution

Four aqueous solutions of 0.1, 1, 10 and 20 mg/L concentrations of each of the proposed dye crystal violet (CV), malachite green (MG) and methylene blue (MB) were prepared by dissolving commercial grade dyes in distilled water. The dyes were obtained from CDH Pvt. Ltd.

Preparation of adsorbents

Natural and easily available materials like FA, BG and RH were used as adsorbents for the dyes. PAC was prepared from agro waste product treated with hot distilled water and dried at 100°C. 50 g of the product so obtained was treated with 50 mL of conc. H₂SO₄ and then it was carbonized at 150°C for 12 hrs. The sorbent was dried and crushed to increase the surface area. The particle size of 150 microns was determined with a standard test sieve⁴. FA and BG were obtained from Chhata Sugar Mill, Mathura. RH was obtained from local factories. Adsorbents were analyzed using standard methods and their properties are presented in Table 1.

Table 1: Characteristics of adsorbents

Parameters or characteristics	FA	RH	BG
	Composition (%)		
Moisture	5.67	4.22	3.22
Ash	5.68	8.36	6.36
Carbon	78.9	81.73	71.73
Silica	3.02	4.64	4.65
Sodium	0.17	0.09	1.00
Potassium	0.27	0.23	0.25
Calcium	0.41	0.32	0.31
Magnesium	0.07	0.01	0.04
Phosphorous	0.06	0.03	0.04
Iron	0.32	0.12	0.14
Properties			
pH	7.34	7.83	7.84
Conductivity (μsm)	0.75	0.62	0.64
Specific gravity	1.10	1.12	1.14
Porosity (mL/g)	0.83	0.72	0.62
Surface area (m ² /g)	328	298	208

Batch studies

The interaction studies were carried out in batch tests. In 6 numbers of 250 mL capacity glass bottles, 0.5 g of adsorbent was added to each of the three sets, each having two bottles for different concentrations of a dye and 50 mL of the dye solution was added to each bottle. The bottle was shaken in a reciprocating shaker at 150 rpm for 5 hrs at room temperature. Then the contents were centrifuged at 2000 rpm for 10 min and the supernatant liquid was filtered using 0.45 μm member filter. The filtrate was analysed for the dye concentration. Dyes were determined in triplicate with respect to each concentration and results were averaged. The uptake of dyes on the sorbent at different concentrations of initial feed was thus calculated and tabulated in Table 2. To study the effects of sorbent dose and

pH on sorption, 1, 5, 10 and 20 g sorbent/L of dye solution and pH values 9.0, 7.5, 6.0 and 4.5 of the medium were taken.

RESULTS AND DISCUSSION

Effect of initial concentration on dye sorption

The effect of initial concentration on the sorbed amount of dyes (mg/g) can be calculated from Table 2. Sorption capacity was found to decrease with increase in contaminant concentration. The higher uptake at lower initial concentration can be attributed to the availability of more isolated dye molecules. The maximum removal was with FA: 69.0% CV, 64.1% MB and 63.6% MG at dye concentration 10 mg/L, sorbent dose 10 g/L, pH 7.5, temperature 25⁰C, contact time 5 hr and rpm 150. Under the same conditions RH: was found to remove 62.2% CV, 53.0% MB and 49.1% MG and for BG it was found to remove 64.2% CV, 63.6% MB and 62.5% MG. The order of dye removal capacities for these chemical (mixed) adsorbents was found FA > BG > RH. The order of removal/sorption of dyes was CV > MB > MG. Adsorption decreased with rise in dye concentration but increased with increase in adsorbent dose.

Table 2: Removal % of dyes by sorbents blended with 10% bentonite at different concentrations and at adsorbent dose 10 g/L, pH 7.5, temperature 25⁰C, contact time 5 hr and rpm 150

Dye	Conc. (mg/L)	FA	BG	RH
CV	1	70.7	67.4	65.9
	5	69.3	65.1	64.3
	10	69.0	64.2	62.2
	15	63.2	62.4	60.1
MB	1	68.5	66.0	60.2
	5	65.6	64.5	54.0
	10	64.1	63.6	53.0
	15	62.0	56.8	51.1
MG	1	67.1	65.5	58.1
	5	64.7	64.0	53.4
	10	63.6	62.5	49.1
	15	51.6	51.0	48.8

Effect of adsorbent dose

The effect of adsorbent dose on the adsorption of dyes using different adsorbents at pH 7.5 and temperature 25°C is depicted in Table 3. It clearly indicates that their percent removal increased with increase in adsorbent dose. It is obvious from this table that as the sorbent dose was increased, percent contaminant removal also increased, but after an optimum dose of 10 g adsorbent per litre of contaminant solution, there is an appreciable change in removal. Further, at lower adsorbent dose, the adsorbent is more easily accessible and because of this, removal per unit weight of adsorbent is higher. The maximum removal was with FA: 69.0% CV, 64.1% MB and 63.6% MG at dye concentration 10 mg/L, sorbent dose 10 g/L, at pH 7.5, temperature 25°C, contact time 5 h and rpm 150. Under the same conditions RH was found to remove 62.2% CV, 53.9% MB and 49.3% MG and for BG, it was found to remove 64.4% CV, 63.5% MB and 62.4% MG. The initial rise in adsorption with adsorbent concentration is probably due to bigger driving force and lesser surface area. Larger surface area of sorbent and smaller size of adsorbate favour adsorption. The rate of adsorption is high in the beginning as sites are available and unimolecular layer increases.

Table 3: Removal % of dyes by sorbents blended with 10% bentonite at different sorbent doses and at dye concentrations 10 mg/L, pH 7.5, temperature 25°C, contact time 5 hr and rpm 150

Dye	Dose (g/L)	FA	BG	RH
CV	1	64.7	61.5	56.8
	5	65.3	63.5	59.2
	10	69.0	64.4	62.2
	20	70.8	69.8	64.8
MB	1	60.2	55.7	50.9
	5	63.0	56.3	52.8
	10	64.1	63.5	53.9
	20	67.1	65.5	62.3
MG	1	50.3	49.0	45.0
	5	51.4	50.4	47.8
	10	63.6	62.4	49.3
	20	66.5	63.6	60.3

Effect of pH

The influence of pH of solution on the extent of adsorption of dyes is depicted in Table 4. The dye removal is highly dependent on pH of the wastewater, which affects the surface charge of the adsorbent and degree of ionization. pH effects were found to be slightly different for different dyes. The optimum pH was 7.5 for all the dyes under investigation. Thus, alkaline medium favoured the dye removal.

Table 4: Removal % of dyes by sorbents blended with 10% bentonite at different pH values and at dye concentrations 10 g/L, adsorbent dose 10 g/L, temperature 25°C, contact time 5 hr and rpm 150

Dye	pH	FA	BG	RH
CV	9.0	60.1	54.3	53.4
	7.5	69.2	64.8	62.9
	6.0	56.2	52.1	50.7
	4.5	53.8	50.1	48.2
MB	9.0	54.2	52.5	49.5
	7.5	64.5	63.4	53.5
	6.0	51.6	48.2	47.8
	4.5	50.5	46.1	45.4
MG	9.0	51.2	48.3	47.1
	7.5	63.3	62.8	49.8
	6.0	47.3	43.8	42.4
	4.5	44.1	41.8	40.9

The optimum pH for dye removal was found in the acidic medium. The reason may be attributed to the large number of H⁺ ions in acidic medium neutralize negatively charged adsorbent surface; thereby, reducing hindrance to diffusion of dichromate ions. At higher pH, the abundance of OH⁻ ions create increased obstacle to diffusion of anions, but can support cation removal by adsorption cum precipitation.

CONCLUSIONS

Conclusions can be drawn from the above results that sorption capacity decreases with increase in dye concentration. The higher uptake at lower initial concentration can be

attributed to the availability of more isolated metal ions or dye molecules. The effect of various parameters affecting the adsorption such as initial dye concentration, adsorbent dose and pH were determined. Adsorption decreases with rise in dye concentration but increases with increase in adsorbent dose. The removal was with FA: 69.0% CV, 64.1% MB and 63.6% MG at dye concentration 10 mg/l, sorbent dose 10 g/l, at pH 7.5, temperature 25^oC, contact time 5 h and rpm 150. Under the same conditions RH: was found to remove 62.2% CV, 53.9% MB and 49.3% MG. The order of dye removal capacities for these (mixed) adsorbents was found FA > BG > RH. The order of removal/sorption of dyes was CV > MB > MG. As the sorbent dose was increased, percent dye removal also increase, but after an optimum dose of 10 g adsorbent per litre of dye solution, there is no appreciable change in removal. The optimum pH was 7.5 for all the dyes under investigation. Thus, alkaline medium favours the dye removal. The modifications and combinations of sorbents to form bentonite blended decolourizers enhanced sorption capacity of sorbents by 10 to 20%.

ACKNOWLEDGEMENT

Author is thankful to be “Care Takers” and Dr. R. P. Singh, Department of Chemistry, St. John’s College Agra for their kind cooperation in order to complete this work.

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Revised : 05.08.2014

Accepted : 08.08.2014