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Kinetics Study of Methyl Orange Adsorption from Aqueous Solutions using Fly Ash Granules as Low Cost Adsorbent

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Fly ash obtained from a thermal power station was granulated using a biopolymer and used as an adsorbent to remove methyl orange (MO) dye from solutions. Uptake of MO from solutions occurred in 30 min of contact and obeyed Langmuir isotherm model. Results point to waste flyash as a promising alternative for removal of azo-dyes such as methyl orange from industrial wastewaters.

Keywords: Adsorption, Biopolymer, Granulation, Methyl orange dye, Wastewater

Introduction

Wastewater emanating from the textile, dyeing and finishing industries cause pollution of the environment, particularly the water resources and soil.[1] Due to high chemical stability and toxicity of dyes, it is necessary to design efficient and cost effective methods of treating dye bearing wastewaters prior to disposal. Fly ash, an abundantly available waste material was used to remove the toxic azo-dye, methyl orange (MO) from aqueous solutions. Biopolymer-based granulation of fly ash aided in ease of handling and disposal after use.

Materials and methods

Fly ash sample and granulation using alginate

Fly ash was obtained from Nashik Thermal Power Plant, Eklahara, Nashik and washed with water, if required, to remove any dirt and activated by heating at 100°C for up to 12 hr. Sodium alginate solution (1% w/v, 100 ml) was added to fly ash powder (10g), mixed thoroughly and extruded drop-wise using a 5 ml syringe into cold $CaCl_2$ (0.1 M) solution. The granules were washed, allowed to harden and stored until use.

Dye sample

Methyl orange powder (100 mgL^{-1}) was added to deionized distilled water to prepare stock solution that was appropriately diluted with deionized distilled water for experiments.

Adsorption studies

Varying amounts of fly ash powder and granulated fly ash were added to MO solutions of varying concentrations (1–20 mgL^{-1}, 5ml, pH 5.5 ± 0.1) in test tubes, mixed and incubated at ambient temperature, c.a. 25°C ± 2°C on an orbital shaker (100 rpm, Orbitek, India) for up to 2 hr. The fly ash was separated by using a Whatman No.1 filter paper and filtrates analyzed for dye content spectrophotometrically at 470 nm. Dye solutions without addition of fly ash/granulated fly ash served as the negative controls, while samples with activated carbon were used as positive controls. The efficiency (%) of dye removal was calculated from the absorbance of samples and controls.[2,3] The uptake capacity (Q_e, mgg^{-1}) was calculated from equilibrium dye concentration (C_f, mgL^{-1}). The kinetics of MO removal by fly ash was studied according to the popular Freundlich and Langmuir isotherm models.

Results and Discussion

Fly ash sample and granulation

As obtained fly ash sample was homogeneous with particle size <5µ and pH_{pzc} of 6.5. In order to facilitate the handling of fine particulates and ease of disposal after use, it was necessary to granulate it. The effectiveness of alginate matrix for granulation of

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nanoparticles has been reported for removal of acid black 1 from solutions.[4] Due to biocompatibility, biodegradability, hydrophility and non-toxicity, alginate is used for immobilization of enzymes, therapeutics, biochemical agents and microorganisms[5]. In the present study the yellowish grey spherical granules of alginate-fly ash composite (3.4 mm diameter) showed good porosity and >40% swelling in aqueous medium.

Dye sample

Methyl orange, a water soluble azo dye is used in textile and paper industries and research laboratories[6]. According to GHS classification, it comes under Category IB and is toxic and carcinogenic with low biodegradability.[6–8] It is difficult to remove from aqueous solutions by conventional methods.[6] The pH of MO sample was adjusted to 5.5 for experiments to ensure that surface binding sites on the adsorbent (fly ash) were positively charged at this pH.

Adsorption studies

Methyl orange was rapidly adsorbed by activated charcoal and fly ash powder with maximum efficiency (>85% and 55%, respectively) attained in 15 to 30 minutes (data not shown). This indicated saturation of available binding sites on the adsorbents. Granulated fly-ash displayed marginally lower efficiency of about 52% owing to altered mass transfer kinetics. It was found that dye removal efficiency of fly ash powder was higher (>44%) at higher adsorbent dosage of 500 mgL^{-1} (Table 1). This was obvious since a larger number of reactive sites on the adsorbent surface were available for binding. However, increasing the adsorbent levels to 1000 mgL^{-1} did not cause significant increase in efficiency, probably due to a masking effect. Similar trend was evident in case of the fly ash granules. As shown in Table 2, maximum removal of MO, i.e. >50% was observed at dye concentration <5 mgL^{-1}. Increase in dye concentration to 10 mgL^{-1} resulted in a sharp decline in the dye removal efficiency (<15%) due to saturation of binding sites. Similar observations were reported for indigo carmine removal using dead biomass of *Pleurotus ostreatus* by Dogan *et al*. (2018).[9]

Since the percent dye removal is often misleading, the results were expressed in terms of specific dye loading capacity (Q_s, μgg^{-1}) on a dry weight basis. As shown in Table 2, at low MO concentration of 1 mgL^{-1}, the values of specific dye loading for activated carbon, fly ash powder and fly ash granules were 4.25, 3.4 and 2.85 μgg^{-1}, respectively. The values increased to 1081, 170 and 164.23 μgg^{-1}, respectively at high MO concentration of 20 mgL^{-1}. In contrast, Table 1 shows that maximum specific dye loadings (70 and 63 μgg^{-1} for powdered and granulated fly ash, respectively) were obtained at low adsorbent concentration of 200 mgL^{-1} and low specific loadings were found at high adsorbent concentration of 1000 mgL^{-1} (51 and 44 μgg^{-1}, respectively). The results indicated that when dye recovery from wastes is desired, it might be more preferable to employ high adsorbent dosages with some compromise over the removal efficiency. However, for elimination of toxicity, high efficiency of dye removal must be achieved by employing higher adsorbent dosages.

The Langmuir and Freundlich adsorption isotherms give useful information on the mechanism of sorption,

Table 1 — Effect of adsorbent dosage on the efficiency of dye removal and specific dye loading capacity of fly ash powder and granules

Adsorbent	200 (mgL^{-1})		300 (mgL^{-1})		500 (mgL^{-1})		1000 (mgL^{-1})	
	%E	Q_s (μg/g)	%E	Q (μg/g)	%E	Q (μg/g)	%E	Q (μg/g)
Fly ash powder	06.21	70	11.11	69	44.44	65	45.97	51
Fly ash granules	05.02	63	10.27	61	42.45	60	44.89	44

Table 2 — Effect of dye concentration on efficiency of MO removal and specific dye loading capacity of fly ash powder, fly ash granules and activated carbon

MO Conc. (mgL^{-1})	Activated carbon		Fly ash powder		Fly ash granules	
	%E	Q_s (μgg^{-1})	%E	Q_s (μgg^{-1})	%E	Q_s (μgg^{-1})
1	92.3	4.25	63	3.4	62.13	2.85
2	91.02	12.23	58.30	11	54.02	10.40
5	90.16	100.1	54.11	64	51.15	62.40
10	87.56	312.0	13.02	74	11.41	72.22
15	85.22	1004	11.04	110	09.12	107.41
20	82.13	1081	6.09	170	5.30	164.23

affinity of the adsorbent and aid in designing large scale processes.[6] Methyl orange adsorption by fly ash granules obeyed the Freundlich and Langmuir isotherms with R^2 values of 0.998 and 0.86, respectively (Figs 1 and 2). This indicated constant adsorption energy and involvement of heterogeneous surfaces.[10–12] The values of Langmuir and Freundlich isotherm parameters are given in Table 3. The R_L value of 0.53 indicated favorable sorption of MO using fly ash.

Based on FTIR spectroscopy, it has been suggested that dye removal is due to interaction of positively charged active sites on the adsorbent with SO_3^{-}—N=N$^-$ group on methyl orange dye.[11] At a solution pH lower than the point of zero charge (pH_{pzc}) of the adsorbent itself, the binding sites on the surface of the adsorbent are predominantly protonated, and hence positively charged that favorably interact with the negatively charged sulfonated dye.[13, 14] In the present work, pH of the dye solution was maintained at 5.5–6.0, since the pH_{pzc} of fly ash sample was 6.5. Since, alginate granulation causes a mere physical entrapment of the fly ash powder, it does not in any way alter the electrochemical properties of the adsorbent. On the other hand, it ensures the retention of a higher concentration of the adsorbent in the granules to enhance the dye loading capacity.

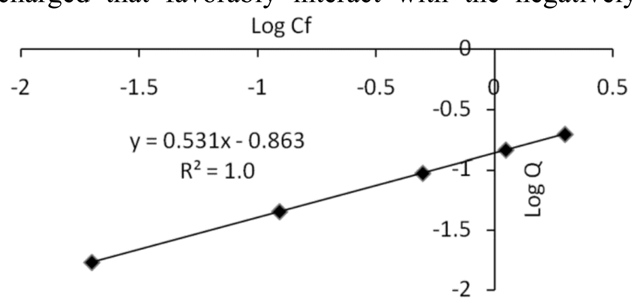

Fig. 1 — Freundlich isotherm for methyl orange uptake by fly ash granules

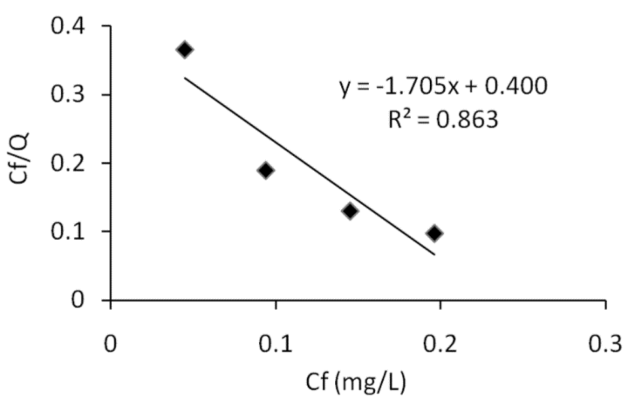

Fig. 2 — Langmuir isotherm for methyl orange uptake by fly ash granules

Table 3 — Parameters for Langmuir and Freundlich adsorption for MO

Langmuir Parameters		Freundlich Parameters	
Qmax (mgg^{-1})	1.4	K	0.01322
b(Lmg^{-1})	0.54	1/n	0.72
`R^2	0.86	R^2	0.998
R_L	0.53	—	—

It must be highlighted that physical and chemical methods are cost/inventory intensive, and cause secondary pollution. Periasamy and Palvannan demonstrated ability of a hypersecretory laccase producing basidiomycetous fungus for removal of dyes, viz. poly R-478 and RBBR, but the biodegradation required 6 days for completion.[15] The present work highlights the advantages of using fly ash for dye removal, viz. lower cost and rapidity. The studies on removal of MO as a model dye, would pave the way for studies on the interaction of other dyes such as methylene blue, rhodamine B, etc. with fly ash for pollution control.

The presence of inorganic nanoparticles in fly ash may lead to explore new uses of the waste. However, the problem of polydispersity and varying chemical composition need to be considered for any large scale application. Based on published literature[16–18], it might be worthwhile to deploy the fly ash nanoparticles for detection, diagnostics and therapeutics.

Conclusions

Fly ash, an abundantly available waste material, demonstrated good potential to remove MO from aqueous solutions in a granulated form. The possibility of selective dye adsorption and/or desorption would aid in the recovery and reuse of dyes.

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