ARTICLE

REMOVAL OF METHYLENE BLUE DYE FROM SOLUTIONS USING GRANULATED FLY ASH

Padmashri A. Pethkar[1], Aniroodha V. Pethkar [2], Pravin M. Nalawade[1]

[1]Dept. of Environmental Sciences, KRT Arts, BH Commence and AM Science College, Nashik, Maharashtra State, Affiliated to Savitribai Phule Pune University, Pune, INDIA

[2]Dept. of Microbiology, Govt. Institute of Sciences, Aurangabad, Maharashtra State, INDIA

ISSN 0976-3104

ABSTRACT

About 80,000 tons of dyestuff is produced in India annually for different industrial applications. Dyes enter the environment through wastewater released from dye manufacturing and dye consuming industries. It is estimated that 10–15% of the dyes are lost in the effluent during the dyeing process. The effluents are highly polluted and are toxic to the aquatic life present in receiving waters. Disposal of fly ash emanating from thermal power stations is another problem which is causing serious global concerns. Utilization of this material as an economical and low-cost product for different applications such as building material, filler and as an adsorbent has been researched. In the present studies, fly ash was utilized as a potential low-cost adsorbent for the removal of methylene blue dye from aqueous solutions. Adsorption studies were carried out in batch experiments with different concentrations of the dye and adsorbent and different exposure times. In order to facilitate the removal of the fine particulate adsorbent after use, the fly ash was granulated in calcium alginate gel. The granules could be used for removal of methylene blue from solutions, albeit with a lower efficiency. The removal of methylene blue varied from 0.0034 to 0.2, mgg-1 respectively when the initial dye concentration was raised from 1 to 20 mgL-1. The dye removal by fly ash granules followed Langmuir and Freundlich adsorption isotherms. The massive amounts of waste fly ash may serve as a valuable resource to reduce water pollution and recover the dyes from wastewaters. The fly ash, being a stable inorganic material can be subsequently put to end-use as filler or a building material.

KEY WORDS
Methylene Blue; fly ash; adsorption; Langmuir and Freundlich isotherms.)

INTRODUCTION

Combustion of coal in modern power plants produces some bottom ash while most of the burnt minerals escape with the flue gasses in the form of fly ash that is subsequently removed from the gas by electrostatic precipitation. About 125 million tons of fly ash is produced in India annually, of which only about 2% is used [1]. The remaining huge amount has raised serious concerns about disposal and/or use. In India about 80,000 tons of dyestuff is produced, of which a large portion is lost in effluents during dyeing process causing water pollution [2]. The present work describes attempts to utilize fly ash as an adsorbent for removal of dyes from solutions. Fly ash is well known as a cost-effective adsorbent and has been used for removal of metals and dyes [3-5]. A variety of cheap and abundantly available materials have been used for the removal of pollutants, but these may require costly processing to generate adsorbents. Use of fly ash, on the other hand, eliminates the time and cost of any further elaborate processing and it is available in huge amounts as a waste material.

Received: 18 May 2016
Accepted: 25 July 2016
Published: 5 Oct 2016

MATERIALS AND METHOD

The Fly ash sample- the fly ash sample was obtained from Eklahara Thermal Power Station located in Nashik, India. The as obtained sample was washed thoroughly with deionized distilled water, dried in an oven at 800 °C for 2 h, sieved to desired particle size (150 μm) and finally stored until use. The morphology of fly ash was studied by scanning electron microscopy (SEM).

Preparation of fly ash granules

Alginate-fly ash composite granules were prepared by admixing fly ash in sodium alginate solution (1 % w/v, 100ml) followed by dropwise extrusion of the solution into a cold solution of CaCl2 (0.1 M) through a 5ml syringe. The granules were allowed to harden by leaving them in CaCl2 solution for 24 h at ambient temperature followed by washing with deionized double distilled water.

Dye sample

A Stock solution of methylene blue dye (100mg.l-1) was prepared by dissolving an appropriate amount of the dye in deionized double distilled water. Working solutions were prepared by suitably diluting the freshly prepared stock solution with deionized double distilled water.

***Corresponding Author**
Email: pmnalawade@gmail.com
Tel: +919580837917

Adsorption studies

Dye removal studies were carried out at ambient temperature, c.a. 25°C±2°C by admixing suitable amounts of the fly ash sample with methylene blue solutions (1-20 mg.dm-3, 5ml) adjusted to pH 7 ± 0.1.in test tubes. The tubes were shaken at 100 rpm using an orbital shaker (Orbitek, India) for up to 2 hr in order to facilitate contact of dye molecules with the adsorbent. After exposure for appropriate time intervals, the fly ash was separated by filtration using a Whatman No.1 filter paper and the solutions analyzed for residual dye content by absorbance measurements using a UV-VIS spectrophotometer at 665nm. Appropriate negative controls of dye samples without fly ash were kept in order to eliminate error due to adsorption of dyes to the filter paper and/or the test tubes. Activated carbon was used as the positive control in the experiments. Similar experiments were carried out using granulated fly ash with activated carbon granules as positive control. Efficiency (%) of dye removal was calculated in order to determine the optimum parameters according to equation 1 as follows:

$$E\,(\%) = (Ci-Cf\,/Ci\,) \times 100 \quad (1)$$

Where, E is the dye uptake efficiency, Ci is the initial dye concentration and Cf is the final dye concentration in mg L-1.

The uptake capacity (Qe) in batch experiments was calculated as follows (equation 2):

$$Qe= V(Ci-Ce)/1000W \quad (2)$$

Where, Qe is the adsorption capacity (mg g-1), Ci is initial dye concentration (mg L-1), Ce is equilibrium dye (mg L-1),W is the amount of fly ash (g) and V is the volume of dye solution (mL).

Data emanating from adsorption studies was plotted to construct isotherms according to the Freundlich and Langmuir models. The linearized form of Freundlich isotherm is represented by equation 3 as follows:

$$Log\ Qe= log\ K+ (log\ Ce)/n \quad (3)$$

Where, Ce is the equilibrium dye concentration (mg L-1), Qe is the amount of dye adsorbed (mg g-1), K is adsorption capacity and1/n is the adsorption intensity. A plot of log Qe versus log Ce gives a straight line of slope 1/n and intercept K.

The capacity of dye uptake was determined by plotting Ce/Qe against Ce, using the Langmuir equation. The linear equation of Langmuir represented as equation 4. The Plot of specific sorption Ce/Qe against equilibrium concentration Ce gave the linear isotherm parameters Qmax and b.

$$Ce/Qe= (1/Qmax\ b) + (Ce/Qmax) \quad (4)$$

Where, Ce is the metal concentration in the solution at equilibrium (mg L-1), Qmax (adsorption capacity) and b (energy of adsorption) are the Langmuir constants.

RESULTS AND DISCUSSION

Fly ash sample- the fly ash sample consisted of near homogeneous particulate matter. The loss in weight after washing with deionized water was negligible. Characterization of fly ash by scanning electron microscopy (Figure 1) revealed characteristic spherical particles of <5μ diameter. Chemically, fly ash consists of oxides of metals that play the vital role in the adsorption behavior [1]. Nalawade and co-workers reported the occurrence of metals in soil in the vicinity of thermal power stations and fly ash dumping grounds providing evidence for the inorganic constituents of fly ash [6-7].

Preparation of fly ash granules- Different methods have been reported for entrapment of biomass and other materials in polymeric matrices. Polymeric material derived from poultry waste was used in the preparation of beads for silver and gold biosorption [8-9]. In the present study, alginate was used as the matrix for preparation of fly ash granules because alginate is a natural, biodegradable, nontoxic and hydrophilic polymer that produces thermostable gel by association with divalent cations [10]. Carboxyl and hydroxyl groups of alginate play an important role in cation exchange capacity and affinity of alginates towards metal ions [10, 11] although the exact mechanism of sorption is not understood. Due to the swelling behavior of alginates, the granules are highly porous with good water retention capacity and thereby display good mass transfer kinetics for sorption of solutes from aqueous media [12-13]. Alginate gels are also used for encapsulation of macromolecular agents and low molecular weight therapeutic agents [14]. The alginate-fly ash composite granules used in present studies were spherical (3.4 mm average diameter), grey in color and had good swelling property and water retention capacity as evidenced from a 40% increase in diameter when soaked in water.

IIOAB JOURNAL
ISSN: 0976-3104

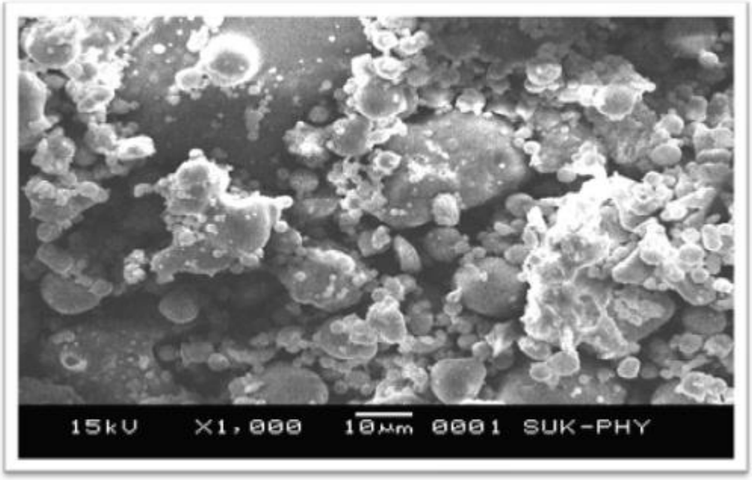

Fig. 1: SEM image of fly ash sample

Adsorption studies- Adsorption occurs due to unbalanced residual forces at the solid or liquid surfaces and is a surface phenomenon in contrast to absorption which is a bulk phenomenon. It was observed that dye uptake was rapid in the initial stages of the contact period (5 to 120 min) and subsequently became slow as the system attained equilibrium [Table-1]. This could be a result of the progressive reduction in the number of available binding sites for the dye with time and the increasing repulsion between the bound and unbound dye molecules. Pre-soaked granules displayed more rapid adsorption than the dry granules as earlier reported for metal biosorption by *C. cladosporioides* biomass beads [9].

Table 1: Effect of time on removal of MB by fly ash, fly ash granules and activated carbon

Time (min)	Dye removal Efficiency (%)		
	Activated carbon (powdered)	Fly ash (powdered)	Fly ash beads
5	68.45	4.7	7.5
10	70.12	7.93	8.78
15	74.80	28.65	34.33
30	85.96	56.43	50.34
60	>99	56.55	50.40
120	>99	56.55	50.81

The simplicity of the molecular structure of methylene blue and the presence of silica, iron and calcium oxides in fly ash indicates that surface adsorption by physico-chemical processes (hydrogen bonding and Van der Waal's forces) is possible without much stearic hindrance. Interestingly, it was observed that the efficiency of dye sorption with activated carbon was very high in the initial 5 minute contact (>95%) while it was low (<10%) in case of fly ash and fly ash granules. The equilibrium values were similar (>50%) for activated carbon and fly ash justifying the use of fly ash as a cost-effective adsorbent for dyes. According to Khan et al. (2009), the hydroxyl groups associated with fly ash play a role in binding to charged pollutants in the wastewater. The adsorbent acquires positive charge below the pHzpc value and negative charge above this value that aid in binding [1]. Weber and Morris demonstrated increase in adsorption capacity with the increase in molecular weight of solutes [16].

Table 2: Effect of dye concentration on removal of MB by fly ash and activated carbon

MB Conc. (mgL^{-1})	Activated carbon		Fly ash powder		Fly ash beads	
	Efficiency (%)	Specific dye uptake (Q)	Efficiency (%)	Specific dye uptake (Q)	Efficiency (%)	Specific dye uptake (Q)
1	92.3	0.0046	63	0.0031	69.03	0.0034
2	93.02	0.0419	54.3	0.0123	55.00	0.0143
5	90.96	0.1074	55.11	0.0691	55.35	0.0692
10	97.56	0.4883	10.02	0.0582	13.41	0.0610
15	93.22	0.9582	9.04	0.1432	10.42	0.1562
20	87.03	1.14	3.09	0.2	5.00	0.21

IIOAB JOURNAL
ISSN: 0976-3104

Table- 2 shows the increase in the dye uptake capacity in terms of mg dye bound per gram of the adsorbent on a dry weight basis as a function of initial dye concentration. Increase in dye concentration from 1 to 20 mg L^{-1} resulted in a 60-fold increase in the dye uptake capacity of granulated fly ash from 0.0035 to 0.21 mg g^{-1}. The increase in dye uptake capacity in a case of activated carbon was to the tune of 250-fold. However, the efficiency of dye sorption reduced at higher concentration of the dye, particularly in the case of fly ash indicating that the fly ash can be used as a polishing treatment to remove residual traces of dye remaining in wastewaters after physicochemical treatments. The studies indicate that it might be necessary to undertake efforts to improve the performance of fly ash by physical and/or chemical treatments.

The process of adsorption is usually studied by plotting the well-known adsorption isotherms, viz. the Langmuir and Freundlich isotherms that provide insight into the sorption mechanism, surface properties and affinity of adsorbent for the adsorbate. Modeling of equilibrium data allows comparison among different adsorbents under different operational conditions, designing and optimizing the processes [10] and also for the comparison of data from different laboratories. In the present studies, it was found that the methylene blue adsorption by fly ash granules obeyed both Freundlich [Figure-2] and Langmuir [Figure-3] adsorption isotherms with R^2 values exceeding 0.95. The data pointed to monolayer coverage with constant adsorption energy according to the Langmuir model and the involvement of heterogeneous surfaces according to the Freundlich model [1, 8, 10, 15].

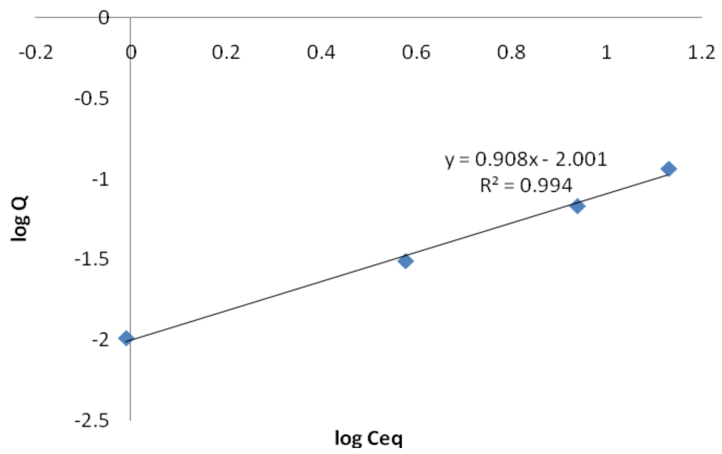

Fig. 2: Freundlich isotherm for methylene blue uptake by fly ash granules

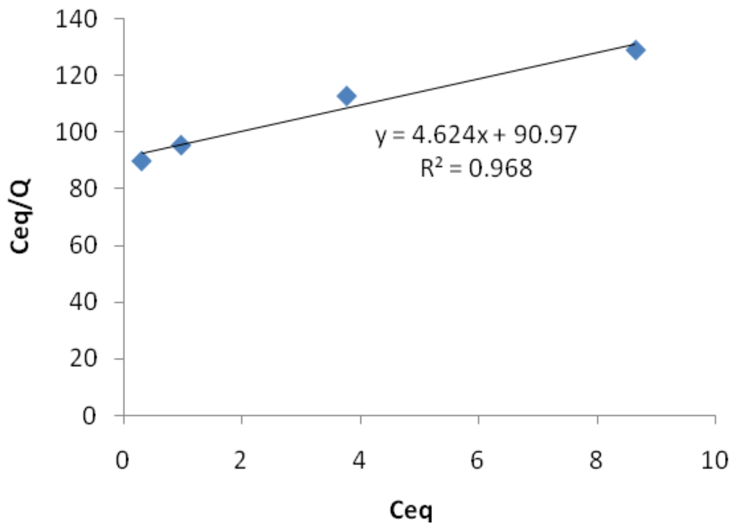

Fig. 2: Langmuir isotherm for methylene blue uptake by fly ash granules

One important characteristic of Langmuir isotherm is a dimensionless constant R_L given by Equation 2 as follows:

$$R_L = \frac{1}{1+bC_0}$$

(2)

Where C_0 (mg dm^{-3}) is the initial concentration of adsorbate and b (dm^{-3} mg^{-1}) is the Langmuir constant. There are several probabilities for R_L value: for linear sorption $R_L= 1$; for favorable sorption $0 < R_L < 1$; for irreversible sorption $R_L = 0$ and for unfavorable sorption $R_L > 1$ [10]. The dye uptake data in the present investigations pointed to favorable sorption kinetics with R_L value of 0.51.

The values of both Langmuir and Freundlich isotherm parameters are given in **Table- 3.**

Table 3: Parameters for Langmuir and Freundlich adsorption

Langmuir Parameters		Freundlich Parameters	
Q_{max}(mgg^{-1})	4.62	K	0.09
b (L.mg^{-1})	0.19	1/n	0.79
R^2	0.967	R^2	0.994

It is worth mentioning that in contrast to most of the attempts towards degradation of dyes, the present work points towards the possibility of recovery of dyes from wastes using waste fly ash. Both the recovered dye and regenerated fly ash beads can be recycled for further dye removal process. The possibility of selective dye adsorption and/or desorption from the fly ash granules needs to be investigated in order to make the process applicable on a large scale for real industrial effluent containing a mixture of dyes.

CONCLUSION

This work indicates that alginate-fly ash granules can be used for removal of dyes from wastewater as exemplified by the uptake of methylene blue dye. The dye adsorption obeyed Langmuir and Freundlich isotherm models. This study highlights the use of granulated fly ash for environmental pollution control that would aid in easy disposal and/or reuse of the fly ash. In the present studies, fly ash was utilized as a potential low-cost adsorbent for the removal of methylene blue dye from aqueous solutions. Adsorption studies were carried out in a batch experiments with different concentrations of the dye and adsorbent and different exposure times. In order to facilitate the removal of the fine particulate adsorbent after use, the fly ash was granulated in calcium alginate gel. The granules could be used for removal of methylene blue from solutions, albeit with a lower efficiency. The removal of methylene blue varied from 0.0034 to 0.2, mgg^{-1} respectively when the initial dye concentration was raised from 1 to 20 mgL^{-1}. The dye removal by fly ash granules followed Langmuir and Freundlich adsorption isotherms.

CONFLICT OF INTEREST
Authors declare no conflict of interest.

ACKNOWLEDGEMENTS
None

FINANCIAL DISCLOSURE
No financial support was received to carry out this project

REFERENCES

[1] Khan TA, Ali I, Singh V, Sharma S. [2009] Utilization of fly ash as low-cost adsorbent for the removal of methylene blue, malachite green and rhodamine B dyes from textile wastewater. *J Environ Protec Sc* 3: 11-22.

[2] Garg VK., Gupta R, Bala A, Yadav RK. [2003] Dye removal from aqueous solution by adsorption on treated sawdust. *Bioresource Technol* 89: 121-124.

[3] Bayat B. [2002] Combined removal of Zinc and Cadmium from aqueous solutions by adsorption onto high-calcium Turkish fly ash. Water Air Soil Pollut.136: 69-92

[4] Yamada K, Haraguchi K, Gacho CC, et al. [2003] Removal of dyes from aqueous solution by sorption on fly ash. In: Proceedings of the international ash utilization symposium. Lexington, Kentucky, USA. 22.

[5] Mohan D, Singh KP, Singh G, et al. [2002] Removal of dyes from wastewater using fly ash-a low cost adsorbent. *Ind Eng Chem Res* 41: 3688-3695.

[6] Nalawade PM, Bhole AD, Mule M. [2012] Assessment of groundwater and surface water quality indices for heavy metals in nearby area of Parli thermal power plant, *Univ J Environ Res Technol* 2 (1): 47-51

[7] Nalawade PM, Solunke KR, Mule M. [2015] Studies on assessment of heavy metals in samples collected from surrounding areas of fly ash dumping ground, *J Environ Res Technol* 5 (3): 131-140.

[8] Pethkar AV, Paknikar KM. [1997] Recovery of silver from low tenor solutions using C. cladosporioides biomass beads, Proceedings of the international biohydrometallurgy symposium. Sydney, Australia. PE8.1-PE-8.2.

[9] Pethkar AV, Paknikar KM. [1998] Recovery of gold from solutions using Cladosporium cladosporioides biomass beads. *J Biotech* 63: 121-136.

[10] Nadeem U, Datta M. [2014] Adsorption studies of zinc (II) ions on biopolymer composite beads of alginate-fly ash. *Eur Chem Bull* 3(7): 682-691

[11] Khotimchenko M, Kovalev V, Khotimchenko Y. [2008] Comparative equilibrium studies of sorption of Pb (II) ions by sodium and calcium alginate, *J Environ Sci* 20: 827-831.

[12] Pethkar AV, Bhagat AP. [2013] Biopolymer stabilized iron sulphide nanoparticles for removal of acid black 1 dye. *Mater Sc Forum* 757: 285-293.

[13] Pinhas MD, Peled HB. [2010] A quantitative analysis of alginate swelling. Carbohyd. *Polym.* 79: 1020-1027.

[14] Mandal S, Kumar S, Krishnamoorthy B, et al. [2010] Development and evaluation of calcium alginate beads prepared by sequential and simultaneous methods, *Braz J Pharma Sci* 46 (4): 785-793.

[15] Moghaddam AAN, Najafpour GD, Ghoreyshi AA, et al. [2010] Adsorption of methylene blue in aqueous phase by fly ash, clay and walnut shell as adsorbents. *W App Sci J* 8 (2): 229-234.

[16] Weber WJ, Morris JC. [1964] Equilibrium and capacities for adsorption on carbon. *J San Eng Div Proc Amer Soc Civl Engr* 90 (SA3): 79.