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Foundry Solid Waste as Adsorbent for the Removal of Basic Dyes from its Aqueous Solution

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Shot blasting dust, an abundant waste material from foundries can be employed as an adsorbent for the removal of basic dyes from aqueous solutions. Methylene blue and malachite green were selected as model compounds for evaluating the adsorption capacity and removal of dye from waste waters. Structural characterization of raw shot blasting dust was done through wet analysis, Fourier transform infrared spectrometry analysis and X-ray diffraction spectroscopy analysis. Surface morphology of raw shot blasting dust was studied through scanning electron microscopy and BET analysis. The effect of pH, initial dye concentration, adsorbent dosage, adsorbent particle size and contact time were evaluated and optimum experimental conditions were verified. Results obtained from the present study revealed that as the amount of adsorbent increases, the percentage removal of basic dyes also increased. For both the dyes an optimum pH 7 was found to be effective. Maximum removal of methylene blue (92.2 %) and malachite green (95.95 %) was observed at neutral pH, adsorbent dosage of 500 mg, temperature 27 ± 2 °C and initial concentration of 10 mg L^{-1}. The adsorption of methylene blue and malachite green followed pseudo second order kinetics and intra particle diffusion model. Study on both the dyes fits the Freundlich, Langmuir and Dubnin-Radushkevich (D-R) isotherms well. The present study confirms the potentiality of an abundant low cost solid waste material and its availability for the removal of basic dyes from aqueous solution.

Key Words: Shot blasting dust, Foundry waste, Adsorption, Methylene blue, Malachite green, Isotherms.

INTRODUCTION

One of the off-suits of industrialization is pollution which is the effluent waste water discharged by the industries and also solid wastes generated by industries. Solid wastes and liquid effluents are a great menace and become a formidable social problem. Many countries including India find it difficult to have a control on it.

Solid waste and liquid effluents from textiles, paper, plastic, leather, food and cosmetic industries pollute soil, air and water, the vital requisites of human life. Among the solid wastes of industries, the one from foundry is yet to be seriously studied. Shot blasting dust, the solid waste from foundries are mostly dumped in specially dug pits for its disposal. There are chances of shot blasting dust to come in contact with stagnated water, which will pollute the soil and hence it needs effective steps to contain the pollution. Otherwise the original power of the soil will decline threatening the agricultural operations. This will in turn lead to health hazards.

Various studies on effluent adsorption have been undertaken by using bagasse fly ash[1], thermal power plant fly ash[2], red mud[3], tripoli[4], coal bottom ash[5], mixture of fly ash and coal[6], diatomite[7], *etc*., Waste from foundries have been used in construction materials and concrete. Studies were also conducted on geo environmental behaviour of foundry sand amended mixture for highway sub bases[8], retaining structures[9], flow able fill[10], asphalt concrete[11], pavement bases[12], *etc.*

Many treatment methods are available for effluent water like coagulation, flocculation, photo catalytic degradation, membrane filtration, microbiological decomposition, electrochemical oxidation, fungus biosorbent and adsorption[13,14]. Among these methods adsorption is considered to be an economical and efficient process for the removal of dyes, heavy metals and hazardous impurities from liquid effluents. But the area of effluents is so vast that every source of effluents and the consequent pollution needs a lot of research study.

The researchers use various materials as an adsorbent which are suitably treated involving considerable cost whereas in our case, the solid waste from the foundry is abundantly available for research and hence shot blasting dust is much more economical. Also the solid waste of one industry, the foundry shall be mixed with the polluted water discharged from the dye industry. Thus raw shot blasting dust eradicates the dye from the effluent. In the process, both the industries are benefited.

In the present study, an attempt has been made to use the shot blasting dust as an adsorbent which can remove the harmful dye from the effluent. Methylene blue and malachite green, cationic dyes are selected as model compound for evaluating the adsorption potential of shot blasting dust. Shot blasting dust is characterized using various spectral techniques and it is investigated to observe the effect of pH, contact time, dye concentration, adsorbent dosage and adsorbent particle size. Results of this study will be useful for future application of shot blasting dust, a foundry waste, an abundant low-cost adsorbent for the removal of cationic dyes.

EXPERIMENTAL

Adsorbent material: Shot blasting dust is dark colour sand mixed with solid material which is obtained from a ferrous alloy foundry in Tamil Nadu, India for the present study. Shot blasting dust is normally used in foundries to remove excess sand from the casting. Hence it is a blend of sand, iron in oxide form and bentonite clay as a binder. It was stirred with double distilled water in a magnetic stirrer for 10-12 h to remove the oily substances present in raw shot blasting dust. The supernatant liquid was filtered. The above procedure was repeated several times until oily substances are completely removed. It was then dried in a hot air oven for 5 h at 110 ºC. The sample was sieved to various particle sizes with the help of a mechanical sieve. Different particle sizes, their yield percentage and adsorption efficiency in the bulk sample is given in Table-1.

TABLE-1
PARTICLE SIZES OF SHOT BLASTING DUST, THEIR YIELD AND ADSORPTION PERCENTAGE

Particle size (µ)	Yield (%)	Adsorption % with methylene blue
>300	01.11	36.7
210	09.09	64.8
150	15.08	50.2
105	15.05	54.8
75	19.97	65.3
53	11.69	63.7
25	20.70	79.8
<25	02.86	94.6

The adsorption capacity of shot blasting dust was analyzed using methylene blue dye solution of 100 mg L^{-1}/50 mL by agitating 500 mg of each sample size for a period of 2 h at a neutral pH at 27± 2 ºC. Based on the study with different particle sizes, shot blasting dust with particle size 75 µ were selected for further studies because it has higher yield percentage and comparatively higher adsorption capacity. Even though smaller sizes had good adsorption capacity, due to their clogging nature during column studies and in industrial applications[15] they are not employed for the present study.

Preparation of synthetic solutions: Typical basic dyes such as methylene blue and malachite green were obtained from a dyeing industry in Tiruppur, Tamil Nadu, India and was used without further purification. The molecular formula and molecular weight of the dyes methylene blue and malachite green are $C_{16}H_{18}N_3SCl$/319.85 g mol^{-1} and $C_{23}H_{25}ClN_2$/ 364.911 g mol^{-1} respectively. Stock solutions of the dyes were prepared by dissolving 1 g of the dye in 1000 mL of double distilled water. Different initial concentrations were prepared by diluting the stock solution. Double distilled water was employed throughout the study as solvent. The pH measurements were made using pH meter. The pH adjustments of the solution were made by 0.1 M HCl or 0.1 M NaOH. The chemicals were of analar grade and all the adsorption experiments were carried out at room temperature (27 ± 2 ºC).

Batch mode adsorption studies: The adsorption of methylene blue was performed by batch experiments. The batch technique was selected because of its simplicity. The experiments were carried out in a mechanical shaker at 150 rpm using 250 mL shaking flasks containing 50 mL of the dye solutions of desired concentrations and initial pH values. The adsorbent shot blasting dust of 1 g was added to each flask and then the flasks were sealed to prevent any change in volume during the experiments. It was agitated for predetermined time intervals at room temperature in a mechanical shaker. Blank samples were run under similar experimental conditions without using adsorbents.

After shaking, the adsorbent was separated by centrifugation and the supernatant solutions were estimated by measuring absorbance at maximum wavelengths using spectrophotometer at the desired wavelength for each dye.

The effect of each parameter like adsorbent dose, adsorbent particle size, different dye concentrations, agitation time, were studied by fixing the values of other parameters. To correct any adsorption of dye on containers, control experiments were carried out in duplicate. There was no adsorption by the container walls.

The amount of dye adsorbed by the shot blasting dust was calculated using the following equation.

$$q_e = \frac{(c_0 - c_e)V}{W} \qquad (1)$$

where q_e (mg g^{-1}) is the amount of dye adsorbed at equilibrium onto shot blasting dust, C_o and C_e (mg L^{-1}) are the initial and equilibrium liquid-phase concentration dye. V(L) the initial volume of dye solution and W(g) the weight of shot blasting dust.

RESULTS AND DISCUSSION

Characteristics of adsorbent: The composition and properties of shot blasting dust is presented in Table-2.

TABLE-2
COMPOSITION AND PROPERTIES OF SHOT BLASTING DUST

Composition	Percentage (%)	Properties	Values
SiO_2	64.95	pH	6.17
Fe_2O_3	44.5	Moisture content (%)	0.598
Clay	0.55	Water soluble matter (%)	28.94
Carbon	Nil	HNO_3 soluble matter (%)	11.08
Volatile matter	Nil	H_2SO_4 soluble matter (%)	11.47
		Surface area (m^2/g)	4.0616
		Micro Pore volume (cm^3/g)	0.001766
		Total Pore volume (Å)	2525.7

Surface characterization: To explore the surface characteristics of shot blasting dust, an FT-IR analysis was performed in the range 4000-450 cm^{-1}. In the spectrum the peak positions showing major adsorption bands were observed at 1082, 796, 695, 470, 550, 2360 and 462 cm^{-1}. Peak at 1082 cm^{-1} reflects the siloxane (Si-O-Si) group stretching vibration[7]. Peaks at 796 and 695 cm^{-1} corresponds to SiO-H vibration. Peak at 550 cm^{-1} and 470 cm^{-1} is characteristic of Si-O-Si bending vibration[7]. A peak at 2360 cm^{-1} may be due to trace of ammonia ions because the shot blasting dust is collected at high temperature and existence of nitrogen in air[15]. The peak at 452 cm^{-1} represents the presence of iron oxide in hematite form[16].

Scanning electron micrograph of shot blasting dust is shown in Fig. 1. It is evident from Fig. 1 and the surface area by BET method available in Table-2 that shot blasting dust has relatively larger number of pore spaces where dyes can be adsorbed. BET surface area for different adsorbents containing silica as their main constituent are shown in Table-3.

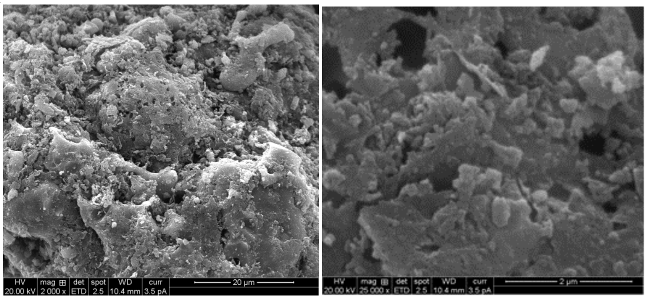

Fig. 1. SEM images of raw shot blasting dust

TABLE-3
BET SURFACE AREA FOR DIFFERENT
ADSORBENTS CONTAINING SILICA

Adsorbent	BET surface area (m^{2}g^{-1})	Reference
Calcined diatomite	7.50	7
Fly ash from aluminium industry	15.6	14
Fly ash from aluminium industry		
After heat treatment 2.50	14.0	
Red mud after heat treatment	10.1	14
Fly ash (CFA)	5.47	17
Fly ash (SFA)	3.26	17
Kaolinite	3.80	18
Fly ash from thermal power plant	2.41	19
Fly ash from thermal power plant	5.77	20
Expanded perlite	2.30	21
Unexpanded perlite	1.22	21
Raw shot blasting dust	4.0616	Present work

XRD spectra for shot blasting dust (Fig. 2) shows peaks at 2θ of 26.7 with high intensity is characteristic of SiO_2 and also some peaks appear at 2θ of 36.5, 39.5, 46, 50.2 and 59.9 confirms quartz and other silicon oxide containing phases[4]. The peak at 2θ of 35 is characteristic of iron oxide in hematite form. The 2θ values for silica and iron oxide are in good agreement with the corresponding JCPDS card numbers 00-033-1161 and 00-024-0072 respectively. It is also observed from the XRD spectra that some low intensity peaks at 2θ 55 and 68.3 may be due to minimum amount of CaF_2 as fluorite in accordance with JCPDS card No. 00-035-0816. The XRD spectra for shot blasting dust before and after treatment with methylene blue are shown in Fig. 2.

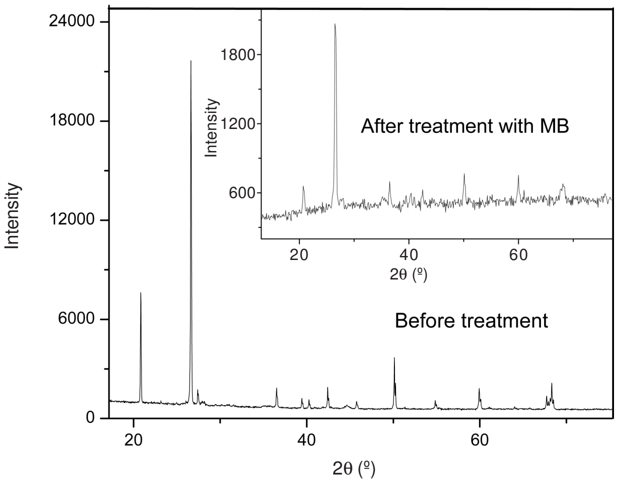

Fig. 2. XRD spectra for shot blasting dust before and after treatment with methylene blue

From the Fig. 2 it is also evident that there is a considerable decrease in the intensity of all the peaks after adsorption with methylene blue dye. This observation confirms that adsorption of methylene blue onto shot blasting dust has taken place.

Effect of adsorbent dosage: The adsorption of methylene blue and malachite green on raw shot blasting dust were investigated at 27 ± 2 ºC by keeping the volume of dye solution and initial dye concentration as 50 mL and 50 mgL^{-1} respectively. Fig. 3 shows the percentage removal of the dyes *versus* shot blasting dust dosage. It was found that by increasing the dosage from 0.1 g to 2.0 g there was an effective adsorption. It is evident from the figure that the percentage removal of both the dyes increased due to the availability of more adsorption sites at higher concentrations of the adsorbent[22]. For methylene blue the percentage of dye removal increased from 8.9 to 88.1 and for malachite green the percentage increased from 23.1 to 96.7. Based on the above data, 1 g of the raw shot blasting dust was used for further experiments.

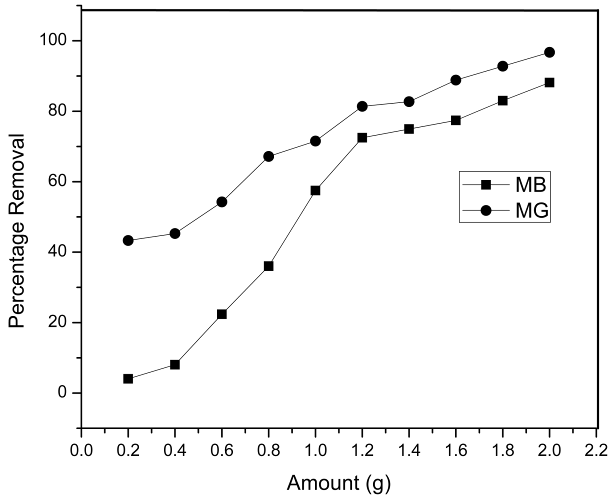

Fig. 3. Variation in adsorption of methylene blue and malachite green onto shot blasting dust dose with a concentration of 50 mg L^{-1}, T = 27 ± 2 ºC, pH = 7

Effect of initial dye concentration: The adsorption experiments were conducted with different adsorbate doses using different dye concentrations ranging from 10 mg L^{-1} to

100 mg L^{-1}. Its behaviour is shown in Fig. 4. It is observed from the figure that as the concentration of methylene blue increased the percentage removal decreased from 92.2 to 55.5 and for malachite green it decreased from 95.95. to 47.11. As expected when the concentration of dye increased the limited capacity of the adsorbent checks any further adsorption of dye and hence the overall removal percentage decreased[7]. The equilibrium controls the maximum adsorption and decreases the final removal percentage due to increasing amount of dye.

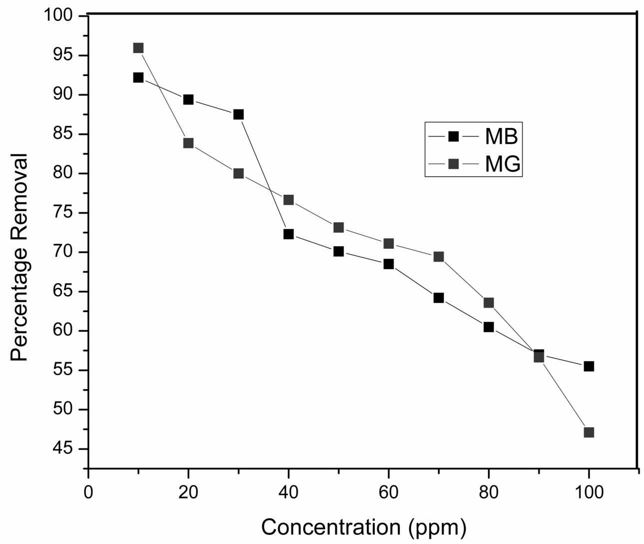

Fig. 4. Variation in adsorption of MB and MG onto shot blasting dust as a function of initial concentration MB and MG, T = 27 ± 2 °C, pH = 7, Dose = 1 g

Effect of contact time: The effect of contact time was studied by agitating 1 g of shot blasting dust with 50 mg L^{-1} of methylene blue and malachite green solutions respectively. Fig. 5 shows the removal percentage of methylene blue and malachite green with respect to the contact time onto raw shot blasting dust. It is evident that the adsorption efficiency increases with increase in time. In the case of methylene blue within 45 min more than 80 % of the dye was removed and for 80 % malachite green removal it took 110 min. Adsorption of methylene blue and malachite green onto shot blasting dust attains equilibrium at 150 min and it was selected as the equilibrium time. In the process of adsorption, initially dye molecules have to first encounter the boundary layer effect and then it has to diffuse from boundary layer film onto adsorbent surface and then finally, it has to diffuse into the porous structure of the adsorbent. This phenomenon will take relatively longer contact time[23].

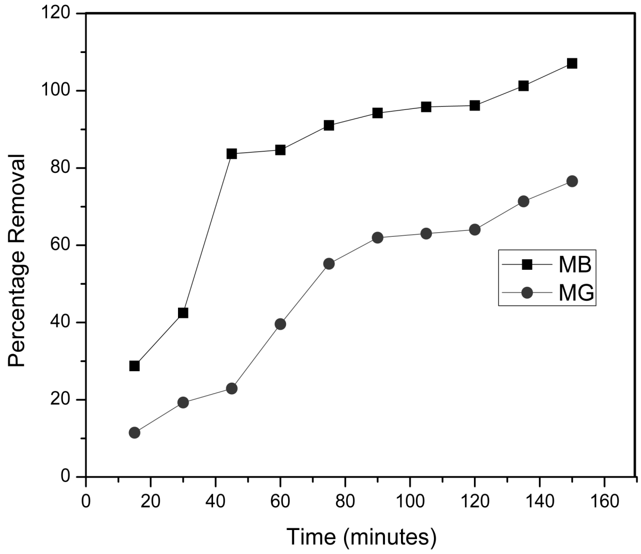

Fig. 5. Effect of contact time on the removal of MB and MG onto shot blasting dust of 50 mg L^{-1}, T = 27 ± 2 °C, pH = 7, Dose = 1 g

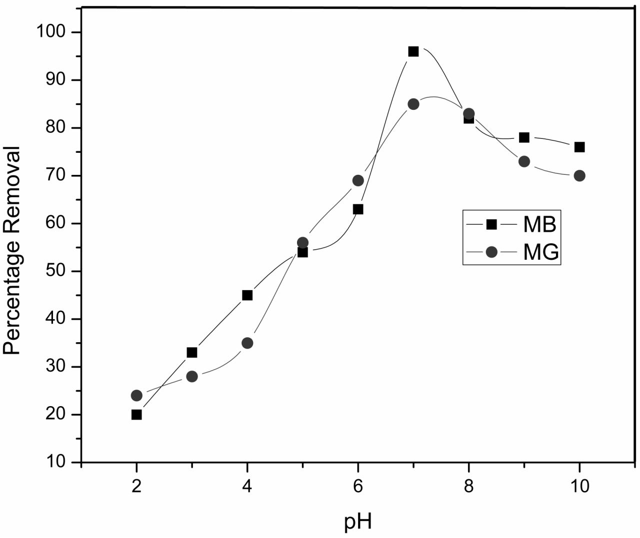

Fig. 6. Variation in adsorption of MB and MG onto shot blasting dust as a function of pH with initial concentration 50 mg L^{-1}, T = 27 ± 2 °C, Dose = 1 g

Effect of pH: pH of dye solution plays an important role in the adsorption process. To determine the effect of pH on the removal of dye its adsorption was studied at varied pH range of 2 to 10 which is shown in Fig. 6. It is known that ionic dyes upon dissolution release coloured dye anions/cations into solution. The adsorption of these charged dye groups onto the adsorbent surface is primarily influenced by the surface charge on the adsorbent which is in turn influenced by the solution pH[24]. Methylene blue and malachite green are basic dyes. In water, they produce cations and reduced ions. As the pH increases the negative charge density on the adsorbent shot blasting dust increases leading to more electrostatic attraction of positively charged dye molecules. Due to this reason, at pH 7 maximum adsorption of methylene blue and malachite green onto shot blasting dust took place. At lower pH, due to the accumulation of H^+ ions on the surface of shot blasting dust, it becomes more positively charged leading to lower adsorption of dye molecules. Similar studies were reported in the adsorption of methylene blue[25] and malachite green by fly ash[2], tuncbilek lignite[26].

Adsorption isotherm: For solid-liquid adsorption system, adsorption isotherm is an important model in description of adsorption behaviour. When the adsorption reaction reaches equilibrium state, the adsorption isotherm can indicate the distribution of dye molecules between the solid phase and the liquid phase. It is significant for understanding the adsorption behaviour to identify the most appropriate adsorption isotherm model. In this paper, Langmuir, Freundlich and Dubinin-

Radushkevich isotherm were employed to investigate the adsorption behaviour.

Langmuir isotherm: The Langmuir adsorption isotherm has been the most widely used adsorption isotherm for the adsorption of solute from liquid solution. It plays an important role in the determination of the maximum capacity of adsorbent. The Langmuir isotherm theory is based on the assumption that adsorption takes place at specific homogeneous sites within the adsorbent, the interaction among adsorbed substance can be negligible and the adsorbent surface is saturated after monolayer adsorption[27]. It also assumes that uniform energies of adsorption onto the surface without transmigration of adsorbate in the plane of the surface[28]. The form of Langmuir isotherm equation is expressed as follows:

$$q_e = \frac{Q_m K_a C_e}{1 + K_a C_e} \qquad (2)$$

where Q_m is the theoretical maximum adsorption capacity per unit weight adsorbent (mg g^{-1}), K_a is Langmuir adsorption constant (Lmg^{-1}), C_e and q_e are defined as in eqn. 1. The Langmuir isotherm eqn. (2) can be linearized into the following form.

$$\frac{C_e}{q_e} = \frac{1}{K_a Q_m} + \frac{1}{Q_m} \times C_e \qquad (3)$$

A plot of C_e/q_e *versus* C_e should indicate a straight line of slope $1/Q_m$ and an intercept of $1/(K_aQ_m)$.

The results obtained from the Langmuir model for the removal of methylene blue and malachite green by shot blasting dust are shown in Table-4.

TABLE-4
COMPARISON OF THE COEFFICIENTS ISOTHERM PARAMETERS FOR METHYLENE BLUE AND MALACHITE GREEN ADSORPTION ON SHOT BLASTING DUST
(1 g, pH 7, INITIAL DYE CONCENTRATION 50 mg L^{-1})

Isotherm model	Methylene blue	Malachite green
Langmuir		
Q_m (mg g^{-1})	4.59	3.457
K_a (L mg^{-1})	0.3184	2.5309
R^2	0.8932	0.9815
Freundlich		
1/n	0.4049	0.7170
KF (mg g^{-1})	1.1178	1.1446
R^2	0.8752	0.9927
Dubnin-Radushkevich		
Q_m (mg g^{-1})	5.9212	8.227
K (mol^2 KJ-2)	9.4×10^{-4}	2.08×10^{-3}
E (KJ mol^{-1})	25.77	16.5
R^2	0.9153	0.9491

The plot of q_e *versus* C_e for the adsorption of methylene blue and malachite green onto shot blasting dust at room temperature according to the non-linear form of Langmuir isotherm model was drawn. Maximum monolayer adsorption of cationic dyes onto shot blasting dust shows that the raw shot blasting dust used in present study has a relatively good adsorption capacity. Strong positive evidence is also obtained from the correlation coefficients R^2 as 0.86 for methylene blue and 0.90 for malachite green on the adsorption. The results of analysis indicated that shot blasting dust is suitable for removal of the cationic dyes methylene blue and malachite green from aqueous solution.

Freundlich isotherm: An earliest known empirical equation employed for non-ideal sorption that involves heterogeneous surfaces systems is called as Freundlich isotherm. The Freundlich equation is expressed as follows:

$$q_e = K_F C_e^{1/n} \qquad (4)$$

where, K_F is a constant for the system, related to the bonding energy. K_F can be defined as the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto adsorbent for unit equilibrium concentration. 1/n is indicating the adsorption intensity of dye onto the adsorbent or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. A value for 1/n below 1 indicates a normal Freundlich isotherm while 1/n above 1 is indicative of cooperative adsorption. Eqn. 4 can be linearized in the logarithmic form [Eq. (5)] and the Freundlich constants can be determined:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad (5)$$

The applicability of the Freundlich adsorption isotherm was also analyzed, using the same set of experimental data, by plotting log q_e *versus* log C_e. The data obtained from linear Freundlich isotherm plot for the adsorption of the methylene blue and malachite green onto shot blasting dust is presented in Table-4. The correlation coefficient shows that the Freundlich model is comparable to the Langmuir model. The 1/n is lower than 1.0, indicating that adsorption of methylene blue and malachite green by shot blasting dust is favourable.

Dubinin-Radushkevich (D-R) isotherm: The isotherm proposed by Dubnin and Radushkevich is useful in estimating the mean free energy and the energy of activation. From the energy of activation it can be predicted whether an adsorption is physisorption or chemisorption. The D-R model has commonly been applied in the following eqn. (6) and its linear form can be shown in eqn. (7):

$$q_e = Q_m \exp(-K\varepsilon^2) \qquad (6)$$

$$\ln q_q = \ln Q_m - K\varepsilon^2 \qquad (7)$$

where K is a constant related to the adsorption energy, Q_m the theoretical saturation capacity, ε the Polanyi potential, calculated from eqn. (8).

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \qquad (8)$$

The slope of the plot of ln q_e *versus* ε^2 gives K [mol^2 $(kJ^2)^{-1}$] and the intercept yields the adsorption capacity, Q_m (mg g^{-1}). The mean free energy of adsorption (E), defined as the free energy change when one mole of ion is transferred from infinity in solution to the surface of the solid, was calculated from the K value using the following relation:

$$E = \frac{1}{\sqrt{2K}} \qquad (9)$$

The calculated value of D-R parameters is given in Table-4. The saturation adsorption capacity Q_m obtained using D-R isotherm model for adsorption of methylene blue and malachite green onto shot blasting dust which is close to that obtained from Langmuir isotherm model (Table-4). If the energy of activation is less than 8 KJ mol^{-1}, the adsorption is physisorption and if it is greater 16 KJ mol^{-1}, the adsorption is chemisorption in nature[29]. The values of E calculated using eqn. (9) is 25.7 KJ mol^{-1} for methylene blue and 16.5 KJ mol^{-1} for malachite green. It indicates that the adsorption of methylene blue and malachite green by shot blasting dust is chemisorption in nature.

Adsorption kinetics: The chemical kinetic describes reaction pathways, along times to reach the equilibrium whereas chemical equilibrium gives no information about pathways and reaction rates. Therefore, a number of adsorption processes for pollutants have been studied in an attempt to find a suitable explanation for mechanisms and kinetics for sorting out environment solution[9]. In the present various kinetic studies like pseudo first order, pseudo second order and intra particle diffusion models were analyzed. Fig. 5 shows the influence of contact time of methylene blue and malachite green adsorption onto shot blasting dust.

Pseudo first-order kinetic model: The pseudo first-order model of Lagergren is based on the assumption that the rate of change of adsorbed solute with time is proportional to the difference in equilibrium adsorption capacity and the adsorbed amount. The pseudo first-order equation is expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad (10)$$

When the boundary conditions $q_t = 0$ at $t = 0$, eqn. (10) can be integrated into the following equation[30]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \qquad (11)$$

where q_e and q_t are the adsorption capacity per unit weight of adsorbent at equilibrium and at time t (min) respectively (mg g^{-1}) and k_1 is the pseudo first-order rate constant (min^{-1}). Linear plot of log (q_e-q_t) *versus* t gives the value for rate constant k_1. The correlation coefficients (Table-5) are relatively low for both the dyes and also the model fits well for first 60 min after that it deviates from the theory. This infers that the adsorption of methylene blue and malachite green on shot blasting dust does not follow first order mechanism.

TABLE-5
KINETIC PARAMETERS OF ADSORPTION OF METHYLENE BLUE AND MALACHITE GREEN ONTO SHOT BLASTING DUST (1 g, pH 7, INITIAL DYE CONCENTRATION 50 mg L^{-1})

	Model coefficients	
Model	Methylene blue	Malachite green
First order kinetic model		
k_1 (min^{-1})	0.056	0.03299
q_e (mg g^{-1})	40.973	69.804
R^2	0.9174	0.8626
Second order kinetic model		
k^2 [g(mg min) $^{-1}$]	1.753×10^{-3}	4.12×10^{-4}
q_e (mg g^{-1})	8.3815	9.8073
R^2	0.97	0.9573
h [mg(g min)$^{-1}$]	0.12311	0.03964
Intra particle diffusion		
k_{diff} (mg g^{-1} $min^{-1/2}$)	3.4177	0.3736
C	0.4368	0.8791
R^2	0.9986	0.9795

Pseudo second-order kinetic model: The pseudo second-order model is based on the assumption that the rate-limiting step involves chemisorption[31]. The equation is represented as follows:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (12)$$

When the initial conditions $q_t = 0$ at $t = 0$, after integration, the linear form of the pseudo second-order equation is given:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e(t)} \qquad (13)$$

where k_2 is the pseudo second-order rate constant (g mg^{-1} min^{-1}). The initial adsorption rate h (mg g^{-1} min^{-1}) at t = 0 is defined as follows:

$$h = k_2 q_e^2 \qquad (14)$$

The plot of t/q_t *versus* t for the adsorption of methylene blue and malachite green dyes are straight lines. From the linear plot the values of h, q_e and k_2 are calculated (Table-5). The correlation coefficients are greater than 0.95 (Table-5) and it is evident that the adsorption of methylene blue and malachite green on shot blasting dust follows pseudo second order kinetic model.

Intra-particle diffusion study: In a rapidly stirred batch reactor, the transport of adsorbent species takes place from the bulk of the solution into solid phase through intra particle diffusion process[32]. It is the rate limiting step in many adsorption processes.

The expression for the intra-particle diffusion model is given by the following equation:

$$q_t = K_{dif} t1/2 + C \qquad (15)$$

where, C (mg g^{-1}) is the intercept and K_{dif} is the intra particle diffusion rate constant (mg g^{-1} $min^{-1/2}$). The values of q_t were found to be linearly correlated with values of $t^{1/2}$ for both methylene blue and malachite green and the rate constant K_{dif} directly evaluated from the slope of the regression line and the values of intercept C provide information about the thickness of the boundary layer, the resistance to the external mass transfer increase as the intercept increase. The results were shown in Table-5.

If the intra-particle diffusion is involved in the adsorption processes, then the plot of the q_t *versus* square root of time would result in a linear relationship and the intraparticle diffusion would be controlling step if this line passed through the origin. When the plots do not pass through the origin, this indicative of some degree of boundary layer control and this further shows that the intraparticle diffusion is not the only rate controlling step, but also other processes may control the rate of adsorption. Such plots may present multi-linearity, indicating that two or more steps take place.

Initially the diffusion of adsorbate takes place through the solution to the external surface of adsorbent. Gradually the intra particle diffusion takes place and at the final equilibrium stage intraparticle diffusion starts to slow down due to extremely low adsorbate concentrations in the solution. The plot of q_t *versus* $T^{1/2}$ do not pass through the origin. It may be concluded that the deviation from the origin may be due to the variation of mass transfer in the initial and final stages of adsorption. The correlation coefficients values from Table-5 indicate that pore diffusion plays a major role for the adsorption of methylene blue and malachite green onto shot blasting dust.

Conclusion

The present study shows that the raw shot blasting dust, an abundant foundry waste can be used as an adsorbent for the removal of methylene blue and malachite green dyes from aqueous solution. Wet analysis of raw shot blasting dust exhibited the presence of silica, iron oxide and small amount of bentonite clay. FT-IR peaks at 1082 cm^{-1} confirmed the presence of SiO_2 and peak at 452 cm^{-1} confirmed hematite form of iron oxide. XRD spectra for raw shot blasting dust further confirmed the structure of silica as quartz, iron oxide in hematite form. XRD spectra after adsorption with methylene blue was shown by a decrease in intensity of the all the peaks. Surface area for shot blasting dust was 4.0616 m^2g^{-1} and total pore volume was 2525.7 Å units as determined by BET analysis.

Presence of pores was captured for raw shot blasting dust before adsorption through scanning electron microscope. The percentage removal of both the dyes was found to vary with initial pH, adsorbent dose, dye concentration and contact time. Maximum adsorption of both the dyes were found at pH 7, shot blasting dust dosage 2 g, initial dye concentration of 10 mg L^{-1} and an equilibrium contact time of 150 min. Various adsorption isotherms like Langmuir, Freundlich and Dubnin-Radushkevich were found to fit the adsorption of methylene blue and malachite green onto shot blasting dust. D-R isotherm predicted that the adsorption is chemisorption in nature. Adsorption of both the dyes was found to follow pseudo second order kinetics. From all the above factors it is proved that the raw shot blasting dust a solid waste from foundries can be effectively employed to treat waste water containing basic dyes.

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