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Development of Mesoporous Geo-Adsorbent Pellets from Low Fire Clay and Cellulose for Removal of Methylene Blue in Aquaculture

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Porous ceramic pellets have been prepared using low fire clay and cellulose as a pore forming agent. The pore size and BET analysis, water absorption capacity and compressive strength of the pellets have been determined. The methylene blue uptake of pellets increased on increasing the percentage of initial cellulose content. Batch mode studies showed that the methylene blue adsorption decreased with increasing dose of pellets, increased with increasing initial dye concentration, while solution pH and presence of co-ions had negligible effect on removal of methylene blue, making them suitable for dye removal over a wide range of pH. The adsorption process followed both the Freundlich and Langmuir adsorption isotherms, whereas the adsorption kinetics followed the pseudo-second-order kinetic model. An inexpensive and simple device consisting of the mesoporous pellets enclosed in a tea ball wire mesh, which can be conveniently dipped and taken out of water in an aquarium and can remove methylene blue, has been developed.

Keywords: Green adsorbent, Methylene blue, Cellulose, Ceramic, Low fire clay, Water.

INTRODUCTION

Chemical substances used in aquaculture can cause water pollution. Some chemicals and their residues, which are used in aquaculture may pose a danger to farm workers through potential toxicity and non-biodegradable nature. Methylene blue is used in various industries like leather, paper, cosmetic, pharmaceutical and also to treat methemoglobinemia (MetHb) [1]. There are a number of health problems, which are linked with methylene blue such as increased heartbeat, jaundice, damage to cardiovascular and gastrointestinal track in human. Methylene blue at a lower concentration range of 0.15 ppm to 2 ppm is used to treat various diseases and fungal infections in fishes (ornamental marine/freshwater finfish, juvenile penaeid shrimp) [2,3].

Activated carbon filters are fitted in most of the aquariums in conjunction with a mechanical filter to remove the coloured and odorous impurities that collects over time. Before methylene blue treatment, the activated carbon filter has to be removed, or else the filter would absorb methylene blue, making it unusable and the treatment would also be unsuccessful. After the methylene blue treatment, aquarium water has to be flushed to eliminate the methylene blue before restoring activated carbon filter in its original place before the mechanical filter. Even though the methylene blue is present at low concentrations, releasing a large quantity of the dye containing water into the environment is an environmental hazard. Therefore, it is imperative to remove methylene blue from the aquarium water after the treatment of fishes with methylene blue.

Amongst different options available to remove dye from water, adsorption is an extensively used procedure due to its straightforward operation, efficiency and simplicity [4,5]. Clay minerals with their ready availability and low-cost have been found to be an adsorbent of choice for removal of dyes and chemicals from water. Clay minerals can be made into porous ceramics by adding pore forming agents prior to calcination [6]. The additional porosity increases the utility of the ceramics and makes them useful as a dye absorbent to control environmental pollution [7].

In this article, we describe the preparation of mesoporous ceramic pellets using cellulose and low fire clay and the testing of a methylene blue removal device containing these ceramic pellets. This device can be used in aquariums to conveniently eliminate methylene blue, which remains after antifungal treatment of fishes at ultralow concentrations at low cost.

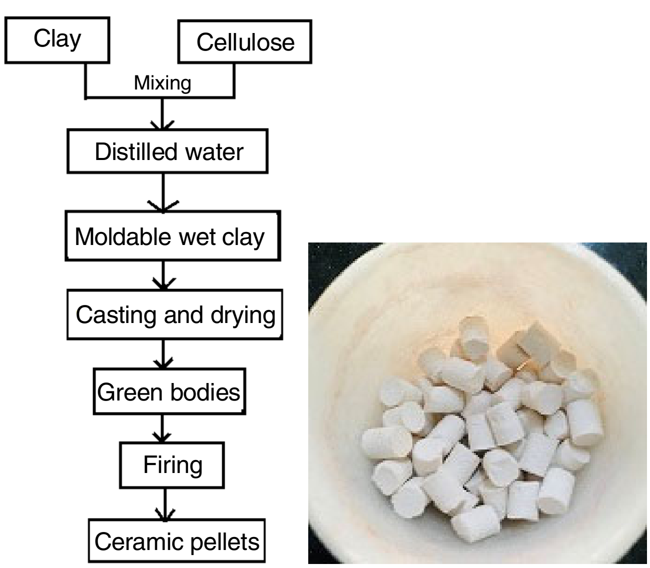
EXPERIMENTAL

For fabrication of moulds to make the ceramic pellets, holes of 5 mm diameter were drilled into a stainless-steel plates of 5 mm thickness. Low fire clay was purchased from Bhoomi Pottery, Mumbai, India and used as such. All chemicals used were of AR grade.

Preparation of porous ceramic pellets: Low fire clay was mixed with cellulose in defined proportions (Table-1) in a pestle mortar for 15 min. and a minimum quantity of distilled water was added to make it into a plastic (workable) stage of clay. The plastic clay was then transferred into the steel mould and left to dry in shade for 4-5 days. The green bodies were then removed from plate and subjected to firing in a muffle furnace. The temperature of the furnace was raised in stages: 1 ºC min^{-1} for 4 h followed by 3 ºC min^{-1} for 2 h to reach a temperature of 650 °C and then 3 ºC min^{-1} for 2.5 h to reach 850 ºC. The temperature of the furnace was maintained at 850 ºC for 1.5 h and then furnace was switched off and it was left to cool overnight with doors closed. Scheme of preparation and the mesoporous ceramic pellets are shown in **Scheme-I**.

TABLE-1
INITIAL CELLULOSE CONTENT, COMPRESSIVE STRENGTH OF PREPARED MESOPOROUS PELLETS

Clay (%)	Initial cellulose (%)	Compressive strength (N/m^2)
100	0	214.5
90	10	98.9
80	20	87.0
70	30	70.5
60	40	45.6
50	50	18.0
40	60 (crumpled on firing)	–



Scheme-I: Flow chart of preparation low fire ceramic pellets (left) and prepared pellets (right)

Characterization of ceramic pellets: IR analysis was carried using Perkin Elmer 4000 FTIR Spectrometer. X-ray fluorescence analysis of clay pellets was done using BRUKER WDXRF Model S8 Series 2, TIGER Spectrometer. Surface morphology was studied and analyzed through JEOL, IT 500 SEM. Determination of BET surface area, pore-size and pore volume of mesoporous pellets was done using N_2 adsorption/desorption isotherm at a temperature of 77 K, Quanta Chrome Instruments, Nova Surface Area Analyser, version 11.05. The compressive strength of the pellets were tested using EI Digital Tablet Hardness Tester Model No.3956 (ranges from 5-500 N, size range 2 mm to 28 mm). Water absorption capacity (W_A), of ceramics was determined according to the ISO 10545 procedure and for this, a defined number of dried pellets were weighed (W_1) and were immersed in boiling water for 2 h. After this, heating was turned off and the pellets remain immersed in water to cool for 4 h (water immersion time). Excess of moisture was removed with a tissue paper and then weighed again (W_2) [8].

$$\text{WA } (\%) = \frac{(W_2 - W_1)}{W_1} \times 100 \qquad (1)$$

Equilibrium studies: For adsorption experiments, 0.5 g of pellets were added to solution 100 mL of methylene blue of known concentrations (0.25, 0.5, 1.0 ppm). The solution was then stirred at a rate of 200 rpm at ambient temperature (25 ºC) to attain equilibrium. Absorbance of the solution was monitored at specified intervals through microprocessor-controlled colorimeter (D.S. Scientific Instruments, India) at a fixed wavelength, 680 nm for methylene blue. Since the water adsorption test indicated that porosity of sample no. 6 (Table-1) was highest in the series, therefore adsorption and kinetic studies were carried out with these pellets.

Tap water trials of methylene blue removal device: To study the ability of the pellets to remove methylene blue in water suitable for aquarium use, the methylene blue solution (1 ppm) was prepared in tap water. The water quality parameters were analyzed at Eco Laboratory Pvt. Ltd. (India) by standard methods. The pellets in different quantities (0.5, 0.75, 1.0 g) were placed inside a stainless-steel tea ball wire mesh (4 cm dia.) and dipped in a 100 mL of the methylene blue solution prepared in tap water. The solution was stirred at low speed of 20 rpm to at room temperature to simulate actual aquarium conditions.

RESULTS AND DISCUSSION

Characterization of mesoporous pellets: XRF analysis of clay showed that it is mainly composed of SiO_2 (64.21 %), Al_2O_3 (24.36%), CaO (4.70%) MgO (4.31%), K_2O (1.22%) with less proportions of other oxides. IR spectra of porous pellets (Fig. 1) showed no peaks in the range of 2500-3500 cm^{-1}, which confirm the absence of cellulose. The adsorption bands at ≈1050 cm^{-1} are associated with strong planar stretching of Si-O. The doublet of quartz (vibrational bands) was observed at 778 cm^{-1} [9], while the bands at 449 cm^{-1} and 454 cm^{-1} are related to bending vibrations of Si-O [10]. The surface morphology, before and after the adsorption of methylene blue molecules has been shown in Fig. 2a-b. N_2 adsorption/desorption isotherm analysis (Fig. 3a-b) showed pore size distribution of pellets ceramic of type IV(H) [11]. The surface area of pellets was found to be 6.420 m^2/g with pore diameter 3.622 nm and with a density of 1.02 g/cc. Pore size analysis showed meso-

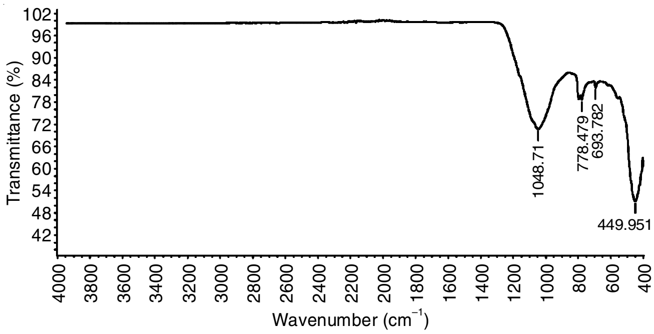


Fig. 1. FTIR spectrum of ceramic pellets (sample No. 6)

porous nature of ceramics (substrate with pore size 2-50 nm are categorized as mesoporous solids) [12,13], which is suitable for easy penetration of dye molecules. Water adsorption capacity (Fig. 4) of the ceramic pellets were found to increase with increase in the initial cellulose content due to increase in porosity of the ceramic pellets.

Effect of different reaction parameters on adsorption behaviour of pellets

Effect of contact time: Variation in adsorption behaviour of pellets with increase in contact time was studied using a series of experiments. Methylene blue solution of various concentrations (0.25, 0.5, 1.0 ppm) were stirred with an adsorbent dose of 5 g/L for 1500 min in duplicate. Eqns. 2-4 were used to calculate the absorption capacities of pellets, where the term q_e and q_t (mg/g) is the absorption capacity at equilibrium and at time t, respectively.

$$q_e = \frac{(C_o - C_e)}{m} \times V \quad (2)$$

$$q_t = \frac{(C_o - C_t)}{m} \times V \quad (3)$$

$$\text{Removal (\%)} = \frac{(C_o - C_t)}{C_o} \times 100 \quad (4)$$

where C_o, C_t and C_e (mg/L) represent methylene blue concentration, at initial stage, at a time 't' and at equilibrium stage, respectively. The term 'V' represents the volume of solution and 'm' is the mass (g) of adsorbent in the experiments [14].

It was observed that methylene blue adsorption on pellets was rapid during the initial 70 min of the reaction and gradually became slower as equilibrium was approached. This may be due to availability of a large number of adsorption sites initially for rapid adsorption, which become progressively filled

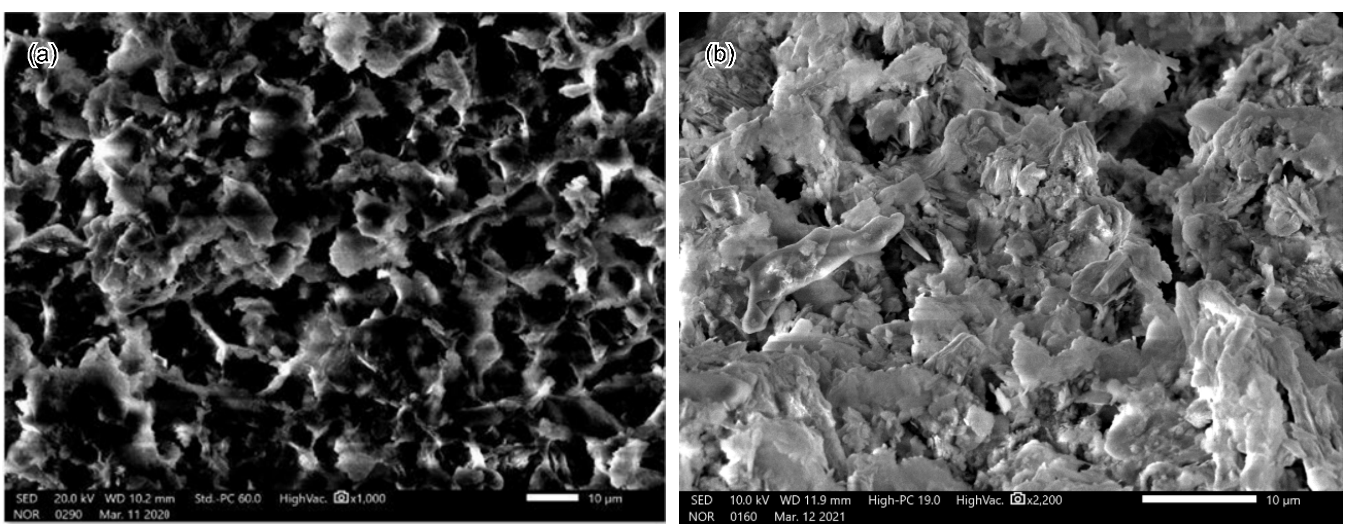


Fig. 2. SEM micrograph of ceramic pellet (Sample No.6) (a) before, (b) after methylene blue adsorption

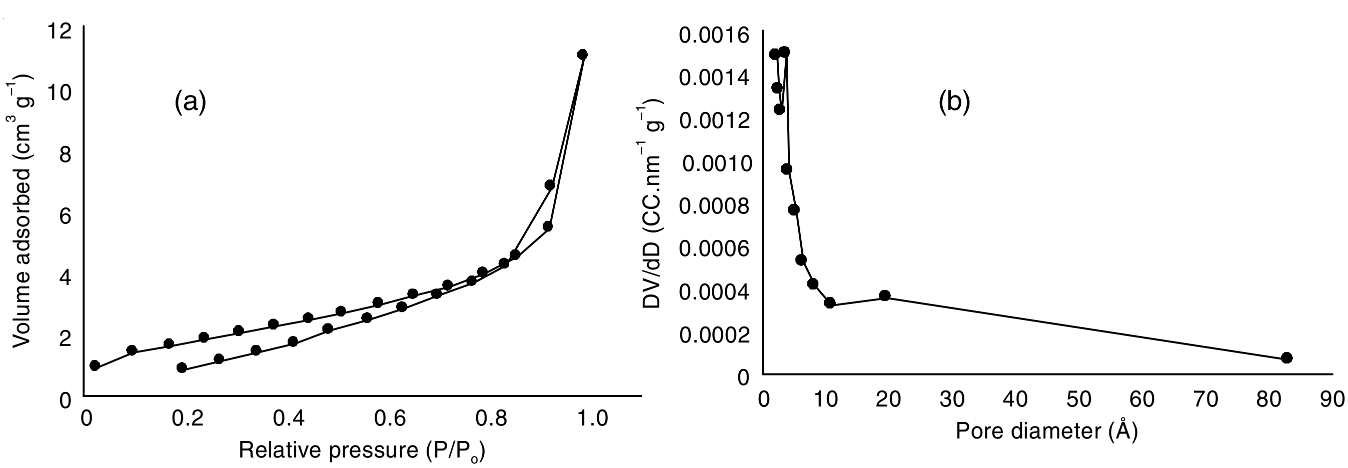


Fig. 3. (a) BET surface area and (b) pore size distribution of ceramic pellets (sample No. 6)

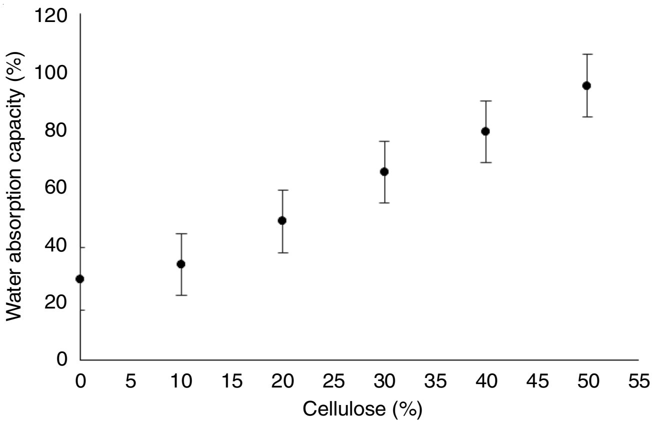


Fig. 4. Variation of water adsorption capacity of pellets with initial cellulose content

with the passage of time. Similar trends were also observed during study of methylene blue adsorption by raw kaolinite, halloysite [15] and silica based ceramic composite [16]. Percentage removal profile showed that 85% of dye removal was achieved at an initial concentration of 1 ppm and a dose of 5 g/L pellet dose.

Effect of initial cellulose content in green body: The q_e value was found to increase with the initial cellulose content (Fig. 5) in the green body. This is expected as increase in the initial cellulose content makes the pellets increasingly porous.

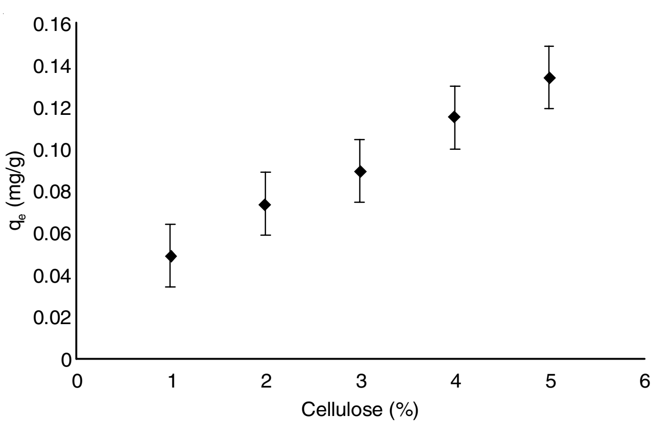


Fig. 5. Variation of equilibrium adsorption capacity (for methylene blue adsorption) with initial cellulose content of pellets

Initial methylene blue concentration: The increase in initial methylene blue concentration leads to increase in value of q_e (Fig. 6), which may be ascribed to increase in the concentration gradient between solution and pellet surface. At lower initial methylene blue concentration, the possibility of uptake of limited methylene blue molecules was higher leading to faster attainment of equilibrium [17]. Present observations are in line with those obtained for methylene blue adsorption by natural clay [18].

Pellet dose: Batch experiments with variable dose of pellets (5, 10, 20, 30, 40 g/L) in fixed methylene blue concentration (1 ppm) showed that the q_e value decreases gradually with increase in pellets dose, which may be due to agglomeration of pellets at higher dosage (Fig. 7) [19].

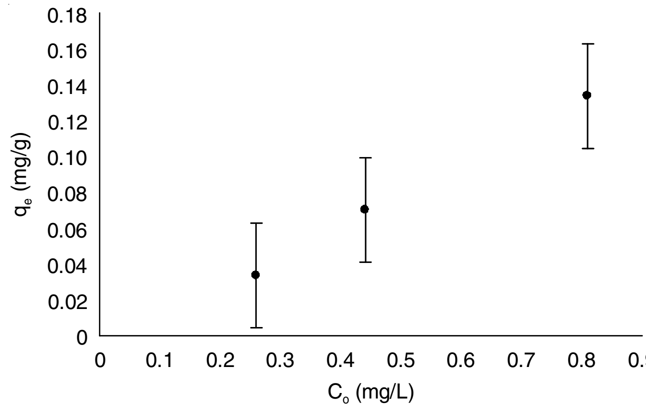


Fig. 6. Variation of methylene blue uptake with increase in initial methylene blueconcentration (sample No. 6)

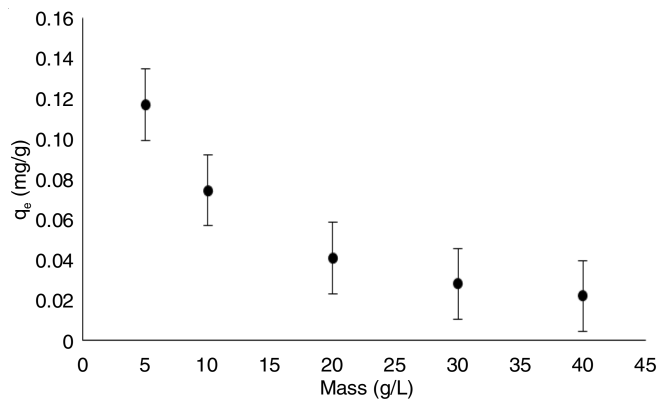


Fig. 7. Variation methylene blue uptake with pellet dosage (Sample No. 6: Initial methylene blue conc. 1 ppm, pH 7)

pH: Experimental studies at different pHs (1 ppm, methylene blue) indicated that the adsorption capacity of ceramic pellets were not affected by the change in initial pH (2-12) of the solution. This may be ascribed due to strong Si-O-Si/Al-O-Al bond, which did not hydrolyses in basic pH (Fig. 8). The pH independent methylene blue adsorption behaviour of the porous ceramic pellets makes them suitable for methylene blue removal over wide range of pH from 2 to 12 much beyond the natural pH range of surface waters (6.5 to 8.5). Similar results obtained for removal of Congo red dye by nanocomposites (iron oxide-alumina) [20] and for cationic dye removal by ceramic prepared from industrial waste coal gangue (pH 2-8) [21].

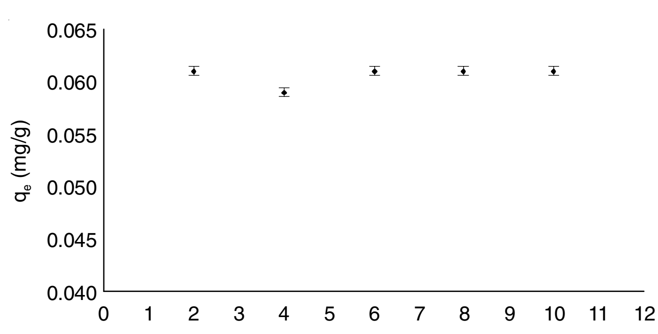


Fig. 8. Effect of initial pH on methylene blue adsorption by pellets (Sample No. 6: initial methylene blue conc. 1 ppm, pH 7)

Co-ions: Results of batch experiments in a concentration of 1 ppm showed that the co-ions reduces the adsorption of methylene blue in the order: blank (1) < HCO_3^- (2) < SO_4^{2-} (3) < Cl^- (4) < NO_3^- (5) < CO_3^{2-} (6), (Fig. 9). This was accounted by the competition for active sites between methylene blue molecules and co-ions present in the solution (Fig. 9).

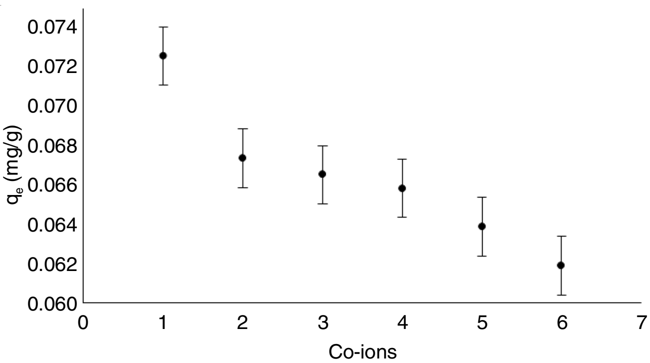


Fig. 9. Effect of co-ions on methylene blue adsorption (Sample No. 6:initial methylene blue conc. 1 ppm, initial co-ion conc. 1 ppm, pH 7)

Adsorption isotherm: Adsorption isotherm models *viz.* Langmuir (eqn. 5,) Freundlich (eqn. 6) and Temkin (eqn. 7) were used for analysis of adsorption experiments. The best fitted isotherm model can provide information about the nature of the adsorption [22]:

$$\frac{C_e}{q_e} = \left(\frac{1}{bQ\max}\right) + \frac{C_e}{Q\max}\left(R_L = \frac{1}{1+bC_o}\right) \quad (5)$$

$$\ln \ln q_e = \ln \ln k_F + \frac{1}{n} \ln \ln C_e \quad (6)$$

$$q_e = B \ln \ln A + B \ln \ln C_e, \left(B = \frac{RT}{b}\right) \quad (7)$$

R_L is a separation factor that helps to decide the favourable or unfavourable nature of the process [23]. K_f and n, Freundlich isothermal constants indicating adsorption power of adsorbent and magnitude of the adsorption, respectively. The graph between ln q_e and ln c_e gives a linear plot with intercept of ln k_f and slope 1/n. 'A' is the Temkin isotherm binding constant and 'B' corresponds to the heat involved during adsorption, can be measured by plotting q_e against ln C_e. T (K) is temperature and R (universal gas constant) has a value 8.314 J/mol K. The R^2 values (Table-2) of adsorption models, indicated that both the Langmuir and Freundlich isotherms were equally fitted for describing the methylene blue adsorption by the porous pellets.

Kinetic study of methylene blue adsorption: Adsorption kinetics is one of the most important variables for designing adsorption experiments. Therefore, to study the kinetics and mechanism involved, kinetic models; pseudo first order, (PFO) (eqn. 8), pseudo second order, (PSO) (eqn. 9), Bangham (BKM) (eqn. 10) and Elovich (EKM) (eqn. 11) intraparticle diffusion (IPD), (eqn. 12) models were applied.

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad (8)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_t} \quad (9)$$

$$\log.1\log\left(\frac{C_i}{C_i - q_t.m}\right) = \log\left(\frac{K.m}{2.303V}\right) + \alpha \log(t) \quad (10)$$

$$q_t = \frac{1}{\beta} \ln \ln(\alpha\beta) + \frac{1}{\beta} l(t) \quad (11)$$

$$q_t = K_{diff} t^{1/2} + C \quad (12)$$

K_1 and K_2 are PFO and PSO kinetic rate constants [24]. K_{diff} is intra-particle rate constant. α and β in Elovich equation represents the rate of methylene blue adsorption and available adsorption sites, respectively [25]. α (< 1) and K_O are Bangham's constants [26].

The kinetic analysis of experimental data is summed up in Table-3. The R^2 value for pseudo second order was found to be higher at all concentration indicating fitting of the pseudo-second-order for adsorption of methylene blue by ceramic pellets. A non-linear graph is obtained for intraparticle diffusion which implies involvement of more than one step during adsorption. Process like intraparticle diffusion and boundary layer diffusion are involved along with the pore diffusion of dye molecules on the surface of adsorbent [27].

Error analysis of adsorption kinetic models: A set of error functions like median absolute deviation (MAD), mean squared error (MSE), root mean square error (RMSE) and normalized standard deviation (NSD) (Table-4) were used to calculate the errors of linear forms of kinetic adsorption models for all concentrations [28,29]. It was found that error values for PSO were lowest.

Study of methylene blue removal device containing pellets: Three trials in duplicate were made using the stainless-steel tea ball wire mesh containing the mesoporous pellets and the time for complete decolorization of methylene blue solution prepared in tap water was determined at a dose of 5, 7.5 and 10 g/L, respectively (Fig. 10). The water quality parameters for the tap water (used in the experiment) was as follows: colour, BDL (DL5); pH, 7.71; TDS 430; Ca^{2+}, 28; Cl^-,48, F^-, 0.89; iron, 0.20, Mg^{2+}; 6.3, NO_3^-, 1.4; SO_4^{2-}, 33; total alkalinity, 284 and total hardness, 96 (all in ppm). This study reveals that these mesoporous pellets can be effectively used to remove

TABLE-2
ISOTHERM DATA FOR THE METHYLENE BLUE ADSORPTION BY MESOPOROUS PELLETS

Langmuir				Freundlich				Temkin			
R^2	Q (mg/g)	B (L mg)	R_L	R^2	1/n	n	K_f (L/g)	R^2	b (K cal/mol)	B	A (L/g)
0.99	0.0648	-4.245	-0.308	0.99	2.022	0.494	0.5128	0.94	4.1065	0.441	1.447

TABLE-3A
KINETIC DATA FOR THE METHYLENE BLUE ADSORPTION BY MESOPOROUS PELLETS

Conc. (ppm)	Pseudo first order		Pseudo second order		Bhangham			Elovich		
	R^2	K_1 (min^{-1})	R^2	K_2 (g/mg min)	R^2	K (mL/g L)	α (min^{-1})	R^2	β (g/mg)	α (mg/g min)
0.25	0.96	0.0057	0.99	0.6005	0.888	183.45	0.313	0.94	172.41	0.00972
0.50	0.96	0.0055	0.97	0.1914	0.928	144.44	0.376	0.93	86.206	0.03588
1.00	0.96	0.0066	0.99	0.9454	0.940	110.464	0.449	0.92	39.840	0.12133

TABLE-3B
KINETIC DATA (IDP) FOR THE METHYLENE BLUE ADSORPTION BY POROUS PELLETS

Conc. (ppm)	R_1^2	R_2^2	K_{diff1} (mg/g $min^{-1/2}$)	K_{diff2} (mg/g $min^{-1/2}$)	$C_1 \times 10^2$ (mg/g)	$C_2 \times 10^2$ (mg/g)
0.25	0.9341	0.9746	1.6×10^{-4}	2×10^{-4}	6.1×10^{-3}	2.94×10^{-2}
0.50	0.9743	0.8381	2.9×10^{-3}	4×10^{-4}	6.9×10^{-3}	5.60×10^{-2}
1.00	0.9907	0.6532	6.6×10^{-3}	6×10^{-4}	1.0×10^{-3}	1.11×10^{-1}

TABLE-4
STATISTICAL ANALYSIS FOR KINETIC MODELS

(Vol. 100 mL, dose: 5 g/L)		MAD $\frac{\Sigma \lvert q_{exp} - q_{cal} \rvert}{n}$	MSE $\frac{\Sigma \lvert q_{exp} - q_{cal} \rvert 2}{n}$	RMSE $\frac{\sqrt{\Sigma (q_{exp} - q_{cal}) 2}}{n}$	NSD (Δq%) $100\sqrt{\frac{\Sigma[(q_{exp} - q_{cal})/q_{exp}]2}{n-1}}$
0.25 ppm	PFO	0.0114	0.000136	0.0116	59.928
	PSO	0.0010	2.74E-06	0.0016	18.374
	BKM	0.0018	5.363E-06	0.0023	16.177
	EKM	0.0062	4.3288E-05	0.0065	48.577
	IPD	0.0014	3.59E-06	0.0018	16.618
0.5 ppm	PFO	0.0111	0.000137	0.0117	45.037
	PSO	0.0036	2.33E-05	0.0048	22.069
	BKM	0.0030	1.694E-05	0.0041	12.195
	EKM	0.0259	0.000694	0.0263	109.517
	IPD	0.0018	5.41E-06	0.0023	20.764
1.0 ppm	PFO	0.0075	7.69E-05	0.0087	29.168
	PSO	0.0044	2.90E-05	0.0053	17.991
	BKM	0.0074	0.0001071	0.0103	13.170
	EKM	0.0784	0.006266	0.0791	196.306
	IPD	0.0028	1.19E-05	0.0034	8.646

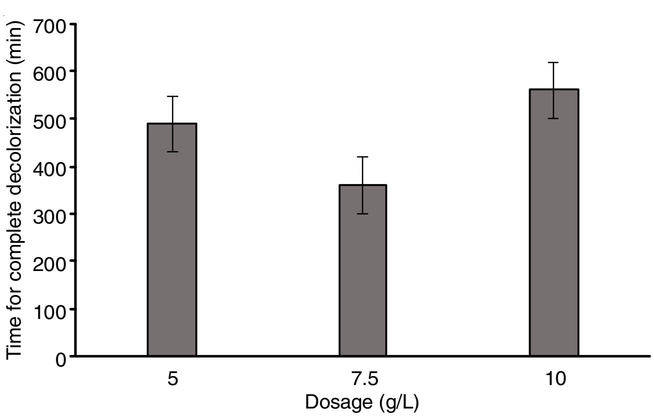


Fig. 10. Time taken by ceramic pellets (Sample No. 6) for decolorization of methylene blue solution (prepared in tap water)

methylene blue in aquarium (after its use in antifungal treatment and transport of fishes).

Conclusion

A porous ceramic pellets were prepared successfully using low fire clay with initial cellulose content of upto 50%. The cellulose burnt off on firing at 850 ºC and porous structure was confirmed by SEM study. The porous pellets were of adequate compressive strength to withstand handling. There were no evidence of remaining cellulose in porous ceramics pellets, which was confirmed by IR studies. Dose dependence studies indicated that the value for equilibrium adsorption capacity decreases with increase in dosage of pellets due to agglomeration of pellets at high pellet dosage. The q_e value increases on increasing the initial methylene blue concentration and initial cellulose content in pellets. The equilibrium methylene blue adsorption capacities of pellets was not affected by change in the initial pH of the solution, which indicates that these pellets are effective adsorbents for methylene blue removal from natural water over a wide pH range. Kinetic studies indicated that both boundary layer and pore diffusion phenomenon were involved during the rate determining step of the adsorption process. Furthermore, error analysis of kinetic models showed that the pseudo-second order reaction kinetics was followed by pellets for methylene blue adsorption. Finally, using a simple device, the viability of these mesoporous ceramic pellets to remove methylene blue at ultralow concentrations used in aquaculture was successfully implemented.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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