Development of Eco-friendly Adsorbent Pellets from Low Fire Clay and Potato Starch for Potential Use in Methylene Blue Removal in Aquaculture

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ABSTRACT

Mesoporous clay-starch ceramic pellets have been prepared using silica-rich low fire clay and potato starch as a pore-forming agent. The ceramic pellets prepared using 30% starch, showed the highest porosity and lowest compressive strength among all the different pellets. Batch mode studies using the pellets showed higher methylene blue adsorption capacity with an increase in time and increased initial dye concentration. The adsorption capacity was found to decrease with increasing pellet dose, while pH had a negligible effect on methylene blue removal which makes them a suitable adsorbent in both acidic and basic mediums. Adsorption isotherm analysis of the process was followed by the Langmuir adsorption isotherm whereas the kinetics analysis fitted well with the pseudo-second-order kinetic model. A low-cost, simple device was made from a stainless-steel wire mesh with mesoporous ceramic pellets enclosed in it, which can easily be dipped and taken out of an aquarium and can remove methylene blue from water.

INTRODUCTION

A number of drugs, dyes, and chemicals are widely used to treat various problems and diseases in fish. Different chemicals used in aquaculture, when get mixed with environmental components, cause various harmful effects (Mabel et al. 2019). Many of the dyes are toxic and carcinogenic in nature, causing threats to humans and other living organisms (Abdel-Halim 2013). Due to their synthetic origin, high molecular weight, and complex structures they are resistant to biodegradation. Discharge of dye-containing water, even in the low concentration affects the process of photosynthesis, chemical oxygen demand, and the quality of water which in turn disturbs the ecological balance (Yemendzhiev et al. 2009).

Methylene Blue (MB) is a cationic dye belonging to an azo group and characterized by an N=N bond. The structure of MB is shown in Fig. 1a:

MB is commonly used for dyeing textiles, leather, and paper. Exposure to MB results in an increased heartbeat, vomiting, jaundice, Heinz body formation, and tissue necrosis in humans (Zeynolabedin et al. 2015) in the long term. MB is also used for the removal of external parasites as well as for fungal infections in fishes at a concentration of 0.15 to 1-2 ppm. Most aquariums are fitted with activated carbon filters before a mechanical filter to filter out the odor and color causing contaminants that accumulate over time.

This activated carbon filter has to be removed before MB treatment, otherwise, the filter would absorb MB, rendering it useless and the treatment would also be ineffective. Post MB treatment, the aquarium water has to be changed to remove the MB before putting in the activated carbon filter back. Discharging a large volume of dye-containing water into the environment, even at low concentrations is an ecological risk. Therefore, it is important to remove MB from the aquarium water post-MB treatment.

Among different techniques of dye removal from water, adsorption is a widely used process due to its effectiveness, cost, simple design, and easy operation (Ahmed et al. 2010). Ceramics are an effective adsorbent for the removal of dyes and chemicals from aqueous systems due to their low cost and natural availability. The use of different additives helps in transforming clay minerals into porous materials and these can be stabilized through calcination. Increased porosity makes them useful to control environmental pollution in relation to dye adsorption (Elimbi et al. 2019).
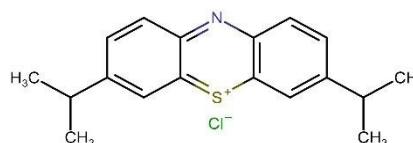

Fig. 1a. Chemical structure of Methylene Blue.

In this paper, we report the preparation of mesoporous ceramic pellets using low fire clay and potato starch and the testing of an MB removal device containing these ceramic pellets. This device can be used in aquariums to conveniently remove MB, remaining after antifungal treatment of fishes at ultralow concentrations at an extremely low cost.

MATERIALS AND METHODS

Preparation of Mesoporous Ceramic Pellets

For making the ceramic pellets, 5 mm holes were drilled into a mild steel plate of 5 mm thickness. The plates were then cleaned and painted to protect from corrosion and these plates were then used as molds for making pellets. Low fire clay was purchased from Bhoomi Pottery, Mumbai, Maharashtra, and was used as such. All chemicals used were of AR grade.

The clay powder and starch were mixed in defined proportion (Table 1) in a pestle mortar for 15 min with a minimum quantity of distilled water to make it plastic (e.g., 8 g clay, 2 g starch, and 5 mL distilled water). The wet clay was poured into the mold and left to dry in shade. The green

pellets were then removed with the help of a cotton-tipped steel rod and placed in a silica crucible. The ceramic pellets were now fired in a muffle furnace and the temperature was raised in stages to reach 850°C. After heating, the furnace was turned off and pellets were left to cool overnight. Ceramic pellets made from clay, starch, and water are named clay-starch ceramic pellets (Fig. 1b). The compressive strength was determined using EI Digital Tablet Hardness Tester, Model No. 3956 (range 2 mm to 28 mm).

Characterization of Starch-Clay Ceramics

XRF analysis was carried out by BRUKER WDXRF Model S8 Series 2, TIGER Spectrometer, IR using the Perkin Elmer 4000 FTIR Spectrometer. Surface morphology by JEOL, IT 500 SEM., determination of pore size, BET surface area, and pore volume of pellets was done with N_2 adsorption/desorption isotherm at a temperature 77K using Quanta Chrome, Nova Surface Area Analyser (ver. 11.05).

Water Adsorption Capacity

To check water absorption capacity (W_{ad}., eqn.1), of pellets,

Table 1: Composition and compressive strength of prepared mesoporous pellets.

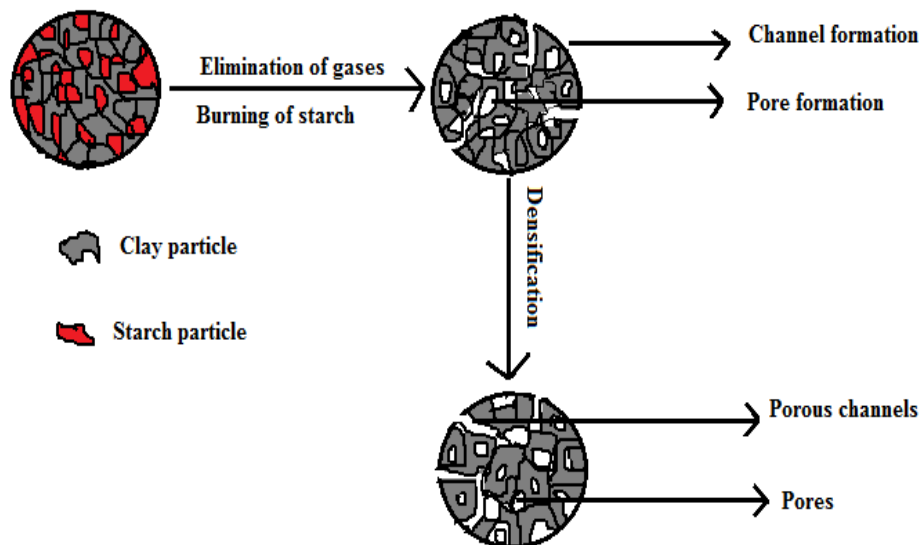| S.No.	Clay [%]	Starch [%]	Compressive Strength [$N.m^{-2}$]
1	100	0	214
2	90	10	110
3	80	20	90
4	70	30	71
5	60	40 [crumbled on firing]	-

Fig. 1b: Formation of clay ceramic pellets using starch as a pore-forming agent.

Fig. 1c: Prepared ceramic pellets.

dried pellets (3 Nos.) were weighed (W_1) and immersed in boiling water for a time of 2 h, and then heating was turned off and the pellets remained immersed in water to cool for 4 h. The pellets were removed from the water, the extra moisture present on the surface of pellets surfaces was removed using a soft cloth, and was re-weighed (W_2).

$$Wad.(\%) = \frac{(W2 - W1)}{W1} X100 \qquad ...(1)$$

MB Adsorption Experiment

MB adsorption experiment was done using batch mode studies. For this, 0.5 g of ceramic pellets were added to MB solution of different concentrations (0.25,0.5,1.0 ppm). The resultant solution was stirred at a speed of 200 rpm. All experiments were carried out at room temperature. The absorbance of the solution was then determined at a wavelength of 680 nm using a microprocessor-controlled colorimeter (D.S. Scientific Instruments). In this study ceramic pellets with initial starch content of 30% (sample no. 4, with the highest porosity) were used to analyze the MB adsorption process.

Tap Water Trials of MB Removal Device

Tap water was used to understand the MB adsorption behavior of ceramic pellets in water suitable for aquarium use. Analysis of different water quality parameters was done at Eco Laboratory Pvt. Ltd. (Mohali) (Table 5) by standard methods. The pellets in specified quantities (0.5, 0.75, 1.0 g) were taken in a stainless-steel tea ball wire mesh of 4 cm dia. and dipped in 100 mL of 1 ppm MB solution in tap water. The solution was then stirred at a speed of 20 rpm at room temperature to replicate the actual aquarium conditions.

RESULTS AND DISCUSSION

Temperature Selection and Preparation of Mesoporous Pellets

Firing is the most critical stage of the ceramic formation as any temperature variation can lead to unsatisfactory results in ceramic durability and color. If fired too high, clay can deform or even melt, if fired too low, ceramics will be dry, rough, and potentially unsolidified. Low fire clays reach maturity at lower temperatures as they need less energy during the firing process. The clay sintering process involves the bonding of clay minerals and the change of clay to ceramics. For making ceramic pellets, the temperature was raised at a rate of $1°C.min^{-1}$ to reach 240°C, $2°C.min^{-1}$ to reach 490°C, and finally, $3°C. min^{-1}$ to reach 850°C

Characterization of Pellets

The spectrum of fired pellets shows bands at $≈1057 cm^{-1}$ are associated with stretching of Si-O bonds (Aroke et al. 2013). The doublet of quartz was observed at $778 cm^{-1}$ (Saikia et al. 2008), and Si-O-Si bonds were observed at $685 cm^{-1}$ (Fig. 2).

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%).

The surface morphology of pellets before and after MB is shown in Fig. 3a and 3b. The specific surface areas and pore diameters ceramic pellets as determined by the BET method and N_2 adsorption/desorption isotherm are shown in Fig.4a and 4b. It was found that the specific surface area of the ceramics was $3.332 m^2.g^{-1}$ with a density of 3.659 $g.cc^{-1}$. The pore volume was found to be $0.008 g.cc^{-1}$ and a pore diameter of 2.453 nm, showing the mesoporous nature of the ceramic pellets. The nitrogen adsorption-desorption isotherms of the samples were classified as a typical type IV isotherm characteristic (Yan et al. 2018, Ambroz et al. 2018) suggesting capillary condensation after multilayer adsorption at mesopores. Water adsorption capacity (Fig. 5) of ceramic pellets was found to increase with an increase in starch content due to an increase in porosity of the ceramic pellets.

Reaction Parameters and Their Effect on Adsorption Behavior of Pellets

Effect of Contact Time

Contact time studies correlate the amount of dye adsorbed onto a fixed mass of adsorbent. It is used to find out the equilibration time for adsorption. The effect of contact time was studied in a time range of 1500 min. Following equations (eqn. 2, 3, 4) were used to determine q_t, q_e, and percentage removal.
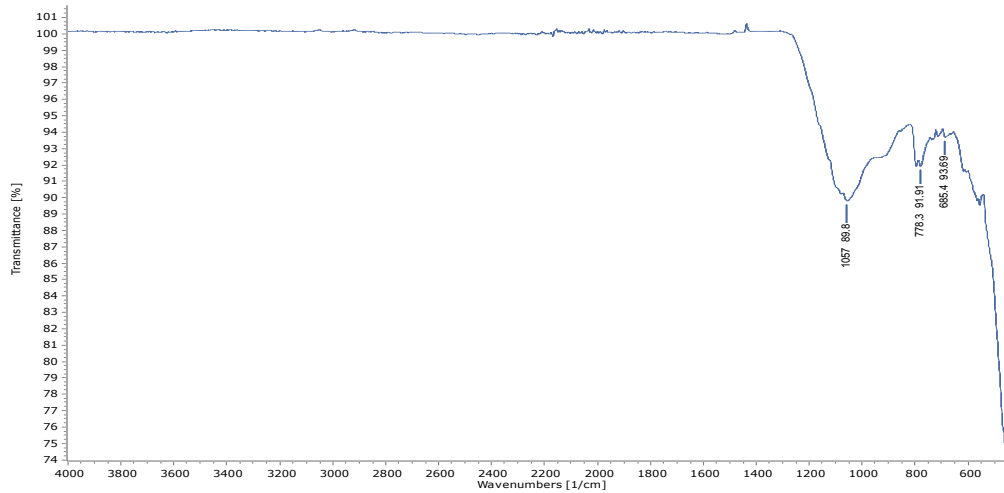
Fig. 2: FTIR Spectra of clay ceramic pellets (sample no.4).

$$qe = \frac{(Co-Ce)}{m} \times V \qquad ...(2)$$

$$qt = \frac{(Co-Ct)}{m} \times V \qquad ...(3)$$

$$\%removal = \frac{(Co-Ct)}{Co} \times 100 \qquad ...(4)$$

The terms C_o, C_t, and C_e indicate the MB concentration during the initial time, at time t and equilibrium, respectively. q_t and q_e (mg.g^{-1}) indicate the amount of MB adsorbed at time t and equilibrium time.

A quick increase in MB adsorption capacity was observed during the first 130 min of reaction time followed by a gradual increase in dye adsorption. Percentage removal was also found to increase with an increase in starch content.

Effect of Pellet Dose

Initial adsorbent dose controls adsorption via available surface area and binding sites. The adsorbent dose was varied from 5 to 40 g.L^{-1} and adsorption capacity was found to be reduced as the dosage increased (Fig. 6). This decrease in adsorption capacity with an increase in dose may be due to
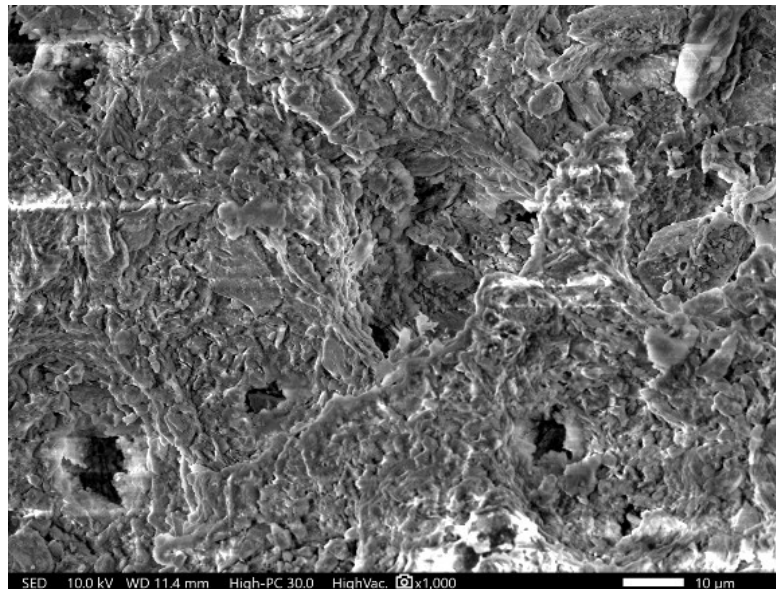

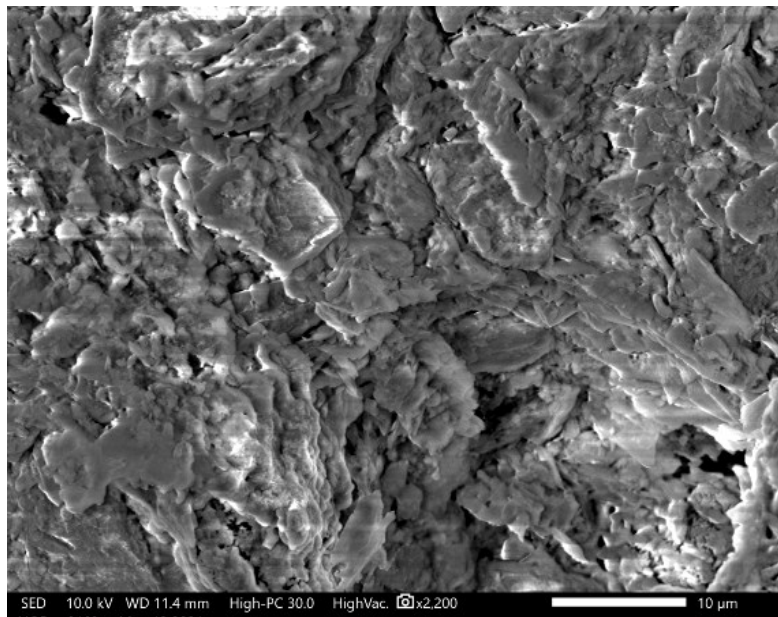Fig. 3a: SEM images of ceramic pellets (sample no.4) before MB adsorption.

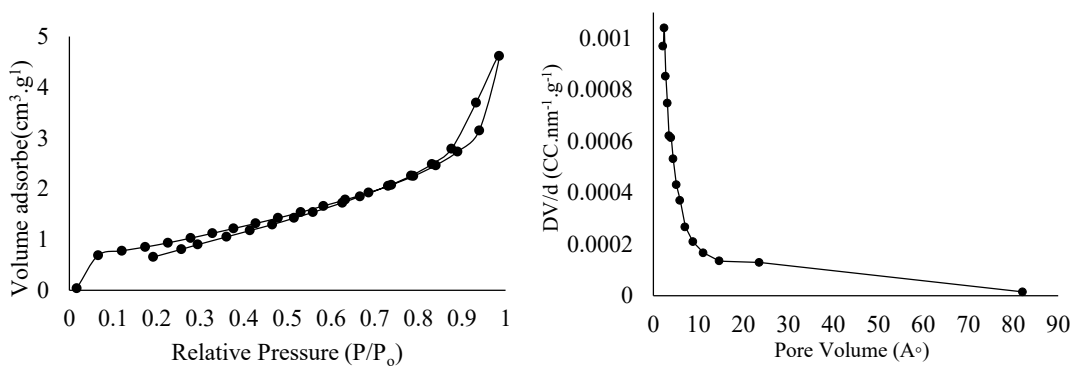Fig. 3b: SEM images of ceramic pellets (sample no.4) after MB adsorption.

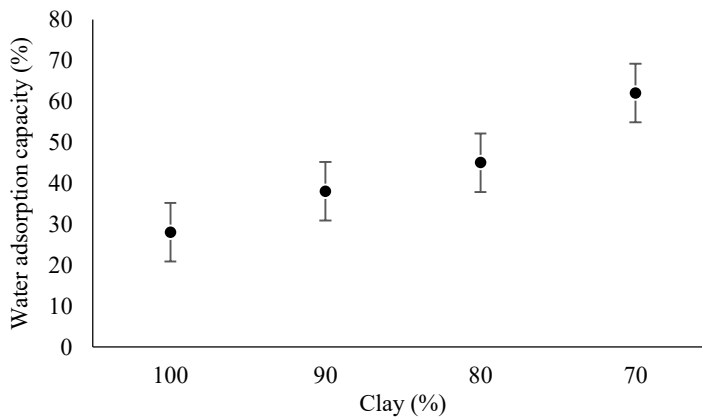Fig. 4: a) BET surface area and b) pore size distribution of ceramic pellets (sample no.4).

Fig. 5: Water adsorption capacity of ceramic pellets with increased starch content in the green body.

saturation of adsorption sites through the sorption process or due to aggregation resulting from a higher dose.

Effect of Initial Dye Concentration

Initial dye concentration plays a crucial role as it drives the solute transfer rate under a higher concentration gradient between MB solution and pellet surface. The adsorption capacity of pellets was shown to increase when the initial MB concentration increased (Fig. 7), as at lower concentration the ratio of the initial number of MB molecules to the available surface area is low, and subsequently, the fractional adsorption becomes independent of initial concentration. Similar results were also obtained for MB adsorption using natural clay (Bentahar et al. 2017).

Effect of pH

The pH of the aqueous solution is an important parameter that controls the adsorption process. The effect of solution pH on the adsorption capacity of MB dye on the pellet surface was performed at different pH levels (pH 2–12) with a fixed dose of 1g.100 mL^{-1} at room temperature. 0.1M HCl/0.1M NaOH was used for pH adjustment. The pH-independent behavior of ceramic pellets makes them suitable to use over a wide pH range (2 to 12), (Fig. 8). Similar results were also noticed during the adsorption of MB on mesoporous Iraqi red Kaolin clay (Jawad & Abdulhameed 2020).

Effect of Co-existing ions

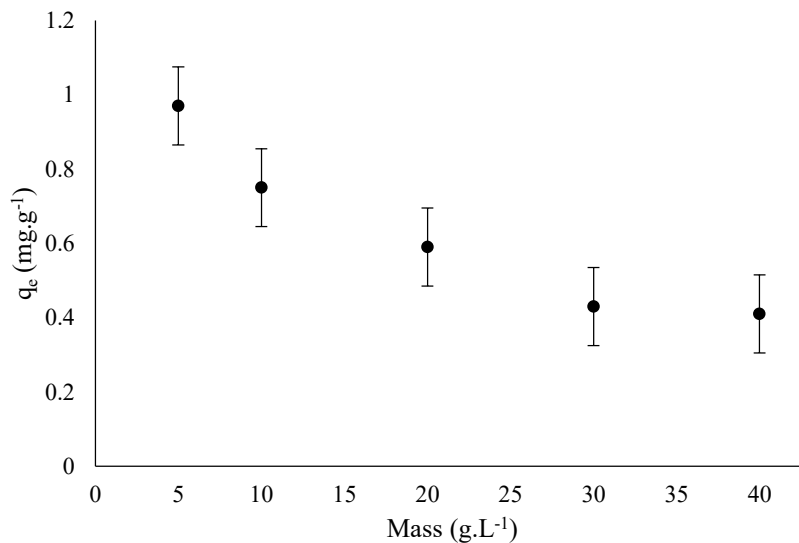The co-ions reduce the adsorption of MB marginally in the

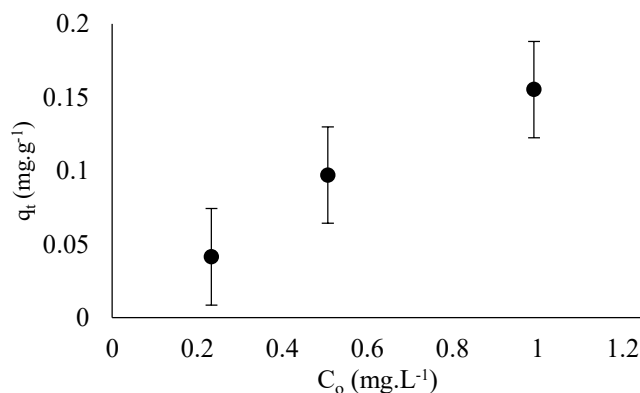Fig. 6: Variation of MB adsorption with increasing pellet dose.

Fig. 7: Variation of MB adsorption with an increase in dye concentration.

order of CO_3^{2-} SO_4^{2-}< HCO_3^-<NO_3^- < Cl^- (Fig.9). This was accounted for by the competition for active sites between MB molecules and co-ions present in the solution.

Adsorption Isotherm Studies

Langmuir Isotherm

The linearized Langmuir equation (eqn. 5, 6) was used to show the surface binding properties of MB with the mesoporous ceramic pellets.

$$\frac{c_e}{q_e} = \left(\frac{1}{bQmax}\right) + \frac{c_e}{Qmax} \qquad \dots(5)$$

$$R_L = \frac{1}{1+bc_0} \qquad \dots(6)$$

Where b is the Langmuir isotherm constant representing affinity between adsorbate and adsorbent (Huang et al. 2020).

Qmax is the maximum adsorption capacity. Feasibility of isotherm can be calculated by using a dimensionless separation factor (Mckay et al. 1982), R_L; $R_L > 1$ is unfavorable; $R_L = 1$ is linear; $0 < R_L < 1$ is favorable; and $R_L = 0$ is irreversible. The value of R_L between 0-1 indicates the favorable nature of the adsorption process (Tahir et al. 2010) (Table 2).

Freundlich Isotherm

The Freundlich equation (eqn. 7) is based upon the assumption that the logarithmic value of enthalpy of adsorption decreases with an increase in the number of occupied sites and it is used to describe the adsorption involving the heterogeneous surfaces. K_F is the Freundlich constant corresponding to the binding energy (Akkaya & Ozer 2005) (Table 2).

$$ln\ ln\ q_e = ln\ ln\ k_F + \frac{1}{n} ln\ ln\ c_e \qquad \dots(7)$$
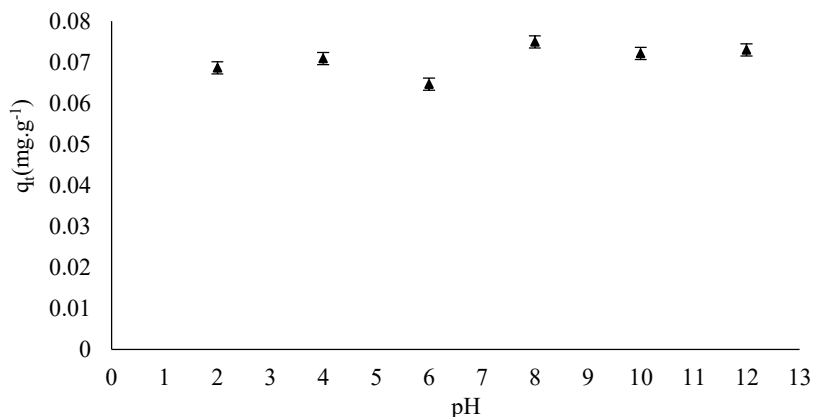

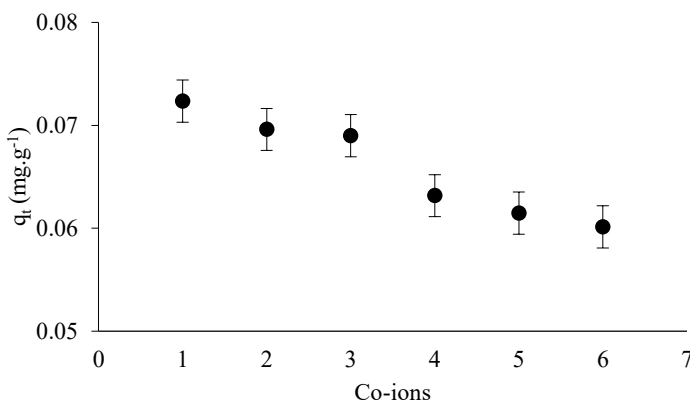Fig. 8: Effect of initial pH on MB adsorption by pellets (initial MB conc.1ppm, pH:7).

Fig. 9: Effect of co-ions on MB adsorption (initial MB conc.1ppm, initial co-ion conc.1 ppm, pH:7).

Temkin Isotherm

The Temkin model (eqn. 8) is used to explain the effect of adsorbate adsorbent interactions. It assumes that the heat of adsorption of all molecules in the adsorbent layers decreases linearly with coverage of the surface.

$$q_e = B \ln \ln A + B \ln \ln C_e \ , \ (B = \frac{RT}{b}) \quad ...(8)$$

Where R is the gas constant, (8.314 J.mol K^{-1}), T is reaction temperature in kelvin. A plot between q_e and $\ln c_e$ gives the values of constants A and B. The Temkin constant b is related to the heat of adsorption (Mohebali et al. 2018) (Table 2).

On comparing the R^2 for different adsorption isotherms used, it was found that the Langmuir isotherm and Temkin model are best suited for the description of the adsorption mechanism.

Kinetic Study of MB Adsorption

Kinetic models can give valuable insight into the adsorption rate and adsorption mechanism. To determine the rate-determining step and to study the kinetics of MB adsorption by pellets, five kinetics models; pseudo-first-order,(PFO) (eqn.9), pseudo-second-order, (PSO) (eqn.10), Bangham (BKM) (eqn.11), Elovich (EKM) (eqn.12), and Intraparticle Diffusion (IPD), (eqn.13), models were applied.

$$log \ (q_e - q_t) \ = log \ q_e - \frac{K_1}{2.303} t \quad ...(9)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_t} \quad ...(10)$$

$$log.\,log \left(\frac{Ci}{Ci-qt.m}\right) = log \left(\frac{K.m}{2.303V}\right) + \alpha log(t) \quad ...(11)$$

$$q_t = \frac{1}{\beta} \ln \ln(\alpha\beta) + \frac{1}{\beta} l(t) \quad ...(12)$$

$$q_t = K_{diff} \ t^{\frac{1}{2}} + C \quad ...(13)$$

K_1 and K_2 are PFO and PSO kinetic rate constants (Dang et al. 2015). $K_{diff.1}$ and $K_{diff.2}$ are the intra-particle rate constants (Balasubramaniam et al. 2018). α and $\frac{1}{\beta}$, the Elovich

equation represents the rate of MB adsorption and available adsorption sites respectively (Sarma et al. 2019). α (<1) and K_O are Bangham's constant (Junghare et al. 2020).

The kinetic parameters of both models are summarized in Table 3a-b. The R^2 value obtained for second-order kinetic (R^2=0.99) is higher than that of other kinetic models for MB adsorption on the pellet surface. For the intra-particle diffusion model, a deviation of the straight line from the origin was observed which indicates involvement of the pore diffusion during rate-controlling step along with intra-particle diffusion during adsorption of dye. Second-order kinetics along with pore and intraparticle diffusion is predominantly followed for MB adsorption by several clay-based adsorbents (Sharma & Qanungo 2021). Furthermore stastical analysis of experimental data (Table 4) using Mean Absolute Deviation (MAD), Mean Squared Error (MSE), Root Mean Square Error (RMSE) and Normalized Standard Deviation (NSD) also indicates second order kinetic model to be well followed.

MB Removal Device Containing Pellets

For MB removal from tap water, a stainless-steel tea ball wire mesh containing the mesoporous pellets was used and all experiments were carried in duplicate (three trials). To study the complete decolorization time using the MB removal device, three sets of experiments were carried out using 5 g.L^{-1}, 7.5 g. L^{-1}, and 10 g.L^{-1} of pellet dose (Fig.10) using 100 mL, 1ppm MB solution. The increase in MB removal by the increase in pellet dose is due to the increase in surface area and the number of active sites. This leads to lower decolorization times. Further increase in pellet dose leads to higher decolorization times due to aggregation and reduction in active sites for adsorption. From this study, it is indicated that the MB removal device containing mesoporous ceramic pellets can be conveniently used in practical settings (post antifungal treatment, transport of fishes, and in aquariums).

CONCLUSION

Mesoporous porous clay-starch ceramic pellets from low fire clay and starch (up to 30 %) were successfully prepared. The mesoporous nature of the pellets was confirmed by BET surface area analysis. The absence of starch in prepared ceramics pellets was confirmed by IR studies. Analysis of the adsorption isotherm and the kinetic data was found to

Table 2: Isotherm data for the MB adsorption by mesoporous pellets.

Langmuir				Freundlich				Temkin			
R^2	Q [mg.g^{-1}]	B [l.mg^{-1}]	R_L	R^2	1/n	n	K_f [l.g^{-1}]	R^2	b [K.Cal.mol^{-1}]	B	A [l.g^1]
0.99	0.2331	11.539	0.079	0.97	0.6017	1.661	2.117	0.99	11.4018	0.0519	1.235

Table 3a: Kinetic data for the MB adsorption by pellets.

Conc. (ppm)	Pseudo1st order		Pseudo 2nd order		Bhangham				Elovich	
	R^2	K_1 [g.mg^{-1}.min^{-1}]	R^2	K_2 [g.mg^{-1}.min^{-1}]	R^2	K [mL.g^{-1}.L^{-1}]	α [min^{-1}]	R^2	β [g.mg^{-1}]	α [mg.g^{-1}min^{-1}]
0.25	0.967	0.0078	0.99	0.2829	0.941	198.437	0.463	0.917	125	0.00376
0.5	0.986	0.0087	0.99	0.0236	0.917	84.8641	0.35	0.943	58.823	0.00509
1.0	0.947	0.0055	0.99	0.0519	0.955	203.200	0.429	0.906	36.363	0.01402

Table 3b: Kinetic data intra-particle parameters for pellets.

Conc. [ppm]	R_1^2	R_2^2	$K_{diff.1}$ [g.mg^{-1}.min^{-1}]	$K_{diff.2}$ [g.mg^{-1}.min^{-1}]	$C_1 \times 10^2$ [mg.g^{-1}]	$C_2 \times 10^2$ [mg.g^{-1}]
0.25	0.9926	0.6112	2.2×10^{-4}	1×10^{-4}	6×10^{-4}	3.64×10^{-2}
0.5	0.9696	0.8292	4.9×10^{-3}	2×10^{-4}	1.2×10^{-2}	9.12×10^{-2}
1.0	0.9836	0.7276	6.6×10^{-3}	1×10^{-4}	3.4×10^{-2}	1.16×10^{-1}

Table 4: Statistical analysis for kinetic models.

[Vol.100mL, dose: 5 g.l^{-1}]		MAD $\dfrac{\sum qexp - qcal}{n}$	MSE $\dfrac{\sum(qexp - qcal)2}{n}$	RMSE $\dfrac{\sqrt{\sum(qexp - qcal)2}}{n}$	NSD($\Delta q\%$) $100\sqrt{\dfrac{\sum[(qexpexp - q_{Cal})/qexp]2}{n-1}}$
0.25 ppm	PFO	0.0020	5.74E-06	0.0023	14.924
	PSO	0.0018	4.87E-06	0.0022	10.680
	BKM	0.0019	6.38E-06	0.0025	6.99
	EKM	0.0026	0.00066	0.0258	164.111
	IPD	0.0012	2.32E-06	0.0015	8.4798
0.5 ppm	PFO	0.0178	0.00032	0.01813	34.3168
	PSO	0.0030	1.4E-05	0.0037	7.1947
	BKM	0.0025	7.49E-06	0.0027	4.0098
	EKM	0.025	0.000656	0.0256	49.45
	IPD	0.0029	1.987E-05	0.00445	6.8106
1.0 ppm	PFO	0.0094	0.00012	0.01105	21.03
	PSO	0.0069	7.262E-05	0.0085	13.003
	BKM	0.0072	0.00011	0.0108	9.3193
	EKM	0.07212	0.0053	0.073	131.35
	IPD	0.0077	0.00016	0.0124	8.83

be of Langmuir type and the pseudo-second-order reaction, respectively. Processes like boundary layer and pore diffusion were found to be involved during the rate-determining step of the adsorption. Error analysis of different kinetic models also favored pseudo-second-order reaction kinetics. The application of these ceramic pellets as a viable MB adsorbent at ultra-low concentrations in aquaculture has been demonstrated.

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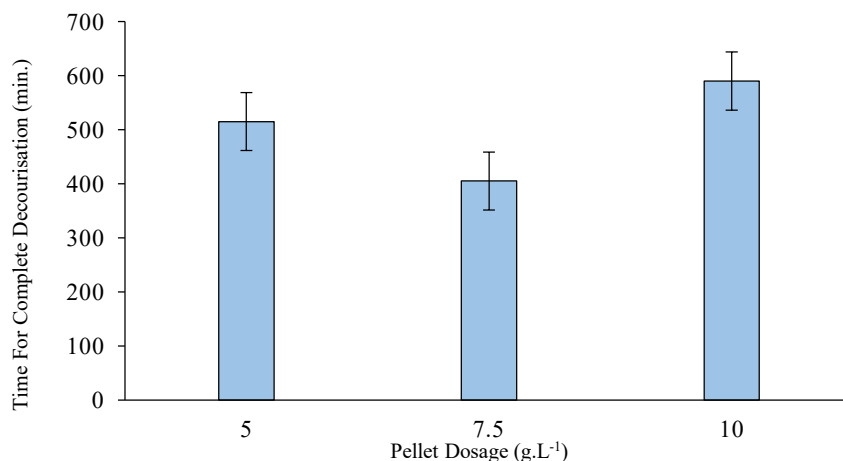Akkaya, G. and Özer, A. 2005. biosorption of acid red 274 (ar 274) on

Fig.10: Time taken by ceramic pellets for complete decolorization of solution.

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