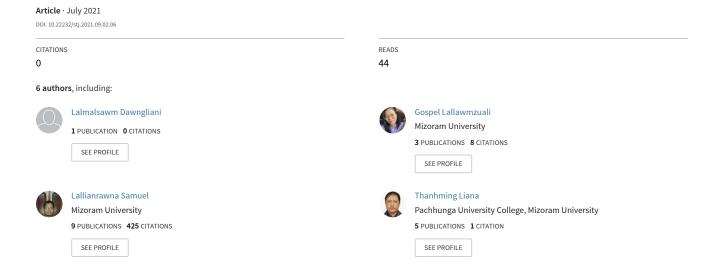
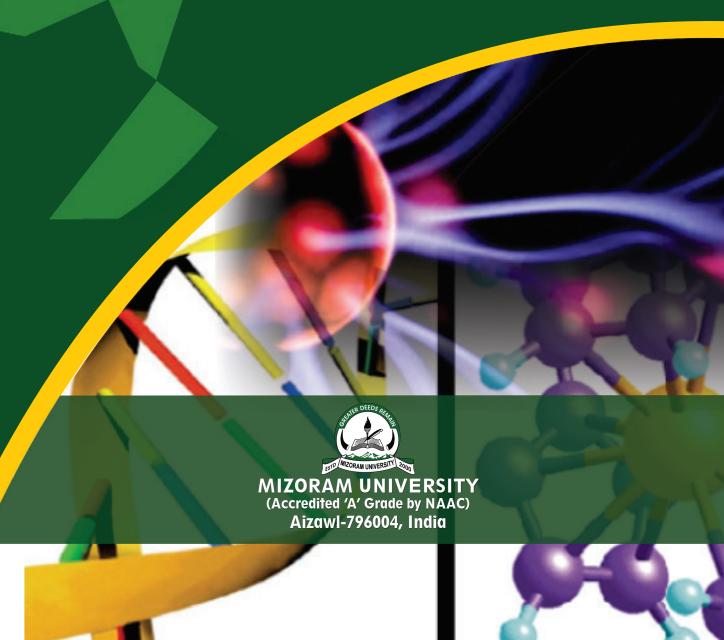
# Potential Application of Indigenous Microorganism Derived Biosorbent in the Efficient Removal of Congo Red from Aqueous Solution



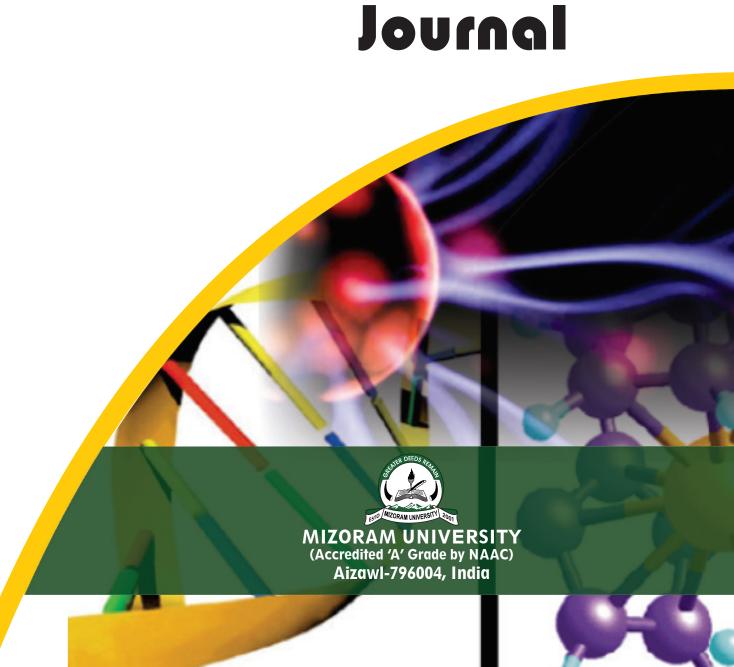
Vol. 9 Issue 2 July 2021 ISSN: 2321-3388

# Science & Technology Journal



Vol. 9 Issue 2 July 2021 ISSN: 2321-3388

# Science & Technology



### **Isolation and Molecular Characterisation of Ginger**

Farr and Rossman, 2010), is attributed to be the major causes of loss from decay of ginger rhizomes which also causes vascular wilt called "fusarium yellows", and several species of *Pythium* and *Fusarium* causing "soft rot", such as *Pythium myriotylum* Drechsler, *Fusarium oxysporum* and *Fusarium solani* (Wang *et al.*, 2003) and *Pythium aphanidermatum* (Edson) Fitzpatrick (Kavita and Thomas, 2008) have been reported in several countries including Taiwan, Malaysia, the USA, Japan (Farr and Rossman, 2010), India (Ravindran and Nirmal Babu, 2005) and Australia (Stirling, 2004).

Identification of major potential ginger diseases and their pathogentogether with their level of intensity has a great implication ondevelopment of disease management strategies. However, it has been a challenging effort to establish appropriate guidelines for the post-harvest management of ginger rhizomes in the ginger growing pockets of Mizoram, mainly due to the lack of knowledge about the main etiological agents associated with soft rot. The goal of this work was to conduct a survey of etiologic and fungi causing soft rot of ginger rhizomes in the main production region in the state of Mizoram, Champhai district, India. Moreover, it was conducted to identify other potential diseases those threaten ginger production with their level of intensity in Champhai district of Mizoram, India.

### MATERIALS AND METHODS

### **STUDY AREA**

The study was conducted at Research and Instrumentation Centre, Department of Zoology, Pachhunga University College, Aizawl, Mizoram during the month of September–October 2020. Sample materials were collected from 4 ginger farms of Champhai district, Mizoram, India: Dulte (CDT), Kawlkulh (CKK), Chawrtui (CT) and Puilo (CPL) (Fig. 1).

### SAMPLE COLLECTION

Rhizomes of Chinese ginger, commonly known as yellow ginger found with symptoms of soft rot were collected for direct isolation and morphological and molecular identification of fungi. From each ginger farms, 5 medium-sized (between 150 and 400 g) rhizomes with rot were collected, for a total of 20 rhizomes and transported to Research and Instrumentation Centre, Pachhunga University College.

### ISOLATION OF FUNGI FROM SAMPLES

Isolation of fungi was undertaken directly from diseased ginger with soft rot symptoms as described by



Fig. 1: Map of sample collection site

Le (Le *et al.*, 2014). Diseased part of the rhizome were thoroughly washed with running tap water, disinfected using 1% sodium hypochloride for 5 minutes and washed repeatedly with sterile distilled water to remove disinfectant and cut into 2-3 mm cube size using sterilized surgical blade. Isolation of fungal pathogens was done by using tissue-transplanting technique. Diseased and healthy ginger tissues were placed in a 1.5% water agar (WA) plates supplemented with 0.3 g/l ampicillin and gentamycin (Himedia). All the inoculated plates were kept in an incubator (Zeistech LS-116 BOD Incubator) at  $25 \pm 1^{\circ}$ C. The cultures were periodically checked and the emerging single mycelial hyphae were transferred to potato dextrose agar (PDA, Himedia) medium by means of hyphal tips

## Potential Application of Indigenous Microorganism Derived Biosorbent in the Efficient Removal of Congo Red from Aqueous Solution

# Lalmalsawmdawngliani<sup>1</sup>, Gospel Lallawmzuali<sup>2</sup>, Samuel Lallianrawna<sup>3</sup>, Thanhmingliana<sup>4</sup>, K. Vanlaldinpuia<sup>5</sup> and C. Lalhriatpuia\*

<sup>1</sup>Department of Chemistry, School of Physical Sciences Mizoram University, Aizawl, Mizoram, India <sup>2</sup>Department of Environmental Science, School of Earth Sciences Mizoram University, Aizawl, Mizoram, India <sup>3</sup>Department of Chemistry, Govt. Zirtiri Residential Science College, Aizawl, Mizoram, India <sup>4,5,\*</sup>Department of Chemistry, Pachhunga University College, Aizawl, Mizoram, India \*Email: clhpuia@gmail.com

**Abstract**—IMO compost was obtained using Indigenous Microorganisms (IMO) as inoculant through anaerobic fermentation process from kitchen waste biomass. The Physico-chemical analysis of the solid was obtained by taking pH, MC, OM, OC, N, K and P content. The biosorbent material was further characterized by SEM, IR and BET analytical techniques. Various physico-chemical parametric studies viz. effect of pH, initial dye concentration and background electrolyte concentrations are performed in the removal of Congo red (CR) dye using the IMO compost. The lower pH condition pH < 6.0 favoured the removal of Congo red and the percent removal was decreased with increase in the CR concentration. The removal of Congo red followed the pseudo-second order rate kinetics and the equilibrium state sorption data was reasonably fitted well to the Freundlich adsorption isotherm. In addition, the minimal effect of background electrolyte concentrations (0.0001 to 0.1 mol/L NaNO<sub>3</sub>) in the removal of CR inferred a specific sorption of Congo red forming 'inner sphere' complexes at the surface of the biosorbent.

Keywords: Biosorbent, IMO Compost, Congo Red, Removal, Kinetics

### INTRODUCTION

The textile and dyestuff industrial effluents are highly contaminated with dyes and Ca 15-50% of dyes are often discharged with effluent from dyeing operations and entered into the water bodies (Lellis  $et\,al.$  2019). It was estimated that the annual dye production exceeds  $7\times10^5$  tons (Robinson  $et\,al.$  2001) and every year, Ca  $2.0\times10^5$  tons of textile dyes are ultimately entered into the aquatic environment through the industrial effluents (Hasanpour & Hatami 2020). These dyestuff effluents are contained with high alkalinity, biological oxidation demand, chemical oxidation demand and total dissolved solids (Verma  $et\,al.$  2012). Not only to their aesthetic deterioration and eutrophication of water bodies some of the dyes, dye precursors or dye degradation

products are found to be toxic, mutagenic or carcinogenic (Chena *et al.* 2021). Therefore, a complete and efficient treatment method to remove effluent dyes from the water bodies is a greater need for the existing treatment plants (Wang *et al.* 2020).

Congo red also known as 3,3'-(biphenyl-4,4'-diyldidiazene-2,1-diyl)bis(4-aminonaphthalene-1-sulfonate) sodium is a water soluble diazo synthetic anionic dye (*cf* Structure 1). Congo red is primarily used as coloring textile, pulp/paper; making paint and as a pH indicator in chemical laboratory and for microbial staining. The synthetic origin and complex aromatic structures of this dye makes to be highly stable and found non-biodegradable (Jabar *et al.* 2020). Several methods are employed in the remediation of

such wastewaters contaminated with dyes viz. ion exchange (Jia et al. 2020), Coagulation (Shi et al. 2007), flocculation or precipitation (Yang et al. 2013) however, they show some restrictions related to the additional environmental concerns or the high cost operation of the treatment process (Adebayo et al. 2020). Similarly, the oxidation of dyes with chemical oxidants viz., chlorine, hypochlorite and ozone are widely employed due to their cost effectiveness, easy availability and fairly efficiency. Although the use of these oxidants is based on the degradation process it causes, in cases, the generation of harmful by-products or sometimes inadequate efficiency in particular towards the recalcitrant chemicals. Moreover, the chlorination and ozonation are accompanied with formation of harmful disinfection by-products (DBPs), such as trihalomethanes and bromate (Krasner et al. 2009). These by-products are potential mutagens or carcinogens and are sometimes even more harmful compared to the parent compounds.

Biodegradation methods involving fungal decolorization, microbial degradation or adsorption by (living or dead) microbial biomass and bioremediation systems are eventually applied for treating industrial effluents where active microorganisms viz. bacteria, yeasts, algae and fungi are able to accumulate and degrade a variety of pollutants (Khan et al. 2013). Nonetheless, the low cost and greener adsorbents are an ever-demanding for the efficient removal of dyes from waste wastewater. Several non-conventional low cost biosorbent materials such as banana peel (Munagapati et al. 2018), biochar (Zhu et al. 2018), fruit leaves (Gupta et al. 2012), coconut shell (Wu et al. 2020), fly ash (Woolard et al. 2002), peat (Fernandes, 2007), rice husk (Costa & Paranhos, 2019), tea waste (Hameed, 2009), Orange peel (Sivaraj et al. 2001), plant nanoparticles (Nayak et al. 2021), etc. are utilized for the removal of dyes from aqueous solution with relatively high efficiency.

On the other hand, composting is one of the most viable and efficient method for a sustainable management of biodegradable solid waste. It is a process which involves in situ degradation of organic solids by the macro-or microorganisms present in the organic waste to organic manure and hence, offer waste to 'value-added' products (Onwosi et al. 2017). Compost is a humus-like porous solid material with high adsorptive capacity and high water holding capacity (EPA, 1998). Compost has been used as a filter medium to remove air pollutants for several years and the high content of organic carbon with porous structure could perhaps, makes it potential adsorbents for the treatment of various organic and inorganic pollutants in the aquatic environment (Pagans et al. 2005; Pennanen et al. 2020). Therefore, EM based compost was

utilized for the removal of Malachite green from aqueous solution (Pushpa et al. 2005). Results demonstrated that the maximum uptake of MG (136.6mg/g) was achieved at pH 8 and the adsorption kinetics followed the pseudosecond order kinetics. In line, compost obtained from kitchen waste, leaf waste, paper waste and water hyacinth waste using Effective Microorganisms was assessed for the removal of Crystal Violet dye from aqueous solutions (Pushpa et al. 2016). The results indicated that the percent removal of CV dye was in the order 89.55 > 86.36 > 86.23> 77.46% using , , , and respectively and further suggested that removal of dyes from aqueous solution was due to the presence of organic carbon in the compost. Similarly, carnation flower waste derived compost was employed as biosorbent in the removal of Cr(VI) from aqueous solution under acidic condition and it was found that 99% Cr(VI) removal was achieved within 3hr of contact and adsorption-coupled reduction was proposed as the removal mechanism (Brandão et al. 2012).

The present communication intended to obtain IMO compost from Kitchen waste biomass materials using Indigenous Microorganisms as inoculant. Further, the obtained material was employed as biosorbent in the removal of Congo red from aqueous solution. The large availability of the biomass waste, efficiency of IMO and minimal use of chemicals in the synthesis of the biosorbent materials could, perhaps, enable the process more cost effective and greener treatment method. To the best of our knowledge, this study is the first systematic study on IMO based Kitchen waste Compost (IMO-compost) onto the biosorption of Congo red from aqueous solution.

Structure 1: Congo red dye

### MATERIALS AND METHODS

### **CHEMICAL AND MATERIALS**

Hydrochloric acid, sodium hydroxide and sodium nitrate are obtained from Merck India Ltd., India. Purified water (18.2 MΩ•cm at 25°C) is obtained from the Millipore Water Purification system (Model: Elix 3) and used for entire solution preparations and other analytical studies. Rice husk powder is procured from the local market. Prior to its use for collecting IMO, it was washed several times with purified water to remove any adhering impurities and then

dried in a room temperature. Quantification of Congo red concentration was done using UV-Visible spectrophotometer (Model: LT-2202-Labtronics, India).

### METHODOLOGY

# COLLECTION OF INDIGENOUS MICROORGANISMS (IMO)

The Indigenous Microorganisms (IMO) was collected from the forest area of the College campus (Pachhunga University College, Aizawl, Mizoram, India) using rice husk as the nutrient source. An indigenous microorganism (IMO) is a beneficial member of soil microorganisms including filamentous fungi, yeasts and bacteria which could enrich the nutrient of soil quality and act as a reserve source for nutrient that play an important role in decomposition of organic matter (Liu et al. 2011). Briefly, a small plastic box (dimension: 30 x 20 x 15 cm) was filled with 200g of semi moist rice husk and was covered with white paper. The box was then covered with a sheet of plastic to protect it from rain and then placed it under the tree in the forest area of the College Campus to avoid direct sunlight. After 4 day, the rice husk was covered with white mould (mycelium) and the smell was mildly sour which indicated the presence of indigenous microorganisms (IMO), named as IMO-1. The obtained IMO-1 was then mixed with a granulated brown sugar in the ratio of 1:1(w/w) to culture/ populate the microorganisms. This mixture was then placed in a plastic container in a cool spot for 5 day to allow the fermentation process to take place and then IMO-2 was obtained. The IMO-2 was then mixed with rice husk in the ratio (1:100 w/w) and fermented rice wash water was added until the mixture appeared semi moist. The mixture was placed in a plastic tray and it was covered with dried leaves and placed at room temperature for 5 day to obtain the final IMO-3. The final IMO-3 was air dried at room temperature and kept in a sealed container for further use.

### PREPARATION OF IMO COMPOST

A biodegradable solid viz. fruit peels, potato peels, banana peels, discarded vegetables etc. were collected from kitchen waste and were initially chopped off to reduce the sizes. A specified compost bin (20 L) having a lid, made of plastic was used to performed anaerobic fermentation of the biodegradable solid waste. About 2 table spoon of the obtained IMO powder was applied to every 2 inch of the biodegradable solid placed in the bin. Once the container was full, the bin was closed tightly to undergo anaerobic fermentation process caused by the microorganisms. After 30 day, the food waste was found pickled by the

white mycelium of the IMO. The pickled was then mixed with a moist coco peat by making a layer in a specified bin with closed lid and was waited for 30 day to obtain the matured compost. The final matured IMO compost was air dried for 24 hr and oven dried at  $50^{\circ}\text{C}$  in a drying oven. It was grounded to a powder and sieved to obtain 100 BSS (British Standard Sieve) mesh size particles (0.150 mm) and stored in airtight polyethylene bottle for further investigation.

### CHARACTERIZATION OF THE IMO COMPOST

The surface morphology and the elemental composition of the IMO compost was obtained by taking the SEM (scanning electron microscopic) images using a scanning electron microscope (Model: Nova Nano FEG-SEM 450, USA) equipped with EDAX. FT-IR data was obtained for the material using a FT-IR machine (Bruker, Tensor 27, USA by KBR disk method). Moreover, the Physico-chemical parametric analysis viz. Organic Carbon (OC), Organic Matter (OM), Moisture Content (MC), pH, N, P and K content was obtained as describe elsewhere (Thakur *et al.* 2012) to assess the quality of the compost.

### PH<sub>PZC</sub> AND BET MEASUREMENTS

The pH<sub>PZC</sub> (point of zero charge) of the sample was obtained by the known method as described previously (Lee *et al.* 2009). Similarly, the specific surface area of the solid was obtained using a BET Analyzer Quanta Chrome Nova 2200e, Surface Area & Pore Size Analyzer, USA.

### BATCH REACTOR EXPERIMENTS

Stock solutions of Congo red dye (50mg/L) was prepared by dissolving appropriate amount of the dye in a purified water. Further, the required Congo red concentration was obtained by successive dilution of stock solutions. 5.0mg/L of Congo red solution (100mL) was taken in polyethylene bottles and the pH was adjusted using concentrated HNO<sub>3</sub>/ NaOH solutions. 0.2g of IMO compost was introduced with these solutions. The bottles were kept in an automatic incubator shaker (Incubator Shaker, TM Weiber, ACMAS Technologies Pvt. Ltd., India) for 24hr at 25±1°C. These bottles were then taken out from the shaker and filtered with 0.45 µm syringe filter and the pH was again checked and reported as equilibrium pH. The filtrates were then taken to its bulk Congo red concentration using UV-Visible spectrophotometer. The absorbance was recorded at 497nm. The calibration curve was obtained with the standard Congo red solutions having the concentrations of

0.5, 1.0, 5.0, 10.0, 20.0 and 25.0mg/L. A good linearity was obtained with  $R^2$  value of 0.9999.

The Congo red concentration dependence study was performed varying the dye concentration from 1.0 to 20.0 mg/L at constant pH $\sim$ 6.0 and at constant temperature 25±1°C. The adsorption process was conducted similarly as detailed above. Results were presented as percent removal of Congo red or adsorption capacity as a function of initial Congo red concentration (mg/L). The sorption data was further utilized to demonstrate the equilibrium state modeling studies using the Langmuir and Freundlich adsorption isotherms as discussed elsewhere (Mittal  $et\ al.\ 2007$ ).

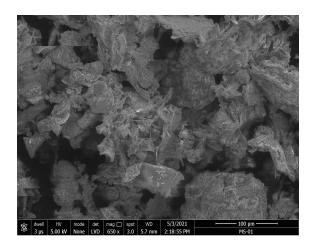
Effect of background electrolyte concentrations dependence sorption was studied varying the background electrolyte (NaNO $_3$ ) concentration from 0.0001 to 0.1 mol/L. The solution pH ( $\sim$ 6.0), Congo red concentration (5mg/L) and temperature (25±1°C) was kept constant throughout the experiments. Results were presented as percent removal of Congo red with the variation of background electrolyte concentrations.

Time dependence sorption of Congo red by the biosorbent was obtained at different time intervals. The initial Congo red concentration  $5.0 \, \text{mg/L}$  with solid dose  $2.0 \, \text{g/L}$  was taken as constant and the sorption experiments were conducted at constant pH  $\sim 6.0$  and at  $25 \pm 1 \, ^{\circ}\text{C}$ . Results were then reported as percent removal of Congo red as a function of time (min).

### **RESULTS AND DISCUSSIONS**

### CHARACTERIZATION OF SOLIDS

The surface morphology of IMO compost was obtained by taking the SEM images of the solid and return in Fig. 1. The SEM image showed a heterogeneous and disordered surface structure. The particles are also aggregated at some places. It was evident that numerous micro pores and meso pores were visible at the surface. Further the elemental composition of the material was obtained by taking EDAX analysis (Fig. 2). The results showed that carbon and oxygen were the main elemental constituents of the solid sample along with several micronutrients, contributing 43.43 and 41.12 weight percent for C and O element respectively.



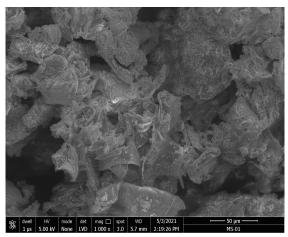


Fig. 1: SEM Image of IMO Compost

The FT-IR spectra of the solid were shown graphically in Fig. 3. The IR-spectra showed a sharp band at around 3286 cm<sup>-1</sup> was assigned to the stretching vibration of O–H, which corresponds to several groups containing hydroxyl group. A less intense band at around 2947cm<sup>-1</sup> was attributed to aliphatic C–H stretching vibrations. Moreover, a low intensity absorption bands at 1450, 1512 and 1604cm<sup>-1</sup> were due to the aromatic C=C stretching vibrations (Droussi *et al.* 2009). Further, a sharp band at around 1018cm<sup>-1</sup> was attributed to C-O stretching of carbohydrates, polysaccharides or polysaccharides like substances present in the solid (Inbar *et al.* 1990).

BET specific surface area, pore volume and pore size of the IMO compost was measured by the  $N_2$  adsorption/desorption method. The  $N_2$  adsorption/desorption curve was illustrated in Fig. 4. The  $N_2$  adsorption/desorption isotherms of IMO compost exhibits a  $N_2$  isotherm close to type IV which inferred mesoporous nature at the solid

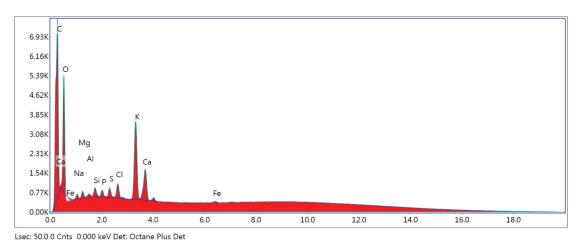


Fig. 2: EDAX Profile of IMO Compost

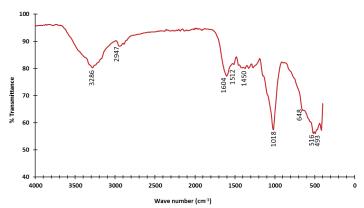


Fig. 3: FT-IR Spectra of IMO Compost

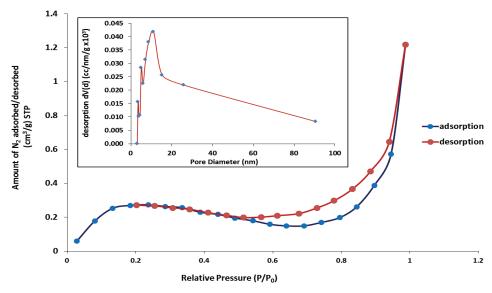


Fig. 4: BET Adsorption/Desorption Isotherms for the IMO Compost

surface. The isotherm curve was found to be H3 type hysteresis loop, suggesting that the non-rigid aggregation of plate-like particles giving rise to slit-shaped pores (Wang *et al.* 2013). This was in agreement with the result obtained with the SEM image. The inset of Fig. 4 showed the typical pore size distribution of the solid sample with three peaks at 3.5, 5.1 and 11.11nm respectively. Moreover, the pore size, pore volume and specific surface area of the solid were found to be 11.114nm, 0.002cm³/g and 1.017m²/g respectively.

Further, the Physico-chemical parameter of the IMO compost was obtained. Three replicate tests were done for each analysis and results were return in Table 1. The relatively high content of the N, P, K value with organic carbon and moisture content suggested that the obtained IMO compost was fairly good enough to apply as fertilizers or soil conditioner. Moreover, the pH value  $\sim\!6.07$  of the compost was again in agreement with the pHpzc value obtained for the sample.

Table 1: Physico-chemical Parameter of IMO Compost

No. of Test	MC (%)	рН	OC (%)	OM (%)	N (%)	P (Kg/ha)	K (kg/ha)
$R_{_1}$	65.36	6.04	4.42	7.62	1.15	35.24	395.72
$R_2$	66.05	6.11	4.60	7.93	1.09	37.25	398.25
R <sub>3</sub>	65.87	6.08	4.54	7.82	1.23	35.54	401.12

### **BATCH STUDIES**

### Effect of pH

The pH dependence sorption data is an important physicochemical parameter which enabled to deduce mechanism involved at solid solution interface. Therefore, the pH dependence sorption of Congo red (5mg/L) was conducted varying the solution pH from pH $\sim$ 2.0 to 10.0. The percent removal of Congo red as a function of pH was represented in Fig. 5. The Fig. clearly demonstrated that at lower pH values i.e., pH $\sim$ 2 – 4, a very high uptake of Congo red was occurred. However, on increasing pH, a gradual decrease in percent removal was observed up to its minimum value at pH Ca 6.0 and then slightly increased with increase in pH up to pH $\sim$ 10.0

These results were explained with the charge carried by solid surfaces and also the ionic charge carried by Congo red in aqueous solutions. It was observed that the  $pH_{pzc}$  of the IMO compost was found to be 6.7. Therefore, the solid carries a net positive charge below this pH and becomes negatively charged beyond this pH values according to the equation (1):

$$\equiv SOH_2^+ \rightarrow \equiv SOH^0 \rightarrow \equiv SO^-$$

$$pH_{PZC}$$
(1)

On the other hand, the Congo red is a benzidine-based anionic diazo dye (Yang  $et\ al.\ 2011$ ) and was carrying negative charge in solution. Therefore, below pH  $\sim$ 6.7, a very high uptake of Congo red was due to a strong electrostatic attraction between the anionic dye and positive surface charge of the solid (Litefti  $et\ al.\ 2019$ ). However, with increase in solution pH i.e. beyond pH $\sim$ 6.7 the solid surface becomes negatively charged and the Congo red molecule also carrying net negative charge and therefore; apparently a strong repulsion between them caused significantly less uptake of Congo red at alkaline condition. Similar results were reported previously for the sorption of Congo red by banana peel (Munagapati  $et\ al.\ 2018$ ). Additionally, the excess OH ions in alkaline solution may compete with the anionic dyes for the limited positively charged sites on the

solid surface thereby decreasing the sorption of the dye (Yang  $\it{et\,al.}\,2011$ ).

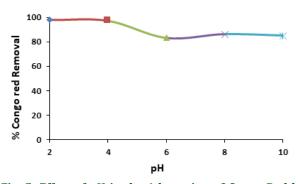


Fig. 5: Effect of pH in the Adsorption of Congo Red by IMO Compost  $\,$ 

### Concentration Dependence Studies

The concentration dependence sorption of Congo red by IMO compost was obtained varying the Congo red concentration from Ca 1.0 mg/L to 20.0 mg/L at pH $\sim$ 6.0 and at 25 $\pm$ 1°C. Results were then presented graphically in Fig. 6.

A very high percent removal of Congo red was not affected significantly by increasing the Congo red concentration from 1.0 to 20mg/L. However, on the other hand, the amount of dye removal was significantly increased with increasing the dye concentration. These results inferred a strong affinity of the dye towards the biosorbent and effective contact between Congo red and heterogeneous solid surface. Similar findings were also reported previously for the sorption of congo red using polyvinyl alcohol/sodium alginate/ ZSM-5 zeolite membrane (Radoor *et al.* 2020). It was stated that the higher initial dye concentration rendered driving force to overcome the mass transfer limit at the solid-solution interface (Litefti *et al.* 2019).

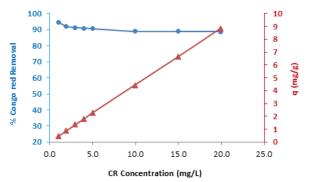


Fig. 6. Effect of Concentration in the Adsorption of Congo Red by IMO Compost

### Equilibrium State Modeling

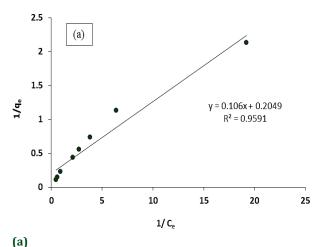
The equilibrium state sorption data was further employed to the linear fitting of Langmuir and Freundlich adsorption isotherm equations (Equations (2) and (3)):

$$\frac{1}{q_e} = \frac{1}{q_m} + \left(\frac{1}{q_m K_a}\right) \frac{1}{C_e} \tag{2}$$

$$lnq_e = lnK_f + (1/n)lnC_e \tag{3}$$

where  $q_e$  and  $C_e$  represent respectively, the amount of Congo red adsorbed and bulk Congo red concentration at equilibrium.  $q_m$  and  $K_a$  are the Langmuir constants indicating the maximum monolayer capacity of solid and strength or affinity of solid towards the sorbing species Congo red, respectively. On the other hand, the  $K_F$  and 1/n represent the Freundlich constants; referring to the maximum sorption capacity and adsorption intensity, respectively. The linear fitting of equilibrium state sorption data was presented graphically in Supplementary Fig. 7. The parameters viz.,  $`q_m$ ' and  $`K_A$ ' for Langmuir isotherm

and ' $K_{\rm F}$ ' and '1/n' for Freundlich adsorption isotherms with the linear regression value were computed and returned in Table 2. The data was reasonably fitted well to the Langmuir and Freundlich adsorption isotherms. However, comparatively, the Freundlich isotherm was better fitted than the Langmuir adsorption isotherm. The applicability of the Freundlich adsorption isotherm suggested that a strong chemical bond was formed between the sorbing species and the surface functional groups with lateral interaction (Tiwari *et al.* 2015).



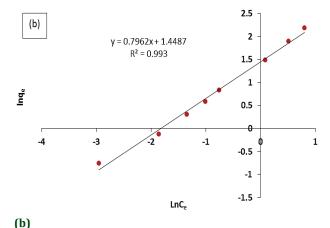


Fig. 7. Adsorption Isotherm Fitting (a) Langmuir, (b) Freundlich, in the Adsorption of Congo Red by IMO Compost

### Kinetic Studies

Further, the time dependence removal of Congo red by IMO compost was obtained by collecting the sorption data at wide range of time intervals i.e., from 5min to 180min. The initial concentration of Congo red was taken at 5.0mg/L at

Table 2: Langmuir and Freundlich Isotherm Parameters for Adsorption of Congo Red on IMO Compost

	Langmuir Isotherm		Freundlich Isotherm				
q <sub>m</sub> (mg/g)	Ka (L/g)	$\mathbb{R}^2$	K <sub>F</sub> (mg/g)	¹/n	$\mathbb{R}^2$		
4.880	46.04	0.9591	4.26	0.796	0.993		

constant pH $\sim$ 6.0. The percent removal of Congo red as a function of time was presented graphically in Fig. 8. It was evident that the material was efficient in the removal of the dye molecule from aqueous solutions since within initial 10-15min of contact, a maximum Congo red was aggregated onto the solid surface and was resulted in maximum percent uptake of the dye. This was then gradually slowed down and an apparent equilibrium was achieved within ca. 45min of contact. This again reaffirmed the affinity of the solid towards Congo red.

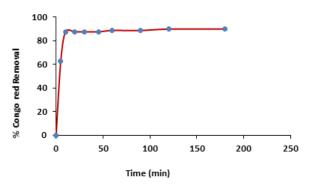


Fig. 8: Percent Congo Red Removal as a Function of Time

The time dependent sorption data was utilized to perform the non-linear form of three kinetic models viz. pseudo-first order (PFO), pseudo-second order (PSO) and fractal-like pseudo-second order (FL-PSO) kinetic modeling (Eq.(4)–(6)):

$$q_t = q_e (1 - \exp(-k_t t)) \tag{4}$$

$$q_{t} = \frac{kq_{e}^{2}t^{\alpha}}{1 + kq_{t}^{\alpha}} \tag{6}$$

where  $q_{i}$  and  $q_{i}$  were the amount of Congo red removed at time 't' and removal capacity at equilibrium, respectively.  $k_1$  and  $k_2$  were the pseudo-first and pseudo-second order rate constants, respectively. Similarly, the constants k and  $\alpha$  were referred to the rate constant and fractal constant, respectively. A non-linear least square fitting was conducted for the estimation of unknown parameters. The estimated values of the unknown parameters along with the least square sum were shown in Table 3. The kinetic simulation data was best fitted to the PSO and FL-PSO models comparing to the PFO model since reasonably low least square sum was obtained for these two models. Additionally, the applicability of the PSO or FL-PSO models pointed that the dye species were bound onto the solid surface by strong chemical forces. Previously, Wanyonyi et al. (2014) reported that the adsorption of Congo red on E. crassipes root followed the pseudo-second order kinetics and assumed that the rate of adsorption was controlled by chemical process involving valence forces through sharing or exchange of electrons between sorbate and the sorbent. Similar results was also obtained in the sorptive removal of Congo red on Polyacrolein (Tang et al. 2020) as well as using bimetallic Cr<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> oxides (Ibrahim, 2019).

# Effect of Background Electrolyte Concentrations

Further, the background electrolytes (NaNO<sub>3</sub>) concentration effect in the sorption of Congo red by the IMO compost was studied which could enable to explain the mechanism involved at solid/solution interfaces. Therefore, the sorption of Congo red by IMO compost was assessed by varying the background electrolyte concentrations i.e., NaNO<sub>3</sub> from 0.0001 mol/L to 0.1 mol/L at initial Congo red concentration

Table 3: Kinetic Parameters Obtained for the Sorption of Congo Red by IMO Compost using Various Kinetic Models

Kinetic Models									
	PFO		PSO			FL-PSO			
$\mathbf{q}_{\mathrm{e}}$	k <sub>1</sub>	s <sup>2</sup>	$\mathbf{q}_{\mathrm{e}}$	$\mathbf{k}_{2}$	s <sup>2</sup>	$q_{e}$	k	α	s <sup>2</sup>
2.014	0.278	0.071	2.109	0.332	0.025	2.052	0.020	2.610	0.014

s2: Least Square Sum

5.0 mg/L and at constant pH~6.0. The percent removal of Congo red was presented as a function of background electrolyte concentrations and presented graphically in Fig. 9. Quantitatively, increasing the background electrolyte concentrations from 0.0001 to 0.1mol/L NaNO, was caused to decrease the percent removal of Congo red from 62.79 to 62.50% (i.e., 0.24% decrease). This result indicated that the 1000 times increase of background electrolyte concentration (NaNO<sub>2</sub>) caused an insignificant decrease of Congo red removal by the IMO solid which inferred that Congo red was adsorbed specifically on the solid forming an 'inner-sphere' complex at the solid surface (Lalhmunsiama et al. 2014). Previously, it was noted that the percent removal of E2 by clay hybrid materials was not significantly affected by 1000 times increasing the NaCl concentrations (Thanhmingliana et al. 2016).

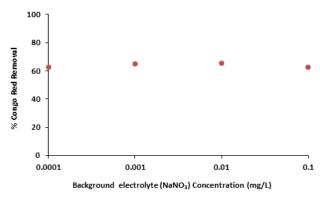


Fig. 9: Effect of Background Electrolyte (NaNO $_3$ ) Concentration on the Removal of Congo Red

### **CONCLUSION**

Biosorbent IMO compost was obtained from biodegradable solid waste employing Indigenous Microorganisms as inoculant using anaerobic fermentation method. The Physical characteristic of the compost was obtained by measuring the MC, pH, OC, OM, N, K and P content. Further, the solid was characterized by IR and BET method. The surface morphology of the solid was discussed with the SEM images. The biosorbent material possessed a heterogeneous structure composed with micro and meso pores onto the solid surface. Further, this material was utilized in the removal of non-biodegradable anionic dyes Congo red from the aqueous solutions under the batch reactor operations. The batch studies enabled that the increase in concentration of Congo red (1.0 to 20.0mg/L) favored greatly the removal of Congo red by IMO compost. The pH dependence data

showed that the lower pH region < 6.0 favored greatly the uptake of Congo red. Further, the equilibrium state sorption data was reasonably fitted well to the Freundlich adsorption isotherm. Moreover, the change in background electrolyte concentrations (0.0001 to 0.1mol/L NaNO<sub>2</sub>) could not affected significantly the percent removal of Congo red which pointed it towards the specific sorption of Congo red onto the solid surface and likely to form an 'inner sphere' complexes at the surface of the biosorbent. The kinetic data showed that the uptake of Congo red was fairly efficient as the apparent saturation between solid/solution was obtained within the contact of 30min. Moreover, the kinetic data was best fitted to the PSO and FL-PSO kinetic models compared to the PFO model. This further suggested that the chemisorption was the primary mechanism involved at the solid-solution interface.

### **ACKNOWLEDGEMENTS**

The authors thank SICART-Gujarat and BIT-Bangalore, India for sample analyses.

### REFERENCES

Adebayo MA, Adebomi JI, Abe TO, Areo FI (2020) Removal of aqueous Congo red and malachite green using ackee apple seed-bentonite composite. Colloid Interf Sci Commun 38: 100311.

Brandão VC, Ágreda, J PFB, Castillo E (2012) Bioadsorption using compost: An alternative for removal of chromium (VI) from aqueous solutions. BioRes 7(3): 2711–2727.

Chena G, Ana X, Li H, Lai F, Yuan E, Xia X, Zhang Q (2021)
Detoxification of azo dye Direct Black G by thermophilic
Anoxybacillus sp. PDR2 and its application potential in
bioremediation. Ecotoxicol. Environ Saf 214: 112084.

Costa JAS, Paranhos CM (2019) Evaluation of rice husk ash in adsorption of Remazol Red dye from aqueous media. SN Appl Sci 1: 397.

Droussi Z, D'orazio V, Provenzano MR, Hafidi M, Ouatmane A (2009) Study of the biodegradation and transformation of olive-mill residues during composting using FTIR spectroscopy and differential scanning calorimetry. J Hazard Mater 164(2–3): 1281–1285.

EPA: An Analysis of Composting as an Environmental Remediation Technology, EPA/530-R-98-008; 1998. US Environmental Protection Agency, Washington, DC. Available from: https://www.epa.gov/sites/production/files/2015-09/documents/analpt\_all.pdf [accessed in June, 2021].

Fernandes AN, Almeida CAP, Menezes CTB, Debacher NA, Sierra MMD (2007) Removal of methylene blue from aqueous solution by peat. J Hazard Mater 144(1–2): 412–419.

Gupta N, Kushwaha AK, Chattopadhyaya MC (2012) Adsorption studies of cationic dyes onto Ashoka (Saraca asoca) leaf powder. J. Taiwan Inst. Chem Eng 43(4): 604–613.

- Hameed BH (2009) Spent tea leaves: a new non-conventional and low-cost adsorbent for removal of basic dye from aqueous solutions. J. Hazard. Mater., 161(2-3), 753-759, 2009. https://doi.org/10.1016/j.jhazmat.2008.04.019.
- (2020)Hatami M Hasanpour Μ, Photocatalytic performance aerogels for organic dyes removal from wastewaters: Review study. J Mol Liq 309: 113094, 2020.
- Ibrahim MM (2019)  $Cr_2O_3/Al_2O_3$  as adsorbent: Physicochemical properties and adsorption behaviors towards removal of Congo red dye from water. J. Environ. Chem Eng 7(1): 102848.
- Inbar Y, Chen Y, Hadar Y (1990) Humic substances formed during composting of organic matter. Soil Sci Socie America J 54(5): 1316–1323.
- Jabar JM, Odusote YA, Alabi KA, Ahmed IB (2020) Kinetics and mechanisms of congo-red dye removal from aqueous solution using activated Moringa oleifera seed coat as adsorbent. Appl Water Sci 10:136.
- Jia Y, Ding L, Ren P, Zhong M, Ma J, Fan X (2020) Performances and Mechanism of Methyl Orange and Congo Red Adsorbed on the Magnetic Ion-Exchange Resin. J Chem Eng Data 65: 725–736.
- Khan R, Bhawana P, Fulekar MH (2013) Microbial decolorization and degradation of synthetic dyes: a review. Rev Environ Sci Biotechnol 12: 75–97.
- Krasner SW, Westerhoff P, Chen B, Rittmann B E, Amy G (2009)
  Occurrence of disinfection byproducts in United States
  wastewater treatment plant effluents. Environ Sci Technol
  43: 8320–8325
- Lalhmunsiama, C. Lalhriatpuia, Tiwari D, Lee SM (2014) Immobilized nickel hexacyanoferrate on activated carbons for efficient attenuation of radio toxic Cs(I) from aqueous solutions. Appl Surf Sci 321(1): 275–282.
- Lee SM, Tiwari D, Choi KM, Yang JK, Chang YY, Lee HD (2009) Removal of Mn(II) from aqueous solutions using manganesecoated sand samples. J Chem Eng Data 54(6): 1823–1828.
- Lellis B, Polonio CZF, Pamphile JA, Polonio JC (2019) Effects of textile dyes on health and the environment and bioremediation potential of living organisms. Biotechnol Res Innov 3: 275–290.
- Litefti K, Freire MS, Stitou M, Álvarez JG (2019) Adsorption of an anionic dye (congo red) from aqueous solutions by pine bark. Sci Rep 9: 16530.
- Liu J, Xu X, Li H, Xu Y (2011) Effect of microbiological inocula on chemical and physical properties and microbial community of cow manure compost. Biomass bioenergy 35: 3433–3439.
- Mittal A, Kurup L, Mittal J (2007) Freundlich and Langmuir adsorption isotherms and kinetics for the removal of Tartrazine from aqueous solutions using hen feathers. J Hazard Mater 146(1–2): 243–248.
- Munagapati VS, Yarramuthi V, Kim Y, Lee KM, Kim DS (2018) Removal of anionic dyes (Reactive Black 5 and Congo Red) from aqueous solutions using Banana Peel Powder as an adsorbent. Ecotoxicol Environ Saf 148: 601–607.
- Nayak SS, Mirgane NA, Shivankar VS, Pathade KB, Wadhawa GC (2021) Degradation of the industrial dye using the nanoparticles synthesized from flowers of plant Ceropegia attenuate. Mater Today 37(2): 2427–2431.
- Onwosi CO, Igbokwe VC, Odimba JN, Eke IE, Nwankwoala MO, Iroh IN, Ezeogu LI (2017) Composting Technology In Waste Stabilization: On the Methods, Challenges and Future Prospects." J environ manage 190: 140–157.

- Pagans EL, Font X, Sanchez A (2005) Biofiltration for ammonia removal from composting exhaust gases. Chem Eng J 113(2–3): 105–110.
- Pennanen T, Srivastava V, Silanpaa M, Sainio T. Compost (2020) Potent biosorbent for the removal of heavy metals from industrial and landfill storm water. J Clean Prod 273, 122736.
- Pushpa TB, Sekaran V, Basha SJS, Jegan J (2016) Investigation on Preparation, Characterization and Application of Effective Microorganisms (EM) Based Composts- An Ecofriendly Solution. Nature Environ. Pollut Technol 15(1): 153–158.
- Pushpa TB, Vijayaraghavan J, Basha SJS, Sekaran V, Vijayaraghavan K, Jegan J (2005) Investigation on removal of malachite green using EM based compost as adsorbent. Ecotoxicol Environ Saf 118: 177–182.
- Radoor S, Karayil J, Parameswaranpillai J, Siengchin S (2020) Removal of anionic dye congo red from aqueous environment using polyvinyl alcohol/sodium alginate/ZSM-5 zeolite membrane. Sci Rep10:15452.
- Robinson T, McMullan G, Marchant R, Nigam P (2001) Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. Biores Technol 77: 247–255.
- Shi B, Li G, Wang D, Feng C, Tang H (2007) Removal of direct dyes by coagulation: The performance of preformed polymeric aluminum species. J Hazard Mater 143: 567–574.
- Sivaraj R, Namasivayam C, Kadirvelu K (2001) Orange peel as an adsorbent in the removal of Acid violet 17 (acid dye) from aqueous solutions. Waste Manage 21(1): 105–110.
- Tang J, Zhang YF, Liu Y, Li Y, Hu H (2020) Efficient ion-enhanced adsorption of congo red on polyacrolein from aqueous solution: Experiments, characterization and mechanism studies. Sep Purif Technol 252: 117445.
- Thakur Rk, Baghel SS, Sharma GD, Sahu RK, Amule PC (2012)
  Training program on advances in Agro-technologies for improving Soil, Plants and Atmosphere system, Oct 11–31. http://jnkvv.org/pdf/Lab%20Manual%202012.pdf.
- Thanhmingliana, C. Lalhriatpuia, Tiwari D, Lee SM (2016) Efficient removal of  $17\beta$ -estradiol using hybrid clay materials: Batch and column studies. Environ Eng Res 21(2): 203–210.
- Tiwari D, Lalhriatpuia C, Lee SM (2015) Hybrid materials in the removal of diclofenac sodium from aqueous solutions: Batch and column studies. J Ind Eng Chem 30: 167–173.
- Verma AK, Dash RR, Bhunia P (2012) A review on chemical coagulation/flocculation technologies for removal of colour from textile wastewaters. J Environ Manage 93:154–168, 2012.
- Wang Q, Gao Y, Luo J, Zhong Z, Borgna A, Guoc Z, O'Hare D (2013) Synthesis of nano-sized spherical Mg3Al–CO3 layered double hydroxide as a high-temperature CO2 adsorbent. RSC Advances 3: 3414.
- Wang X, Deng B, Yu L, Cui E, Xiang Z, Lu W (2020) Degradation of azo dyes Congo red by MnBi alloy powders: Performance, kinetics and mechanism. Mater Chem Phys 251:123096.
- Wanyonyi YC, Onyari JM, Shiundu PM (2014) Adsorption of Congo Red Dye from Aqueous Solutions Using Roots of Eichhornia crassipes: Kinetic and Equilibrium Studies. Energy Procedia 50: 862–869.
- Woolard CD, Strong J, Erasmus CR (2002) Evaluation of the use of modified coal ash as a potential sorbent for organic waste streams. Appl Geochem 17(8): 1159–1164.

- Wu L, Zhang X, Thorpe JA, Li L, Si Y (2020) Mussel-inspired polydopamine functionalized recyclable coconut shell derived carbon nanocomposites for efficient adsorption of methylene blue. J Saudi Chem Soc 24: 642–649.
- Yang Y, Wang G, Wang B, Li Z, Jia X, Zhou Q, Zhao Y (2011) Biosorption of Acid Black 172 and Congo Red from aqueous solution by nonviable Penicillium YW 01: Kinetic study, equilibrium isotherm and artificial neural network modeling. Biores Technol 102(2): 828–834.
- Yang Z, Yang H, Jiang Z, Cai T, Li H, Li H, Li A, Heng R (2013) Flocculation of both anionic and cationic dyes in aqueous solutions by the amphoteric grafting flocculant carboxymethyl chitosan-graft-polyacrylamide. J Hazard Mater 254–255: 36–45.
- Zhu Y, Yi B, Yuan Q, Wu Y, Wang M, Yan S (2018) Removal of methylene blue from aqueous solution by cattle manurederived low temperature biochar. RSC Adv 8: 19917– 19929.