

NJC

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Synthesis of copper-isonicotinate metal-organic frameworks simply by mixing solid reactants and investigation of its adsorptive properties in the removal of fluorescein dye

Adedibu C. Tella^{1*}, Samson O. Owalude¹, Christianah A. Ojekanmi¹ and Oluwatobi S. Oluwafemi^{2*}

¹Department of Chemistry, P.M.B.1515, University of Ilorin, Nigeria.

²Department of Chemistry, Cape-peninsula University of Technology, P.O. Box 652, Cape Town 8000, South Africa.

Abstract

The formation of [Cu(INA)₂] (INA= isonicotinate) metal-organic frameworks (MOFs) by a highly efficient and environmentally method simply by mixing and heating solid reactants without milling has been investigated. The materials were characterized using elemental analysis, FT-IR spectroscopy and powder x-ray diffraction (PXRD) and scanning electron microscopy (SEM). Comparison of PXRD patterns of the materials with pattern simulated from single crystal X-ray diffraction data allowed identification of the products. The adsorption properties of the [Cu(INA)₂] was studied using fluorescein dye (FS). The adsorption data followed both Langmuir and Freundlich equations but was best suited to the Langmuir model. The adsorption data were also correlated with Temkin and Dubinin-Radushkevich adsorption model and the results showed that adsorption process is physical. These results indicate that the adsorption of FS on the [Cu(INA)₂] is partly due to electrostatic interaction between fluorescein and the adsorbent. Compared with the traditional synthetic techniques, this method for the synthesis of MOF was found to be highly efficient, environmentally benign and useful for the large scale production.

Keywords: MOFs, PXRD, adsorption isotherms, fluorescein dye

*Corresponding author: ac_tella@yahoo.co.uk and oluwafemi.oluwatobi@gmail.com

Introduction

Metal organic frameworks (MOFs) have attracted significant attention during the past decade due to their high porosity, tunable structures and controllable surface functionalities.¹ Many MOFs have been synthesized by a variety of solvent- based methods, ranging from solvothermal conditions over several days to reflux for several hours.²⁻⁵ Recently, alternative synthetic methods which introduces energy into the reaction systems have been described e.g. electrochemical, sonochemical methods, microwave heating and introduction of mechanical energy by mechanochemistry.⁶⁻⁷ The first solvent-free mechanochemical synthesis of a microporous metal-organic framework [Cu(INA)₂] using ball-mill was reported in 2006 by James *et al.*⁸ Since then, there has been an increasing interest in the use of mechanochemical method to prepare metal-organic frameworks and metal complexes. Most of the studies carried out on the synthesis of metal organic frameworks in solid state involved the use of ball-mills.⁹⁻¹¹ However, ball-mills have some limitations such as temperature control, low yields and contamination of the products by ball materials. All these make the use of this method for large scale production unfeasible. Hence, development of highly efficient and environmentally friendly synthetic methods for MOFs has become an emerging challenge to the synthetic chemist. Thus, we report the synthesis of [Cu(INA)₂] in the solid state via a facile, highly efficient and environmentally benign method simply by mixing together appropriate reactants without co-milling. Synthesis of porous and non-porous metal-organic frameworks directly from metal oxide precursors using a similar approach known as “accelerated aging” have been reported.¹²⁻¹⁴

Removal of hazardous materials from the environment has continued to be of interest due to the negative effects on the environment and human health. Adsorptive removal of toxic components

from fuels, waste-water and air is one of the most attractive approaches for environmental remediation. The commonly employed adsorbent materials are alumina silica, metal hydroxides and activated carbon.¹⁵⁻¹⁷ MOFs have also been widely investigated for the adsorptive removal of various hazardous materials from the environment due to their high porosity and variable pore geometry.¹⁸⁻²¹

Dyes typically have complex aromatic molecular structures which are stable and difficult to biodegrade. The conventional methods of removing dyes include, coagulation and flocculation, oxidation or ozonation and membrane separation.²²⁻²⁴ These methods have not received prominent attention because they are not cost effective. In contrast, an adsorption technique is by far the most versatile and widely used. However, there are few reports on the use of MOFs to remove dyes from solutions.²⁵⁻²⁷ To the best of our knowledge, there has been no report on the use of $[\text{Cu}(\text{INA})_2]$ as an adsorbent to remove dye from aqueous solution. We herein report the results of our findings on the adsorption of fluorescein dye by MOF $[\text{Cu}(\text{INA})_2]$ which was synthesized by simply mixing copper acetate monohydrate and isonicotinic acid at room temperature without co-milling.

EXPERIMENTAL

Materials and Instrumentation

All reagents were purchased from Sigma-Aldrich and were used without further purification. Infra-red spectra were obtained from the samples in the form of KBr pellets using a Perkin Elmer FTIR spectrometer. Metal analyses were performed by atomic absorption spectroscopy with Perkin-Elmer Spectrometer, model 3110. UV-Vis spectra were obtained on an Aquamate v4.60 spectrophotometer. The analyses of carbon, hydrogen and nitrogen were carried out on a Perkin-Elmer 204C microanalyser. Powder XRD analysis was performed on a Syntag PADS diffractometer at 294 °K using Cu $K\alpha$ radiation ($\lambda = 1.54059 \text{ \AA}$). Each sample was analyzed

between 4.0 and 40.0° 2 θ with a total scan time of 5.0 min. Ball-milling was performed using a RetchMM2000. The synthesis of [Cu (INA)₂] metal-organic framework by mixing of solid reactants (**MSR**), mixtures were prepared using molar ratio of reactants as reported in literature.^{8,28,29} Synthesis using the ball-milling method (**BSR**) followed the procedure described in reference 8.

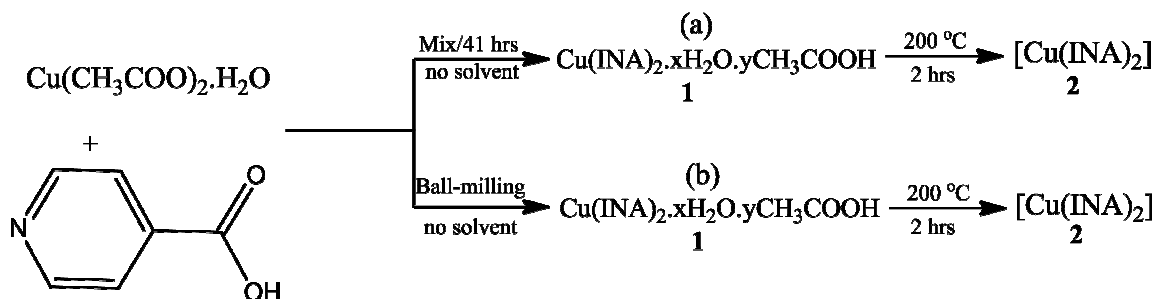
Synthesis by mixing of solid reactants (MSR)

Approximately 500 mg of each reactant was ground individually at room temperature in air for 30 seconds using a mortar and pestle. Copper acetate monohydrate (203 mg, 1 mmol) and isonicotinic acid (252 mg, 2 mmol) ground separately, were mixed together manually in a vial for 1 minute. The mixture was characterized by FT-IR and PXRD prior to storage. The mixture was then stored at room temperature for 41 hours, with constant shaking at interval of 10 hours. The formation of the product was evident by the colour change from green to blue. The material obtained was desolvated by heating at 200 °C for 2 hours, (Yield 80 %, Mol. wt = 308 g mol⁻¹, elemental analysis for [C₁₂H₈N₂O₄Cu]: calcd. C, 46.75; H, 2.60; N, 9.09; Cu, 20.62 % found: C, 45.51; H, 2.71; N, 8.94; Cu, 21.00 %. IR (KBr, cm⁻¹): 3680, 3260, 3136, 3091, 1620, 1605, 1556, 1500, 1417, 1376, 1321, 1230, 1057, 867, 775, 700, 669, 615, 574, 470.

Synthesis by ball-milling of solid reactants (BSR)

For comparison purpose, ball-milled synthesis was carried out by adopting the procedure of Pichon *et al.*⁸ Copper acetate monohydrate (203 mg, 1 mmol) and isonicotinic acid (252 mg, 2 mmol) were carefully weighed into a Retsch MM 200 stainless steel ball-mill vessel equipped with steel balls (20 g). The vessel was closed and the milling was carried out at room temperature at a speed of 25 Hz for 10 minutes. The material obtained was desolvated by heating at 200 °C for 2 hours. Yield 72 %, Mol. wt = 308 g mol⁻¹, elemental analysis for [C₁₂H₈N₂O₄Cu]:

calcd. C, 46.75; H, 2.60; N, 9.09; Cu, 20.62 % found: C, 45.95; H, 2.66; N, 9.16; Cu, 20.75 %.
 IR (KBr, cm⁻¹) 3660, 3227, 3115, 3084, 1615, 1600, 1553, 1500, 1410, 1384, 1321, 1232, 1061, 867, 777, 700, 667, 627, 579, 475.



Scheme 1: Synthetic methods (a) Mixing (b) Ball-milling

Adsorption experiment

A batch equilibrium technique was used to study the adsorption of fluorescein on the [Cu(INA)₂] synthesized using the MSR method (scheme 1a). Adsorption experiments were carried out in 250 mL flasks and the total volume of the reaction solution was kept at 50 mL. The flasks were shaken at 165 rpm for 2 hours in an incubator shaker. The adsorption conditions such as contact time, pH, temperature, dye concentration and adsorbent dosage were optimized to determine the maximum removal of fluorescein dye over [Cu(INA)₂]. The effect of adsorbent dosage on the dye removal was investigated at different adsorbent dosages between 5 and 40 mg. The effect of contact time on the dye removal was studied up to equilibrium, which was reached within 360 minutes. The effect of the initial fluorescein dye concentrations were studied in the range 3 to 18 mg/L. The effect of temperature was investigated between 310 – 328 °K. The effect of the pH on the removal of the dye was studied in the range 3 to 11 using 0.1M HCl or 0.1M NaOH. After adsorption, the adsorbent and the supernatants were separated by centrifugation at 1500 rpm for 10 min. The supernatants were analyzed for residual dye concentration using a UV-visible

spectrophotomete, by monitoring the absorbance changes at λ_{max} of 490 nm. The amount of dye adsorbed per gram of adsorbent (Q_e) was calculated using equation (1)

$$Q_e = \frac{(C_o - C_e)V}{w} \quad (1)$$

Where C_o and C_e are the initial and equilibrium liquid phase concentrations of the dye in mg/L respectively, V is the volume of the solution in L and w is the amount of adsorbent used in g. The equilibrium data were analyzed using the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich adsorption isotherm models.³⁰⁻³³ The data on the effect of contact time were fitted into the pseudo-first-order and pseudo-second-order kinetic equations and the characteristic parameters were determined.

Results and discussion

Characterization of the adsorbent

The metal-organic framework of copper isonicotinate [$\text{Cu}(\text{INA})_2$] (**2**) has been prepared by mixing copper acetate salt and isonicotinic acid in the appropriate ratio and allowed to stand for 41 hrs with intermittent shaking and by ball milling. The structure of **2** consists of infinite chains of copper ions bridged by carboxylate ligands.⁸ The material synthesized by MSR and that formed by BSR techniques were characterized by comparison of their elemental analysis data, infra-red spectra and PXRD patterns. The agreement between the theoretical and the experimentally determined CHN values for both materials indicate that the compounds are pure. Also, similarity of the elemental analysis data of the material from the two methods shows that they are the same.

Infra-red spectroscopy

Fig. 1 shows comparison of the infra-red spectra of $[\text{Cu}(\text{INA})_2]$ obtained from both methods. The absence of an absorption band at 1700 cm^{-1} suggests that the carboxylic groups of the ligand isonicotinic acid in the MOFs obtained are de-protonated.³⁴ The IR bands in both products from MSR and BSR methods show a strong absorbance at $\sim 1600\text{ cm}^{-1}$ (ν_{COO^-} asymmetric) and $\sim 1553\text{ cm}^{-1}$ (ν_{COO^-} symmetric stretch). The absence of carbonyl ($\text{C}=\text{O}$) stretching vibration IR bands between 1655 and 1730 cm^{-1} in the two MOFs shows that the HINA is fully coordinated.³⁵ In addition, the presence of an absorption band at $\sim 775\text{ cm}^{-1}$ indicates the formation of Cu-O coordination bond in these compounds.³⁶ The $\text{C}=\text{N}$ stretch is shifted from 1555 cm^{-1} to 1500 cm^{-1} in both products due to the participation of the nitrogen of the pyridine ring in the coordination. The IR spectra of **1** produced by MSR and BSR are identical providing further evidence that they are the same material. Heating of **1** at $200\text{ }^\circ\text{C}$ for 2 hours produced material **2**. The infra-red spectra of both materials show a slight difference due to the removal of glacial acetic acid and water from material **1** (see supplementary materials)

X-ray powder diffraction analysis

The PXRD pattern of the MSR mixtures measured 10 hours after mixing exhibited some new peaks suggesting partial reaction had occurred as shown in Fig. 2. The reaction as reported is self-propagating and the reaction started as soon as the reactants got in contact, with the release of glacial acetic acid which serves as fluid.⁸ The progress of the reaction was monitored by PXRD as shown in Fig. 2. It can be seen that once the two reactants were brought into contact via shaking every 10 hours, the reaction proceeded to completion without grinding or ball-milling. The colour changed from green to blue as the reaction approached the endpoint. PXRD

patterns of compound **1** made by the MSR method and that obtained using BSR are identical as shown in Fig. 3.

The single crystal diffraction data for the empty framework of $[\text{Cu}(\text{INA})_2]$ reported by Lu and Babb,³⁷ was obtained from the Cambridge Structural Database (CSD) (ref. code UFUMUD). Its PXRD pattern was simulated from the single crystal data using Mercury 1.3 software and compared to that of the material **1** obtained by MSR. **1** contains glacial acetic acid and water, but this was readily removed by heating, to produce **2**. The PXRD patterns of **1** (MSR) and the simulated pattern of UFUMUD are very similar, with some discrepancies due to the presence of acetic acid and water in the former (Fig. 3). Far better agreement is seen when compound **1** (MSR) is heated at 200 °C for 2 hours to remove water and glacial acetic acid, producing **2** (Fig. 3).

Scanning Electron Microscopy (SEM) study

The SEM images of the product **2** from the MSR and BSR methods are shown in Figure 4. The morphologies of MOF crystals obtained from MSR are homogenous, which indicates the crystallized phase. The MSR sample contained crystals that are larger, with defined faces and edges than those obtained from ball-milling. The SEM image of the ball-milled product is not homogenous due to concomitant nucleation and crystal growth. A cursory look at the images of the product obtained from two the methods revealed a close correspondence in term of phases.

Correspondence between the products from mixing of solid reactants, ball-milling and single crystal data was ascertained by comparing the analytical data (CHN), infra-red spectra, SEM and powder diffraction patterns. In all cases, the data are almost identical suggesting they are same materials.

Dye adsorption studies

The removal of fluorescein dye from aqueous solution through adsorption on $[\text{Cu}(\text{INA})_2]$ was investigated under different conditions of contact time, dye concentration, pH, temperature and adsorbent dosage to maximize the adsorption efficiency.

Effect of initial dye concentration

The effects of initial dye concentrations were studied at 298 K for 12 hours using 0.025 g of adsorbent. As shown in Fig. S8, the amount of fluorescein dye adsorbed on $[\text{Cu}(\text{INA})_2]$ increased with increase in concentration up to 15 mg/L and reaches a constant value thereafter. The result implies that at low concentrations of the dye solutions, there still existed unoccupied adsorption sites that became occupied with increase in concentration.³⁸ At this concentration, all the adsorption sites have been saturated with the dye molecules.³⁹

Effect of contact time

The effect of contact time was investigated at room temperature for the adsorption of fluorescein dye on porous $[\text{Cu}(\text{INA})_2]$ and the plot of removal efficiency at different contact times is shown in Fig. S9. The adsorption rate increased with time at the initial stages of the sorption process and reached equilibrium value after 6 hours. This has been attributed to great amounts of unoccupied active sites on $[\text{Cu}(\text{INA})_2]$ and high concentrations of the dye molecules at the initial stage resulting in the high adsorption rates.²⁶ As the adsorption process continues, the active sites becomes occupied and there is decrease in the dye molecules in the solution, uptake rates thereby decreases until equilibrium was obtained after 6 hrs.

Effect of temperature

The effect of temperature was studied using 0.02 g of the adsorbent. The results obtained from the above two studies of optimum initial concentration and time were used here. From Fig. S10, it can be observed that the adsorption value of fluorescein on $[\text{Cu}(\text{INA})_2]$ reached a maximum at 45 °C. This result showed that temperature is another factor that can influence the amount of dye adsorbed from solution.

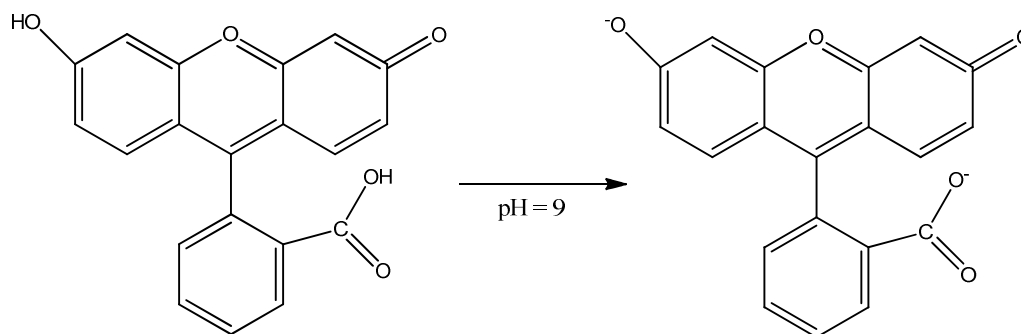
Effect of Adsorbent dosage

The results obtained from the above three studies of optimum initial concentration, time and temperature were used here. It can be observed from Fig.S11 that the adsorption value increased with increase in adsorbent dosage. This is attributed to increased adsorbent surface area and availability of more adsorption sites.⁴⁰ A slight decrease in the adsorption value with increase in the adsorbent dosage from 0.03-0.04 g may be due to the conglomeration of the adsorbent.

Effect of pH

The results obtained from the above four studies of optimum initial concentration, time, temperature and adsorbent dosage were used here. The adsorption of fluorescein dye is highly dependent on the pH of the solution. It is only stable at within pH 7-9,⁴¹ so the adsorption study was carried out at pH values 7 and 9. The amount of fluorescein dye adsorbed at pH 7 was 41.5 mg/g for $[\text{Cu}(\text{INA})_2]$ while at pH 9 it was, 50.9 mg/g. This is attributed to the fact that the flourescein dye in aqueous solution at the pH of 9 will exist in dianionic form with the negative charge on both the carboxylate and the phenolate groups as shown in scheme 2.^{42,43} $[\text{Cu}(\text{INA})_2]$ has positively charged Cu(II) sites (Lewis acid) with a reported pore size of $12.7 \times 11.4 \text{ \AA}$,⁴⁴ this pore size will be too small to contain the fluorescein dye molecules. The mechanism of fluorescein adsorption on $[\text{Cu}(\text{INA})_2]$ may therefore be explained in terms of electrostatic

interaction between the negatively charged dye molecules and the positively charged $[\text{Cu}(\text{INA})_2]$ adsorbent.⁴⁵ Similar adsorption mechanism of anionic dyes via electrostatic interaction has been reported.^{46,47}



Scheme 2: Chemical structures of fluorescein

Adsorption isotherms

Adsorption isotherms show the relationship between the amount of dye adsorbed and the concentration of the dye at constant temperature. For solid–liquid adsorption system, the adsorption isotherm is an important model in the description of adsorption behavior. When the adsorption reaction reaches equilibrium state, the adsorption isotherm can indicate the distribution of dye molecules between the solid phase and the liquid phase.⁴⁸ It is significant to understand the adsorption behavior in order to identify the most appropriate adsorption isotherm model. To describe the equilibrium nature of adsorption in this study, various isotherm equations such as Langmuir, Freundlich, Temkin and Dubinin-Radushkevich equations have been used.²⁻⁸

The linear form of Langmuir's isotherm model for adsorption in solution is given by the equation 2

$$\frac{C_e}{q_e} = \frac{1}{K_L Q_m} + \left(\frac{1}{Q_m} \right) C_e \quad (2)$$

Where C_e is the equilibrium concentration of the adsorbate (mg/L), q_e the amount of adsorbate per unit mass of adsorbate (mg/L), and Q_m and K_L are Langmuir constants related to adsorption capacity and rate of adsorption, respectively.

The logarithmic form of Freundlich model for adsorption in solution is given by the equation 3 below:

$$\log Q_e = \log K_f + 1/n \log C_e \quad (3)$$

Where Q_e is the amount of dye sorbed at equilibrium per gram of adsorbent (mg/g), C_e is the equilibrium concentration of the dye in the solution (mg/L), and K_f and n are the Freundlich model constants. The numerical value of $1/n$ reported in Table 1 is less than 1 which indicates that adsorption capacity is only slightly suppressed at lower equilibrium concentrations.⁴⁹

The linear form of the Temkin isotherm equation has been commonly applied in the form of equations 4 and 5.

$$q_e = \left(\frac{RT}{b_T} \right) \ln AT + \left(\frac{RT}{b_T} \right) \ln C_e \quad (4)$$

Equation 4 can also be written as

$$q_e = RTB \ln AT + B \ln C_e \quad (5)$$

where $B = RT/b_T$

B is the Temkin constant related to the heat of adsorption (J/mol), AT is the equilibrium binding constant (L/mg), b_T is the Temkin isotherm constant, R is the universal gas constant (8.314 J/mol/K) and T = Temperature at 298 K.

The D-R isotherm, apart from being analogue of Langmuir isotherm, is more general than Langmuir isotherm as it rejects the homogenous surface or constant adsorption potential.⁵⁰ It is expressed as:

$$\ln q_e = (q_s) \exp(-B_D \varepsilon^2) \quad (6)$$

and in linear form we have

$$\ln q_e = \ln q_s - B_D \{RT \ln(1 + 1/C_e)\}^2 \quad (7)$$

Where $\varepsilon = (1 + 1/C_e)$

Here q_e = amount of adsorbate in the adsorbent at equilibrium (mg/g), q_s = theoretical isotherm saturation capacity (mg/g), B_D = Dubinin-Radushkevich isotherm constant relating to energy (mol^2/kJ^2).

The regression coefficient values R^2 show the applicability of the isotherms to the absorption process. Table 1 shows that Langmuir isotherm has the highest R^2 value of 0.9994, therefore, it fits most to the absorption process. The isotherms have R^2 values of increasing order $0.894 < 0.957 < 0.961 < 0.994$ corresponding to Freundlich < Temkin < Dubinin-Radushkevich < Langmuir. The corresponding plots of the adsorption models are given in the supplementary material.

The D-R isotherm, apart from being an analogue of Langmuir isotherm is more general than Langmuir isotherm as it rejects the homogenous surface or constant absorption potential.⁵⁰ The equilibrium parameter R_L calculated from the Langmuir isotherm shows that the absorption is favourable since it is between 0 & 1⁵¹ and the maximum monolayer coverage capacity Q_m is 66.67 mg/g. A unique feature of D-R isotherm model is the fact that it is temperature dependent. Q_s was found to be 70.81 mg/g and mean free energy E is 1290.99 J/mol from the D-R isotherm plot. The fact that the data fits the Langmuir isotherm better than the Freundlich isotherm suggests that the absorption of fluorescein onto $[\text{Cu}(\text{INA})_2]$ is monolayer sorption rather than adsorption on a surface having heterogeneous energy distribution.⁵²

Table 1: Isotherm parameters for fluorescein dye adsorbed onto [Cu(INA)₂].

Langmuir	Freundlich	Temkin	Dubinin-Radushkevich
Q_m (mg/g) = 66.67	K_f (mg/g(L/mg) ^{1/n}) = 23.39	$B = 26.32$	B (mol ² /kJ ²) = 3×10^{-7}
K_L (L/mg) = 1.364	$n = 1.105$	$b_T = 96.344$	Q_s (mg/g) = 70.81
$R_L = 0.047$	$1/n = 0.91$	A_T (L/mg) = 3.049	E (J/mol) = 1290.99
$R^2 = 0.994$	$R^2 = 0.894$	$R^2 = 0.957$	$R^2 = 0.961$

Adsorption kinetics

The experimental data on the effect of contact time at 298 K were fitted into the pseudo-first-order rate equation (Eq. (7)) and the pseudo-second-order rate equation (Eq. (8)) to analyze the adsorption kinetics of the fluorescein dye molecules on [Cu(INA)₂]:

$$\ln (q_e - q_t) = \ln q_e - k_1 t \quad (7)$$

where k_1 is the rate constant for the first-order model for the adsorption process (min⁻¹). The values of k_1 can be calculated from the slope of the plots of $\ln (q_e - q_t)$ versus t .⁵³ For the pseudo-second-order, equation 8 applies:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (8)$$

where k_2 is the rate constant of the pseudo-second-order model for the adsorption process (g mg⁻¹ min⁻¹).⁵⁴ From the plot of t/q_t against t values of k_2 and q_e can be determined.

The kinetic parameters for the sorption of the fluorescein dye molecules on [Cu(INA)₂] at 298 K are summarized in Table 2. The plot of $\ln (q_e - q_t)$ versus t and t/q_t versus t are shown in the supplementary materials Fig. S6 and S7 respectively. The pseudo-second-order kinetic plot showed a better fit to the data (i.e., higher correlation coefficient = 0.982) than the pseudo-first-

order kinetic model (correlation coefficient = 0.977). This result is consistent with the literature reports.⁵⁵

Table 2. Adsorption kinetic parameters for the adsorption of fluorescein onto [Cu(INA)₂] at 298 K.

Adsorbent	Q _e exp (mg/g)	Pseudo-first-order			Pseudo-second-order		
		k ₁ (min ⁻¹)	Q _e (cal) (mg/g)	R ²	k ₂ (g(mgmin ⁻¹))	Q _e (cal) (mg/g)	R ²
mCu-INA	7.49	0.010	125.84	0.977	5.594 x 10 ⁻⁵	125	0.982

This study has demonstrated that fluorescein dye can be efficiently removed from water using a MOF-type material [Cu(INA)₂] via specific interaction between dye and the adsorbent. The adsorption of fluorescein over [Cu(INA)₂] at various temperatures showed that the adsorption capacity increased with increasing adsorption endothermic similar to previous studies.^{56,57}

Conclusions

In this study, we present for the first time an efficient new method for the synthesis of MOFs under solvent-free condition. We also demonstrated that the method can provide a real alternative to ball-milling and solution based methods. The method is simple and environmentally friendly and can be applied to important industrial processes. The adsorption of fluorescein dye was studied to examine the potential of [Cu(INA)₂] in removing dyes from water solution. The adsorption data was best fitted into the Langmuir isotherm model. The adsorption data were analyzed using pseudo-first-order and pseudo-second-order kinetic equations and the results showed that the adsorption process followed the pseudo-second-order kinetics. These

results suggest that the adsorption of fluorescein on the MOFs is partly due to electrostatic interaction between fluorescein and the adsorbent. Based on this study, [Cu(INA)₂] can be suggested as a potential adsorbent to remove dye from aqueous solution.

Acknowledgement

ACT is grateful to the Royal Society of Chemistry for the award of JWT Jones Fellowship and to Professor Stuart James of Queen's University, Belfast, United Kingdom for the facilities to carry out the research. The authors would also like to thank Professor Susan Bourne of University of Cape Town, South Africa, for helpful discussions.

References

1. O. M. Yaghi, M. O. Keefe, N. W. Ockwig, H. K. Chae, M. Eddaoudi and J. Kim, *Nature*, 2003, **432**, 705.
2. Y-K. Seo, G. Hundal, I. T. Jang, Y. K. Hwang, C-H. Jung and J-S. Chang, *Microporous Mesoporous Mater.*, 2009, **119**, 331.
3. V. I. Isaeva, O. P. Tsachenko, T. R. Bruera, V. D. Nissenbaum, I. V. Mushin, W. Grunert and L. M. Kustov, *Russ. J. Phys. Chem.*, 2011, **85**, 532.
4. D. T. Lii, D. J. Bozzuutto and C. L. Cahii, *J. Chem. Soc. Daltons Trans.*, 2005, 2111.
5. J. Y. Lee, D. H. Olson, L. Pan, T. L. Emge and J. Li, *Adv. Funct. Mater.*, 2007, **17**, 1255.
6. E. Haque, N. A. Khan, J. H. Park and S. H. Jhung, *Chem. Eur. J.*, 2010, **16**, 1046.
7. N. A. Khan, E. Haque and S. H. Jhung, *Phys. Chem. Chem. Phys.*, 2010, **12**, 2625.
8. A. Pichon, A. L. Garay and S. L. James, *CrystEngComm.*, 2006, **8**, 211.
9. W. Yuan, T. Friscic, D. Apperley and S. L. James, *Angew. Chem. Int. Ed.*, 2010, **49**, 3916.
10. A. Pichon and S. L. James, *CrystEngComm.*, 2008, **10**, 1839.
11. W. Yuan, J. O. Connor and S. L. James, *CrystEngComm.*, 2010, **12**, 3515.
12. F. Qi, R.S. Stein and T. Frisci, *Green Chem.*, 2014, **16**, 121.

13. C. Mottillo, Y. Lu, M-H. Pham, M.J. Cliffe, T-O. Do and T. Frisci , *Green Chem.*, 2013, **15**, 2121.
14. M.J. Cliffe, C. Mottillo, R.S. Stein, D-K. Bu ar and T. Frisci , *Chem. Sci.*, 2012, **3**, 2495.
15. G. Ciardelli, L. Corsi and M. Marussi, *Resour. Conserv. Recycl.*, 2001, **31**, 109.
16. S. Y. M. Josefa and E. De Oliveira, *Adv. Environ. Res.*, 2003, **7**, 263.
17. A. Mittral, A. Malviya, D. Kaur, J. Mittral and L. Kurup, *J. Hazard. Mater.*, 2007, **148**, 229.
18. D. J. Malik, V. Strelko, M. Streat and A. M. Puziy, *Water Res.*, **36**, 1527.
19. A. R. Millward and O. M. Yaghi, *J. Am. Chem. Soc.*, 2005, **127**, 17998.
20. Z. Zhao, X. Li, S. Huang, Q. Xia and Z. Li, *Ind. Eng. Chem. Res.*, 2011 **50**, 2254.
21. S. R. Caskey, A. G. Wong-Foy and A. J. Matzger, *J. Am. Chem. Soc.*, 2008, **130**, 10870.
22. J. J. Orfao, A. I. Silva, J. C. Pereira, S. A. Barata, I. M. Fonseca, P. P. Faria and M. F. Pereira, *J. Coll. Inter. Sci.*, 2006, **296**, 480.
23. T. G. Glover, G. W. Peterson, B. J. Schj ndler, D. Britt and O. M. Yaghi, *Chem. Eng. Sci.*, 2011, **66**, 163.
24. P. K. Malik and S. K. Saha, *Separ. & Purif. Technol.*, 2003, **31**, 241.
25. A. A. Adeyemo, I. O. Adeoye and O. S. Bello, *Toxicol. & Environ. Chem.*, 2010, **94**, 1846.
26. C. Kannan, K. Muthuraja and M. R. Devi, *J. Hazard. Mater.*, 2013, **244–245**, 10.
27. N. A. Khan, Z. Hasan and S. H. Jhung, *J. Hazard. Mater.*, 2013 **244–245**, 444.
28. K. Fujii, A. L. Garay, J. Hill, E. Sbircea, Z. Pan, M. Xu, D. C. Apperley, S. L. James and K. D. M. Harris, *Chem. Commun.*, 2010, **46**, 7572.
29. T. Friscic, I. Halasz, V. Strukil, M. Eckert-Maksic and R. E. Dinnebier, *Croat. Chem. Acta.*, 2010, 85(3), 367.
30. I. Langmuir, *J. Am. Chem. Soc.*, 1916, **38**, 2221.
31. H. M. Freundlich, *J. Phys. Chem.*, 1906, **57**, 385.
32. M. I. Temkin and V. Pyzhev, *Acta Phys. Chim. USSR*, 1940, **12**, 327.
33. A. O. Dada, A. P. Olalekan, A. M. Olatunya and O. Dada, *J. Appl. Chem.*, 2012, **3**, 38.
34. K. Nakamoto, Infrared and Raman spectra of inorganic and coordination compounds, 1978, 3rd edition, John Wiley, New York.
35. L-G, Qui, L-N, Gu., G. Hu and L-D. Zhang, *J. Solid State Chem.*, 2009, **182**, 502.

36. S. A. Orefuwa, H. Yang and A. J. Goudy, *Microporous Mesoporous Mater.*, 2012, **153**, 88.
37. J. Y. Lu and A. M. Babb, *Chem. Commun.*, 2002, 1340.
38. N. Kannan and M. M. Sundaram, *Dyes and Pigm.*, 2001, **51**, 25.
39. Z. Eren and F.N. Acar, *Desalination*, 2006, **194**, 1.
40. S. A. Umoren, U. J. Etim, and A. U. Israel, *J. Mater. Environ. Sci.*, 2013, **4**, 75.
41. S. A. Smith and W. A. Pretorius, *Water SA.*, 2002, **28**, 403.
42. S. Pirillo, V. Pedroni, E. Rueda and M. L. Ferreira, *Quim. Nova*, 2009, **32**, 1239.
43. R. Sjoback, J. Nygren and M. Kubista, *Spectrochim. Acta A*, 1995, **51**, L7.
44. Y-H. Liu, Y-L Lu, H-L Tsai, J-C. Wang and K-L. Lu, *J. Solid State Chem.*, 2001, **158**, 315.
45. E. Haque, J. E. Lee, I. T. Jang, Y. K. Hwang, J-S. Chang, J. Jegal and S. H. Jhung, *J. Hazard. Mater.*, 2010, 181, 535.
46. B.K. Jung, Z. Hasan and S. H. Jhung, *Chem. Eng. J.*, 2013, **234**, 99.
47. E. Haque, J.W. Jun and S. H. Jhung, *J. Hazard. Mater.*, 2011, **185**, 507.
48. I. A. Tan, A. L. Ahmad and B. H. Hameed, *J. Hazard. Mater.*, 2008, **154**, 337.
49. R. Saha, K. Mukherjee, I. Saha, A. Ghosh, S.K. Ghosh and B. Saha, *Res. Chem. Intermed.*, 2013, **39**, 2245.
50. M. M. Dubinin, *Chem. Rev.*, 1960, **60**, 235.
51. H. Chen, J. Zhao, J. Wu and G. Dai, *J. Hazard. Mater.*, 2011, **192**, 246.
52. M. A. Rauf, S. B. Bukallah, F. A. Hamour and A. S. Nasir, *Chem. Eng. J.*, 2008, **137**, 238.
53. M. S. Chiou and H. Y. Li, *J. Hazard. Mater.*, 2002, **93**, 233.
54. Y. S. Ho and G. McKay, *Proc. Biochem.*, 1999, **34**, 451.
55. S. Chen, J. Zhang, Q. Yue, Y. Li and C. Li, *Desalination*, 2010, **252**, 149.
56. S. Wang, L. Li, H. Wu and Z. H. Zhu, *J. Coll. & Inter. Sci.*, 2005, **292**, 336.
57. E. Haque, J. W. Jun and S. H. Jhung, *J. Hazard. Mater.*, 2011, **185**, 507.

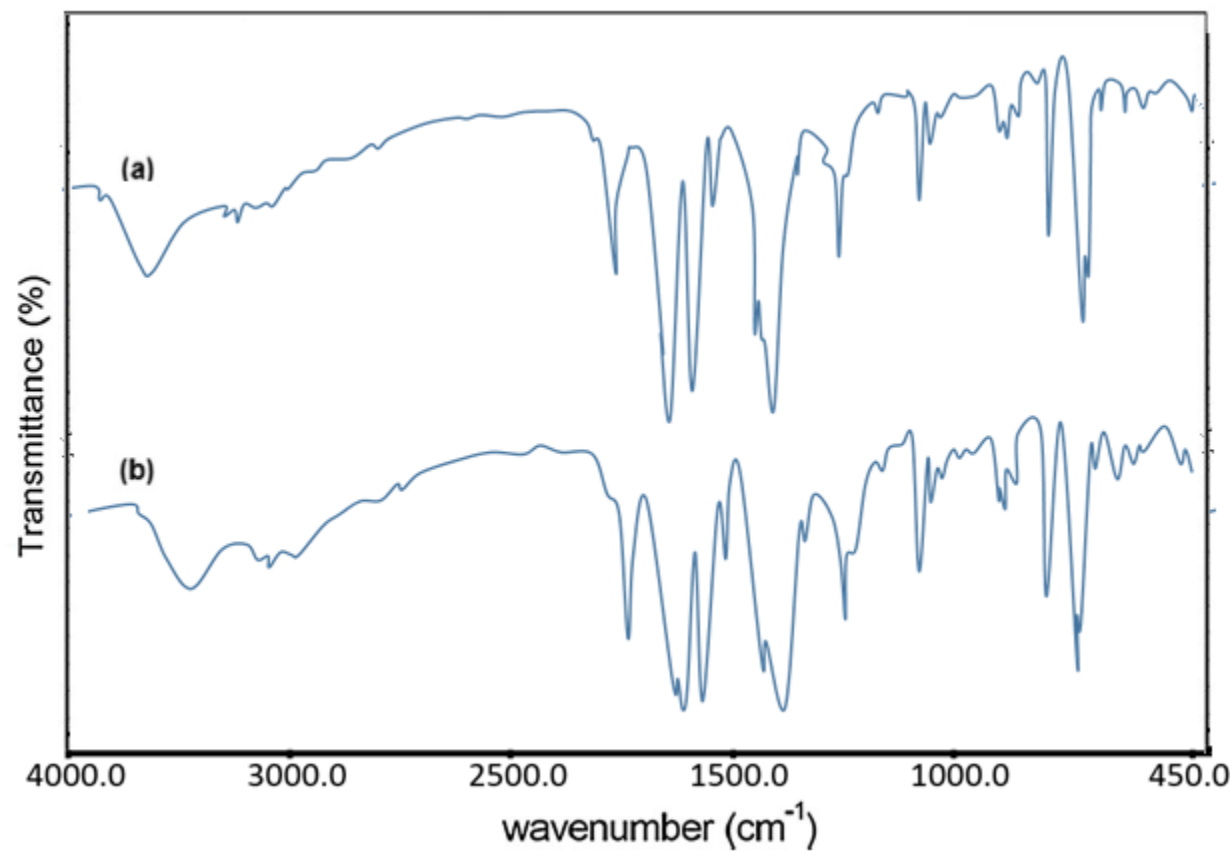


Fig. 1. FT- IR spectra of [Cu(INA)₂] **(a)** (MSR method) and [Cu(INA)₂] **(b)** (BSR method).

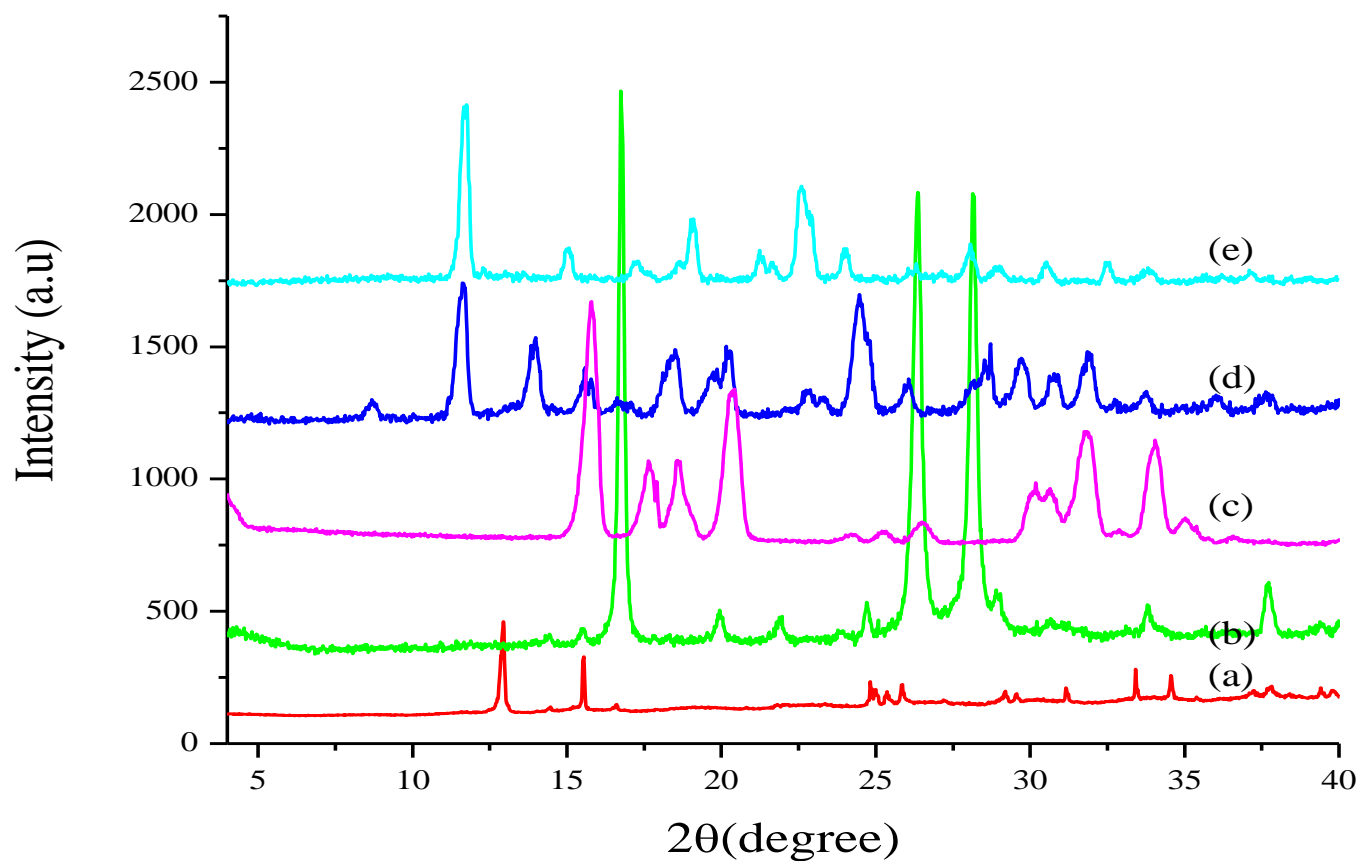


Fig.2. PXRD patterns of reactants (a) $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (b) HINA and reaction product (c) $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ + HINA after 10 hrs (d) 20 hrs (e) 41 hrs.

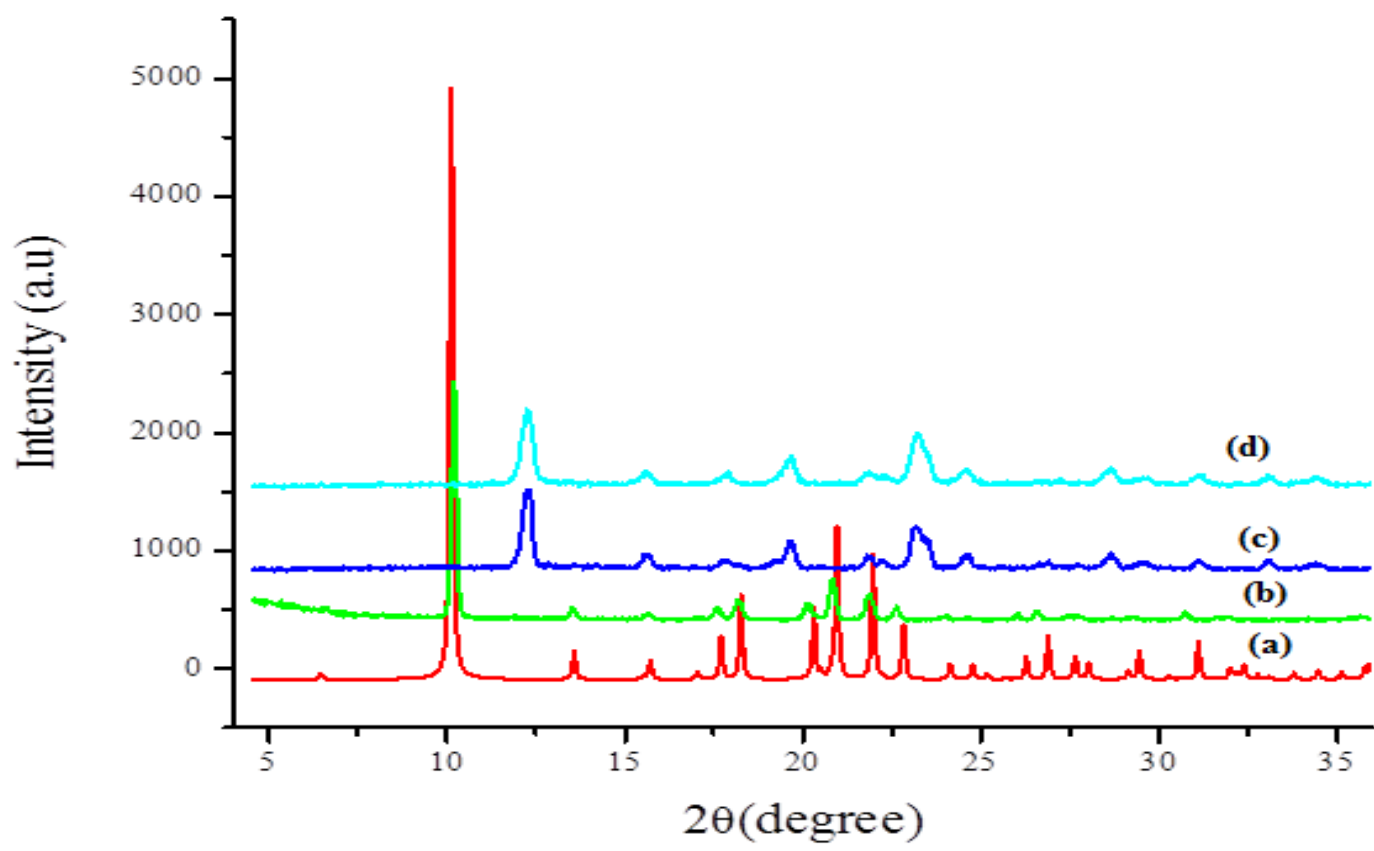
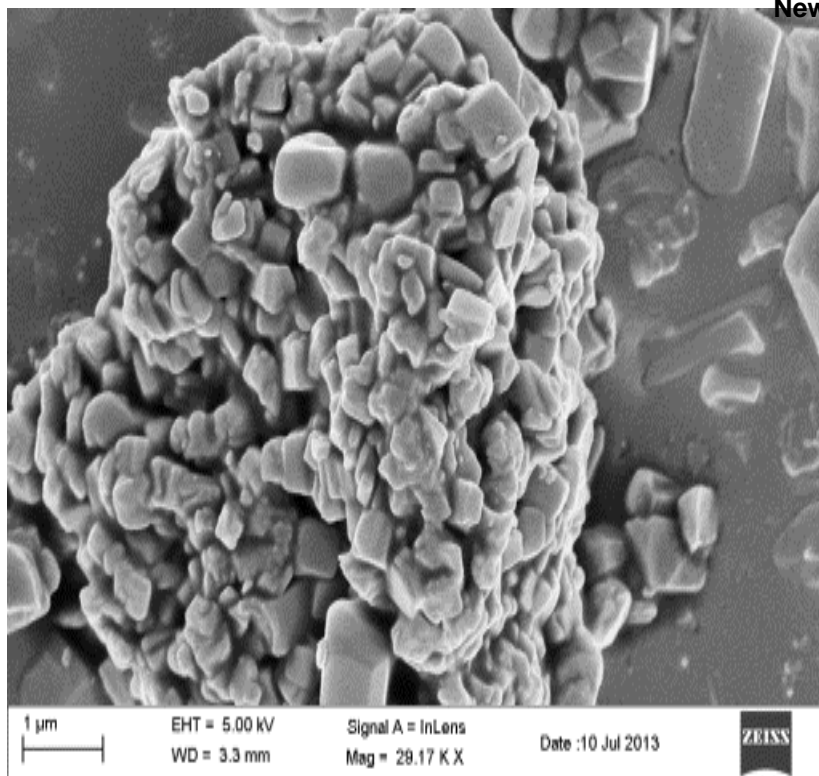
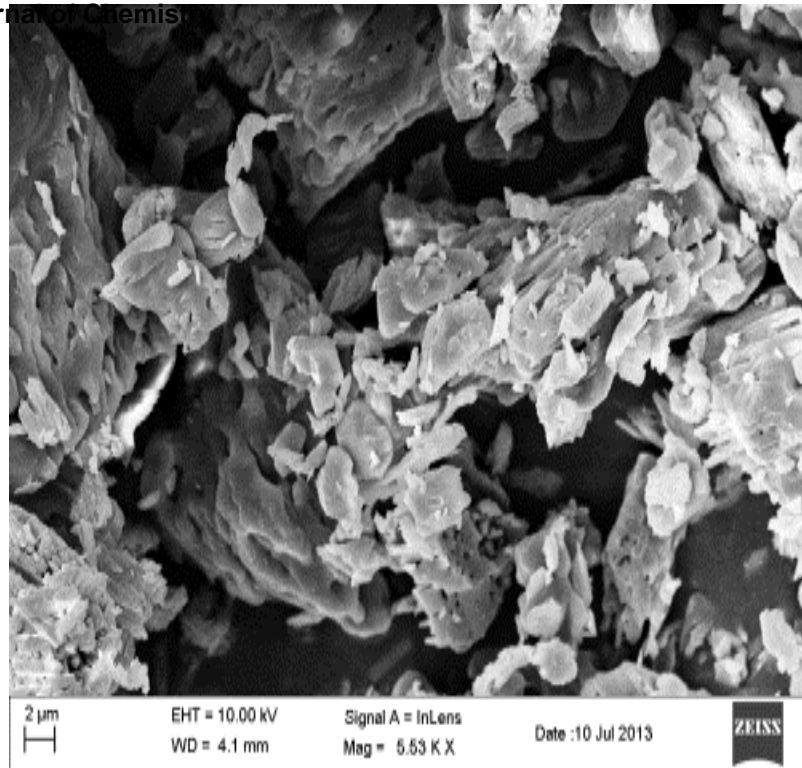


Fig. 3. PXRD patterns of the Cu(INA)₂ (a) [Cu(INA)₂] simulated from single crystal data (UFUMUD) (b) Product 2 (c) Mix for 41 hrs (Product 1a) (MSR) (d) Ball-milling(Product 1b) (BSR)

New Journal of Chemistry Accepted Manuscript



(i) [Cu(INA)₂] (MSR method)



(ii) [Cu(INA)₂] (BSR method)

Fig. 4: SEM images of samples prepared by (i) MSR and (ii) BSR methods.