



# Magnesium oxide entrapped Polypyrrole hybrid nanocomposite as an efficient selective scavenger for fluoride ion in drinking water

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## Abstract

Aim of this work is to synthesizing a new highly efficient adsorbent as of magnesium oxide ( $\text{MgO}_2$ ) entrapped Polypyrrole (Ppy) nanocomposite preparation for toxic pollutant of fluoride removal form drinking water. The synthesized  $\text{MgO}_2$ /Ppy hybrid nanocomposite shows an extraordinary defluoridation capacity of  $4328 \text{ mg F}^- \text{ Kg}^{-1}$  in the room temperature through batch adsorption technique. It was performed to know the effect of various parameters such as contact time, initial concentration, pH, competitor ions and temperature. The structural and morphological changes on the fluoride adsorbent in before and after were analyzed by using XRD, FTIR & SEM techniques. The adsorption isotherm of Freundlich, Langmuir, & Dubnin - Radushkevich isotherms were studied and the fluoride adsorption is well fixed with Langmuir isotherm model. The kinetic model studies were carried out by both diffusion and reaction based models. The mechanism of fluoride on the  $\text{MgO}_2$ /Ppy nanocomposite is mainly influence the interaction of electrostatic adsorption and ion-exchange. The reusability and regeneration studies were performed for the reusability of the nanocomposite.

**Keywords** Adsorption · Fluoride · Isotherm · Magnesium · Polypyrrole

## 1 Introduction

Fluoride is an essential element for living systems related to the total amount consumed. Fluoride ions to cause significant properties in human through intake of water [1]. The existence of fluoride has favorable effects on the maintenance of teeth and bones at low concentrations, however various adverse problems would be increased such as, neurological damage, bones softening teeth mottling and so on within an excessive exposure [2]. The World Health Organization (WHO) has suggested the maximum permissible concentration of fluoride ion in drinking water between 0.5 & 1.5 mg/L [3]. Henceforth, an excessive quantity of fluoride in drinking water requisite is removed using suitable technologies and materials.

Certain technologies have been established for fluoride removal from water such as ion exchange, precipitation, nanofiltration, reverse osmosis, Donnan dialysis electro dialysis,

and adsorption [4–8]. Several disadvantages, i.e. production of unwanted chemicals, waste removal issues minimum economic feasibility, high maintenance cost, scaling, fouling, and membrane degradation are associated with some exciting techniques such as precipitation, electro dialysis, Donnan dialysis and membrane process. Therefore, adsorption and ion exchange method are expansively accepted technologies as these are reasonably effective in decreasing to the tolerable limit of fluoride concentration. Adsorption has extra advantage due to low operational maintenance cost, and simple procedure [9]. Abundant, waste, natural and synthetic materials have been tested as an adsorbent for fluoride removal from drinking water. The perfect fluoride removal adsorbent have some favorite characteristics such as low cost, quick uptake, easy regeneration, good adsorption capacity and greater physical characteristics such as inability to block the pores of the filter. Unfortunately, most inorganic adsorbent materials have all of these features. In spite of the fact that nanomaterial has high surface areas, yet they need different adsorbing functional groups. On the conflicting, organic polymers hold a large number of multifunctional groups but still their small specific area due to aggregation, limits their small specific area. The synthesis of hybrid/core-shell nanocomposites as absorbent with both multifunctional groups and the high surface area

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has recently gained considerable attention in wastewater treatment.

Polypyrrole (Ppy) is a well-known conducting polymer that has fascinated the researchers for various applications due to its facile synthesis, high electrical conductivity, excellent biocompatibility, redox and ion exchange properties [10, 11]. Ppy chains have positively charged nitrogen atoms that may easily become major active sites for the adsorption of anions and also has an anion exchanger behavior due to the presence of exchangeable counter anions doped in its chains [12]. Highly reactive of Magnesium nanoparticles derived adsorbents are well known for wastewater treatment. The majority of the magnesium derived adsorbents were prepared by high temperature hydrolysis [13, 14]. The power type of metal oxides has practical problem for water purification purpose and inconvenience in solid/liquid separation, because of low hydraulic conductivity and leaching of metal/metal oxide along with purified water. To overcome the above problem, more environmental friendly, cost effective and efficient materials need to be developed [15]. The MgO is comparatively low cost material than other metal oxides.

Based on the view, in this work was planned to synthesize magnesium oxide fabricated with Polypyrrole polymer matrix (MgO<sub>2</sub>/Ppy) for fluoride removal studies. The effects of parameter such as contact time, competitive ions dosage, initial concentration, on the fluoride removal efficiency of MgO<sub>2</sub>/Ppy were studied. Finally its real field applicability was also tested.

## 2 Experimental section

### 2.1 Materials and methods

Anhydrous Magnesium chloride (MgCl<sub>2</sub>), Sodium fluoride (NaF), Sodium hydroxide (NaOH), Ammonia (NH<sub>3</sub>) and all other chemicals were used as received form Sigma-Aldrich, India. Pyrrole was bought from CDH-Central Drug House, New Delhi. 1000 ppm of fluoride stock solution was prepared by dissolving 2.21 g of sodium fluoride in 1000 mL of double distilled water. All the chemicals are analytical grade and used as without any other purification.

### 2.2 Synthesis of MgO<sub>2</sub>/Ppy nanocomposite adsorbent

#### 2.2.1 Synthesis of MgO<sub>2</sub> nanoparticles

The initial precursor of nano MgO<sub>2</sub> was synthesized by 20.0 mL of MgCl<sub>2</sub> solution was dropped very slowly by using injection in 1000 mL of double distilled water under safe condition (fume hood) with constant mechanical stirring with 1000 rpm. The pure white colored solution was appeared and

it was treated with 1:4 ratio of dilute ammonia solution up to the pH of the liquid reached neutral (~6.8). The white colored precipitate obtained and it was completely washed with double distilled water. The obtained precipitated was dried in hot air oven at 80 °C for 24 h. Then the white precipitate was crushed with ball mill and get a uniform sized nano MgO<sub>2</sub> powder.

#### 2.2.2 Synthesis of MgO<sub>2</sub>/Ppy nano composite

The adsorbent nanocomposite was synthesized by chemical oxidative polymerization method using Iron (III) Chloride as an oxidant. Initially 0.5 g of MgO<sub>2</sub> nanoparticles was dispersed in 50 mL of DD (double distilled) water and continuously stirred for 1 h. Then 0.5 mL of Pyrrole was dropped by using syringe into the solution and it again stirred for 50 min. 1.35 g of Iron(III) chloride was then added into the above mixture, the mixture was constantly stirred for 6 h and then left unstirred for polymerization to overnight without any disturbance. The resulted MgO<sub>2</sub>/Ppy nanocomposite was filtered and washed with double distilled water followed by ethanol and then dried in a hot air oven at 80 °C for 12 h. The obtained MgO<sub>2</sub>/Ppy nanocomposite used for as an adsorbent of fluoride removal.

### 2.3 Batch adsorption studies

The defluoridation studies were done by batch adsorption method to the effect of contact time, competitive anions, temperature, solution pH, and initial concentration. The adsorption methodology were done in thermostat shaker with 200 rpm at 25 ± 1 °C using 100 mL of 3 ppm F<sup>-</sup> solution in a conical flasks at neutral pH. The parameters were varied with respective of experiments. The effects of pH value, contact time, adsorption isotherms, coexisting ions and adsorbent dose on the equilibrium adsorption capacity were studied. The adsorbent dosage was kept as 0.5 mg for all the investigates except for the adsorbent dosage study. The 0.1 mol/L NaOH or HCl, were used to adjust the solution pH. The fluoride ion concentration in the solution was calculated as described by the following equation

$$DC = \frac{C_i - C_e}{m} V \times \text{mg F.g}^{-1}$$

Where, DC-defluoridation capacity, C<sub>i</sub> (mg/L) is the initial fluoride ion concentration, C<sub>e</sub> (mg/L) is the equilibrium fluoride ion concentration, V is the volume of the fluoride solution in litre and m is the mass of adsorbent in gram.

The concentration of fluoride ion was measured using fluoride ion selective electrode Thermo Orion Bench top multi parameter kit (Model: VERSA STAR92) with ±1 significant

digit of relative accuracy,  $0.02 \text{ mg}\cdot\text{L}^{-1}$  of detection limit, and  $\pm 2\%$  of the reproducibility. The pH measurements were carried out with the same instrument in addition with a pH electrode. The other water quality factors were examined by standard methods [16]. The pH at zero point charge ( $\text{pH}_{\text{zpc}}$ ) of the adsorbent was measured by pH drift method [17].

## 2.4 Instrumentation studies

The solution pH was altered by using an proper amount of hydrochloric acid/sodium hydroxide, monitored with a pH meter (Orange pH 303, India). The adsorbent equilibrated with an orbital incubator shaker (Biotechnics, India). The fourier transform infra red (FTIR) spectra for the adsorbent were obtained using a Bruker Tensor 27 series model FTIR spectrometer by mixing 0.2 gram of the sorbent with 1.0 gram Potassium bromide and taking readings in the range of  $400\text{--}4000 \text{ cm}^{-1}$  at a  $4 \text{ cm}^{-1}$  resolution, with 16 scans. The powder X-ray diffraction (XRD) spectra of the adsorbent were obtained using monochromatic nickel-filtered copper radiation (40 kV, 30 mA) in a wide angle X-ray diffractometer (XPRT-PRO system with  $2 \mu$  angle). The scanning electron microscopy (SEM) micrograph and mapping studies were done using a VEGA 3 TESCON model.

## 2.5 Statistical tools

The Microcal Origin (Version 8.5) software used for the computations studeis. The suitable and best model of the fit was found out using the standard deviation (sd), and chi-square ( $\chi^2$ ) analysis and regression correlation coefficient (r) values.

# 3 Results and discussion

## 3.1 Effect of contact time

The fluoride ion removal investigations of the  $\text{MgO}_2/\text{Ppy}$  nanocomposite adsorbent were carried out with various interval of time period in the choice of 10–60 min at 303 K with starting fluoride concentration of 10 mg/L with an adsorbent measurement as 50 mg. From the results, the defluoridation capacity of  $\text{MgO}_2/\text{Ppy}$  nanocomposite adsorbent was found to be  $3836 \text{ mg F}^-/\text{Kg}$  and it attained equilibrium at 50 mins (Fig. 1a). After the time of 50 mins, which was attains the equilibrium stage of the adsorbent by the surface of the  $\text{MgO}_2/\text{Ppy}$  nanocomposite adsorbent was maximum filled with fluoride ion [18]. Then, 50 min was fixed as an appropriate contact time with maximum fluoride ion removal efficiency by  $\text{MgO}_2/\text{Ppy}$  nanocomposite.

## 3.2 Effect of dosage

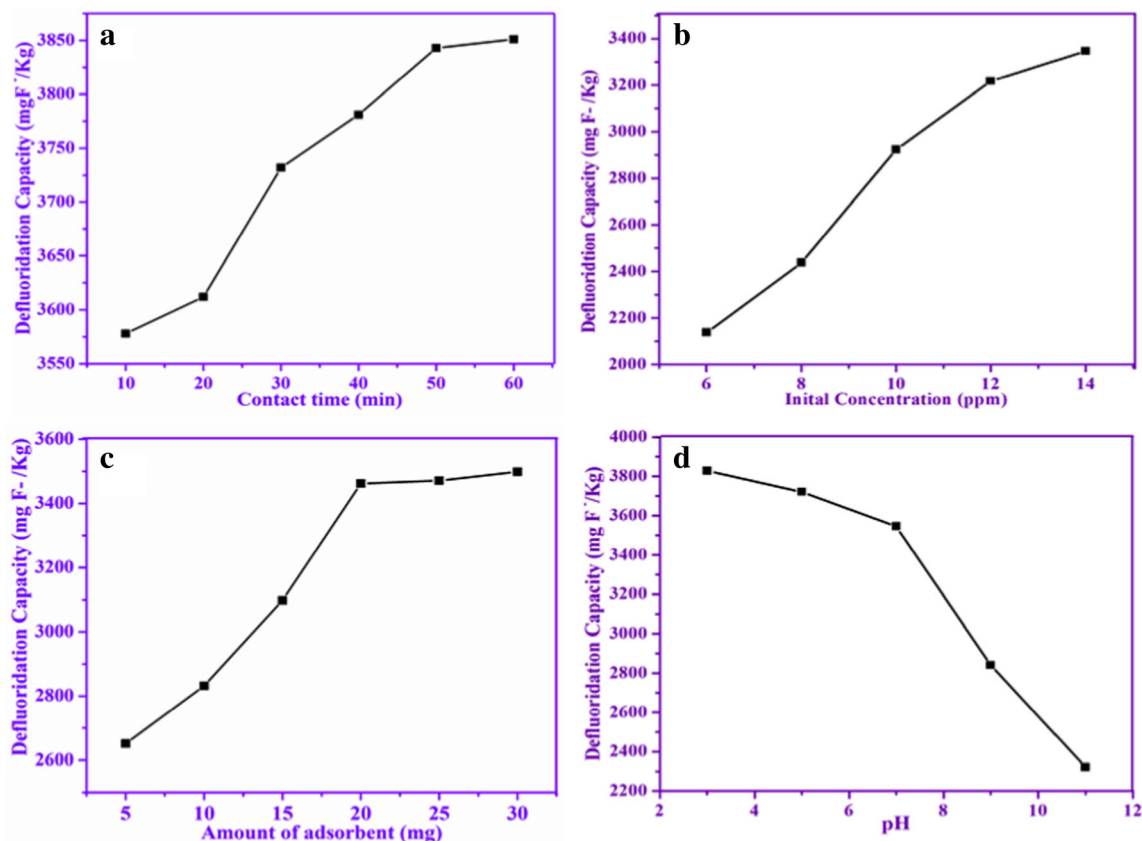
The adsorption limits of  $\text{MgO}_2/\text{Ppy}$  nanocomposite adsorbent for fluoride ions reduced with the adsorbent dosage increased from 5 to 30 mg. Fig. 1c shows the fluoride ion adsorption limits versus adsorbent dosage (mass of composite/volume of solution) at pH concentration of neutral ( $7.0 \pm 0.5$ ). The most extreme adsorption limit was found by utilizing 20 mg of  $\text{MgO}_2/\text{Ppy}$  nanocomposite adsorbent. The efficiency of fluoride removal is directly proportional to active sites of the adsorbent [19]. The most extreme fluoride removal of  $98 \pm 1\%$  was acquired utilizing 20 mg of composite. In this study, adding sorbent quantities greater than 20 mg did not effect in any substantial increase in the fluoride removal efficiency. This looks to be due to overlapping that decreased the active sites available in the adsorbent [20].

## 3.3 Effect of initial concentration

We studied the effect of changing the initial fluoride ion concentration in replicated drinking water on the adsorption efficiency of adsorbent, using values from  $6.0 \text{ mg}\cdot\text{L}^{-1}$  to  $14 \text{ mg}\cdot\text{L}^{-1}$  (Fig. 1b). At an initial fluoride ion concentration of  $6.0 \text{ mg}\cdot\text{L}^{-1}$  the DC were  $2143 \text{ mg F}^-/\text{Kg}$  for the 20 mg of  $\text{MgO}_2/\text{Ppy}$  composite at 303 K in pH  $7.0 \pm 0.5$ . When the fluoride ion concentration was increased to  $8.0 \text{ mg}\cdot\text{L}^{-1}$ , the DC enhanced  $2526 \text{ mg F}^-/\text{Kg}$ , at final  $14 \text{ mg F}^-/\text{Kg}$  the DC was  $3484 \text{ mg F}^-/\text{Kg}$  at the same conditions. The fluoride ion removal efficiency was increased with increasing the fluoride ion concentration at same condition. Since, adsorption efficiency was directly proportional to the concentration of fluoride ions in the solution [21].

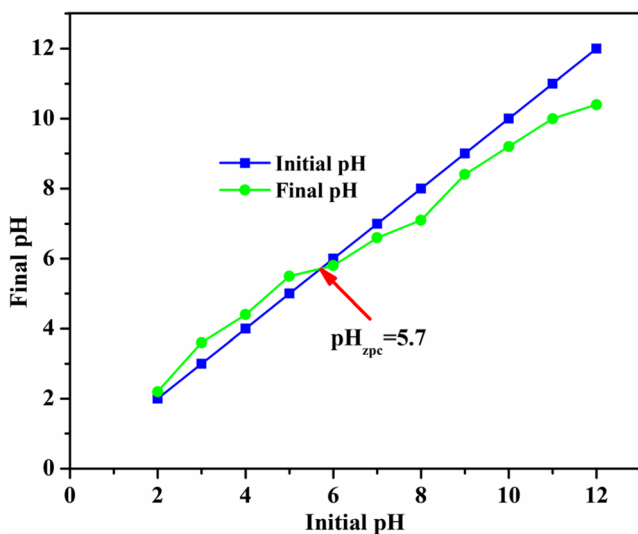
## 3.4 Effect of pH

The result of solution pH was inspected for the composite such  $\text{MgO}_2/\text{Ppy}$  nanocomposite at various initial pH values of 3.0, 5.0, 7.0, 9.0, and 11.0. Fig. 1d shows the adsorption capabilities of the  $\text{MgO}_2/\text{Ppy}$  nano composite was considerably affected by solution pH. In general, the surface of the adsorbent is positively charge due to the lower  $\text{pH}_{\text{zpc}}$  than neutral pH of the adsorbent ( $\text{pH} > \text{pH}_{\text{zpc}}$ ), and negatively charged means the  $\text{pH}_{\text{zpc}}$  is greater than neutral pH ( $\text{pH} < \text{pH}_{\text{zpc}}$ ). The  $\text{pH}_{\text{zpc}}$  value of  $\text{MgO}_2/\text{Ppy}$  nano composite adsorbent was found to be 5.7 (showed in Fig. 2). The observed  $\text{pH}_{\text{zpc}}$  value of the  $\text{MgO}_2/\text{Ppy}$  nanocomposite adsorbent has less positive charge is due to the adsorbent has more electropositive magnesium ion. The positive charge on the surface



**Fig. 1** a Effect of contact time of the MgO<sub>2</sub>/Ppy nanocomposite at 300 K, b Effect an Initial concentration of MgO<sub>2</sub>/Ppy nanocomposite at 300 K. c Effect of Dosage of the MgO<sub>2</sub>/Ppy nanocomposite at 300 K, d Effect of Various pH of the MgO<sub>2</sub>/Ppy nanocomposite at 300 K

is easier to attract the fluoride ion from drinking water. The outcome exposes that the maximum defluoridation capacity was taking place at pH 3.0, and the pH was increased from 3.0 to 11.0 defluoridation capacity reduced drastically.



**Fig. 2** pH zero point charge (pH<sub>zpc</sub>) studeis for the MgO<sub>2</sub>/Ppy nanocomposite adsorbent

When the medium pH was lower, the surface of the MgO<sub>2</sub>/Ppy nanocomposite was positively charged and protonated, than the fluoride ions were moved to the positively charged surface, hence favoring fluoride adsorption onto the surface results in the increase in defluoridation capacity of the composite. But in the pH ranges of 9.0 and 11.0 shows the adsorption capacity is lower, because the surface of the MgO<sub>2</sub>/Ppy nanocomposite adsorbent covered with more negatively charged species, so the competition of F<sup>-</sup> and OH<sup>-</sup>, fluoride adsorption is decreases [22].

### 3.5 Effect of foreign-ions

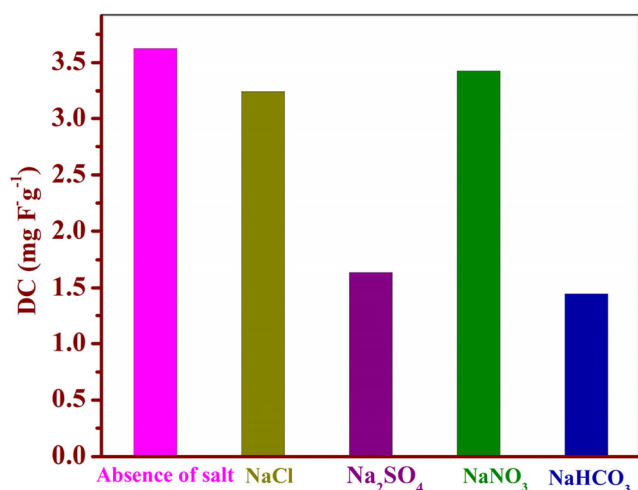
The common foreign ions such as chloride, sulphate, nitrate, & bicarbonate ions are occur in water in addition with fluoride ions, and they may encounter with fluoride for the active sites of the adsorbent during adsorption. To calculate the defluoridation capacity of MgO<sub>2</sub>/Ppy nanocomposite in the existence of other ions with 10 mgL<sup>-1</sup> initial fluoride ion solution was shifted individually into 200 mg·L<sup>-1</sup> initial concentrations of chloride, sulphate, nitrate and bicarbonate ions. The impact of the various foreign ions on

fluoride adsorption of the composite at pH 7 is shown in Fig. 1d. It was detected that all of the foreign ions affected a little with the fluoride ion adsorption onto the MgO<sub>2</sub>/Ppy nanocomposite, but bicarbonate and sulphate caused substantial result on the defluoridation capacity of the MgO<sub>2</sub>/Ppy nanocomposite. The weakening in the defluoridation capacity of the MgO<sub>2</sub>/Ppy nanocomposite in the presence of sulphate and bicarbonate ions is primarily due to the increase in the solution pH which decreases the active sites on the adsorbent surface for fluoride adsorption of the composite [23]. The defluoridation capacity of the various competitive ions shows in Fig. 3.

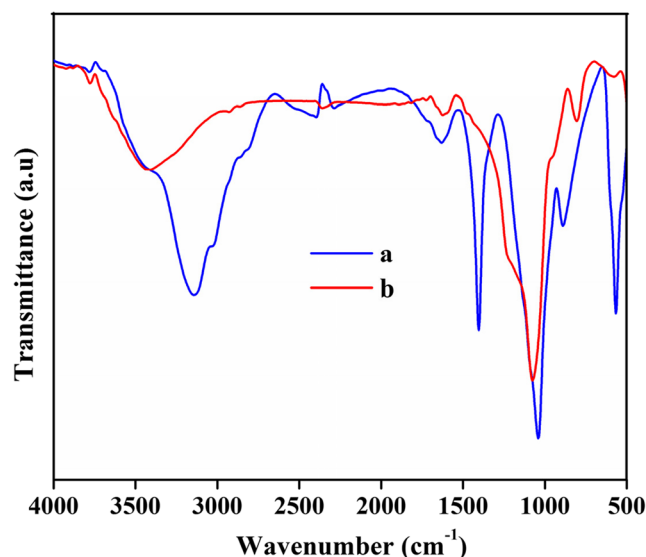
### 3.6 Chemical characterization

#### 3.6.1 FTIR analysis

The FTIR spectrum of fluoride ion before and after adsorbed MgO<sub>2</sub>/Ppy nanocomposite as shown in Fig. 4. In the spectrum, the band at 1142 cm<sup>-1</sup> and 1086 cm<sup>-1</sup> is due to the hydroxyl group bending vibration in metal oxide (Mg-OH). The band appeared in the range of 743–480 cm<sup>-1</sup> is due to the metal oxide bonding (Mg-O-Mg) [24]. The peak appeared in 2436 cm<sup>-1</sup> in the spectrum, which shows the Mg-F composition. The peaks at 1543 and, 1023 cm<sup>-1</sup> were assigned to vibrations of C-N, C-H respectively. The broad and sharp peak at 3445 cm<sup>-1</sup> suggested that the stretching peak of N-H group in Polypyrrole [25] and the intensity of the N-H group peak was decreased due to the fluoride adsorption and formation of fluoride adsorbed MgO<sub>2</sub>/Ppy nanocomposite.



**Fig. 3** Effect of Co-ions influencing the fluoride adsorption by the MgO<sub>2</sub>/Ppy nanocomposite at 300 K



**Fig. 4** FTIR spectrum of (a) MgO<sub>2</sub>/Ppy nanocomposite and (b) Fluoride adsorbed MgO<sub>2</sub>/Ppy nanocomposite

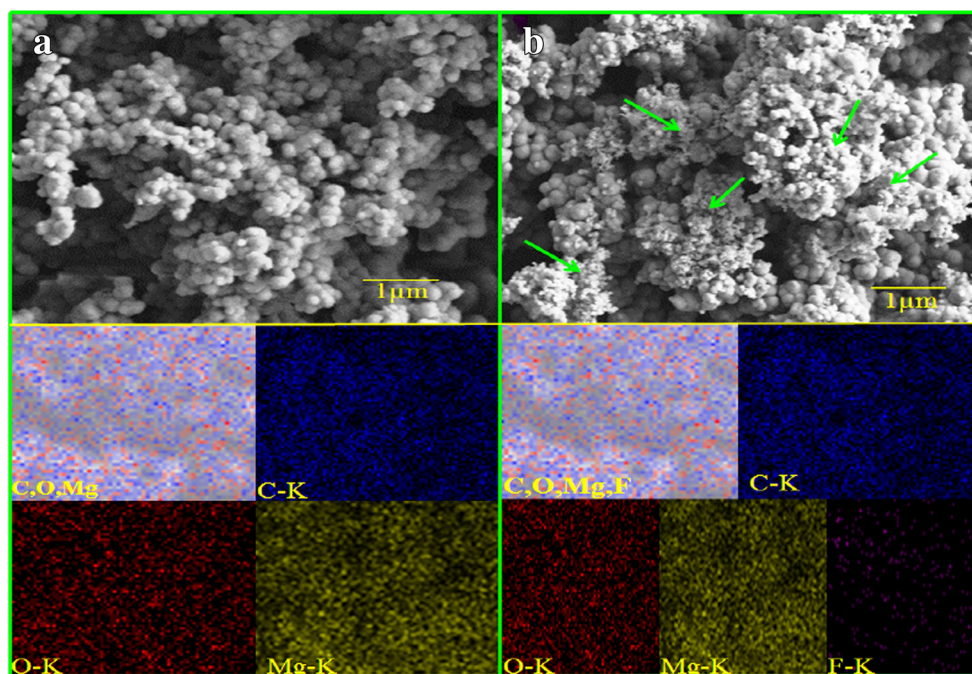
#### 3.6.2 SEM analysis

SEM micrographs of MgO<sub>2</sub>/Ppy nanocomposite of before and after fluoride adsorption were investigated and presented in Fig. 5. Before, the adsorption the adsorbent has the regular spherical shape with uniform size and after the fluoride removal the adsorbent shows the white color powder like particles are dispersed on the surface of the global regular spheres, which is represented as a fluoride ion and which indicated by green color arrows in the image. The elemental mapping studies of the adsorbent was confirms the presence of elements in the before and after adsorption of fluoride by MgO<sub>2</sub>/Ppy nanocomposite adsorbent.

#### 3.6.3 XRD analysis

The XRD pattern of MgO<sub>2</sub>/PPy nanocomposite adsorbent (Fig. 6) shows no distinct peaks for magnesium oxide which suggests its amorphous Mg(OH)<sub>2</sub> structure. The XRD spectra of MgO<sub>2</sub>/PPy nanocomposite (Fig. 5a), showed a broad amorphous diffraction peak in the range of 15degree < 2θ < 30degree which is the characteristic peak for PPy monopolymer due to the scattering of PPy chains at interplanar spacing. Moreover, no noteworthy alteration noticed in XRD patterns of MgO<sub>2</sub>/PPy nanocomposite after F<sup>-</sup> adsorption (Fig. 5b) suggests that the F<sup>-</sup> interaction with the nanocomposite has not affected its crystalline structure.

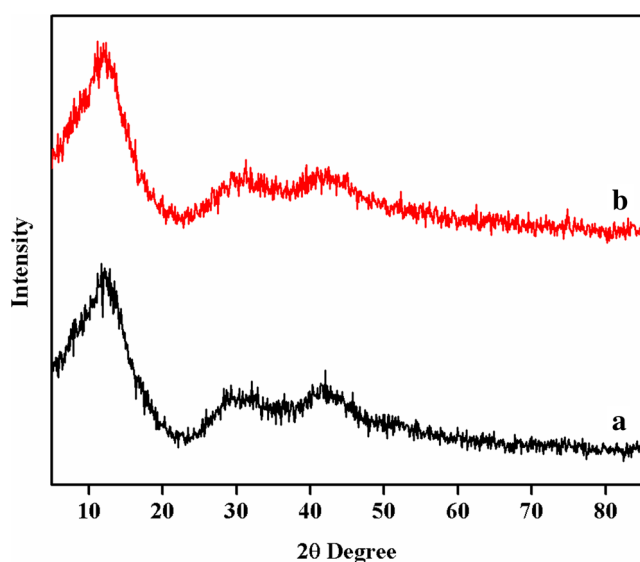
**Fig. 5** SEM & Elemental mapping images of (a) MgO<sub>2</sub>/Ppy nanocomposite (b) Fluoride adsorbed MgO<sub>2</sub>/Ppy nanocomposite



### 3.7 Adsorption isotherms

The fluoride adsorption limit of MgO<sub>2</sub>/Ppy nanocomposite was assessed by using distinct isotherms specifically Freundlich [26], Langmuir [27] and Dubnin–Radushkevich [28] isotherms. The estimations of Freundlich isotherm constants  $1/n$  and  $k_F$  were found out from the intercept and slope of the plot for  $\log C_e$  Vs  $\log q_e$  (Table 1). The  $n$  values are lying in between

1 to 10, and the values of  $1/n$  are lying in between 0 to 1, it shows that the system and conditions were suitable for adsorption fluoride. The higher  $r$  value showed the well fit of Langmuir isotherm compared with other two isotherms. The Langmuir adsorption isotherm model constants  $b$  and  $Q^\circ$  were calculated from the intercept and slope of the plot for  $C_e$  versus  $C_e/q_e$  and the outcomes given in Table 1. The estimations of  $Q^\circ$  value was found to rise with the expansion in temperature, which showed adsorption limit expanded with ascend in temperature. The higher  $r$  value shows the applicability of Langmuir adsorption isotherm. The possibility of the adsorption isotherm can be tried by ascertaining the dimensionless constant partition factor/equilibrium parameter (RL).



**Fig. 6** XRD spectrum of a) MgO<sub>2</sub>/Ppy nanocomposite nanocomposite b) Fluoride adsorbed MgO<sub>2</sub>/Ppy nanocomposite

The linear plots of  $\ln q_e$  vs.  $\epsilon^2$  shows the suitability of D–R isotherm. The values of D-R isotherm parameters like  $K_{DR}$ ,  $X_m$ , and  $E$  are given in Table 1. The range of  $E$  value from 1.0–8.0 kJ·mol<sup>-1</sup> indicating physical adsorption (physisorption) and from 9.0–16.0 kJ·mol<sup>-1</sup> for chemical adsorption (chemisorption). The result of Langmuir and D-R isotherm was recommended that the mechanism of fluoride ion adsorption by the adsorbent overcome the chemisorption compared to physisorption. The acquired  $E$  values are 8.7261, 9.2507 and 9.9031 kJ·mol<sup>-1</sup> for 303, 313, and 323 K, respectively, which indicates the defluoridation mechanism of MgO<sub>2</sub>/Ppy nanocomposite is physical in nature. The best fit isotherm was distinguished by utilizing the error analysis and non-linear data information. In view of the above values the suitable

**Table 1** Adsorption isotherm parameters of the MgO<sub>2</sub>/Ppy nanocomposite

Isotherms	Parameters	Temperature		
		303 K	313 K	323 K
Freundlich	1/n	0.1780	0.1872	0.2211
	n	5.6052	5.3521	4.5201
	$k_F(\text{mg.g}^{-1})(\text{L.mg}^{-1})^{1/n}$	3.1872	3.3006	3.4041
	r	0.9918	0.9997	0.9999
	sd	0.0074	0.0219	0.0246
	$\chi^2$	0.2021	0.3410	0.4232
Langmuir	$Q^\circ(\text{mg.g}^{-1})$	4.7081	4.9032	5.3789
	$b(\text{L.g}^{-1})$	1.7277	1.8113	1.5326
	$R_L$	0.0344	0.0391	0.0212
	r	0.9999	0.9999	0.9979
	sd	0.0137	0.0293	0.0341
	$\chi^2$	0.3891	0.8762	0.9785
Dubnin - Radushkevich	$X_m(\text{mg.g}^{-1})$	4.8271	4.7293	4.6751
	$E(\text{kJ.mol}^{-1})$	4.7261	4.9031	4.2507
	r	0.9808	0.9317	0.9262
	sd	0.0250	0.0551	0.0654
	$\chi^2$	0.7659	1.4709	1.8203

isotherm fit was ordered as: Langmuir > Freundlich > D–R isotherm for fluoride sorption by MgO<sub>2</sub>/Ppy nanocomposite and thus fluoride ion adsorption by MgO<sub>2</sub>/Ppy nanocomposite takes after Langmuir isotherm which demonstrates the homogenous adsorption. The graphical plots of Langmuir, Freundlich and Dubnin-Radushkevich isotherms are shown in Fig. 7a, b, and c respectively.

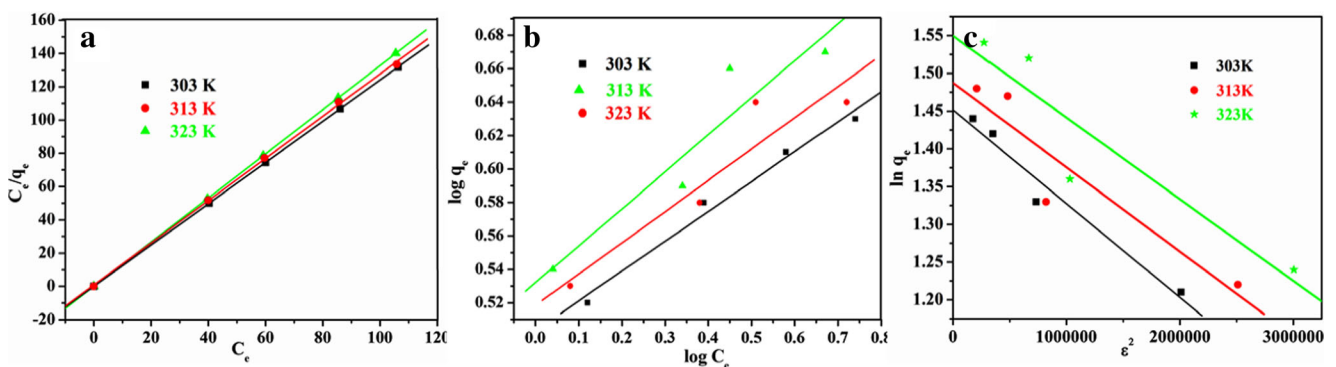
### 3.8 Thermodynamics parameters

The thermodynamic parameter, such as standard entropy change ( $\Delta S^\circ$ ), standard enthalpy change ( $\Delta H^\circ$ ) and standard free energy change ( $\Delta G^\circ$ ) are temperature dependent and

furthermore connected with the adsorption feasibility [29, 30]. The Khan and Singh method [16] is used for to calculate the values and results are presented in Table 2. The randomness and endothermic nature of fluoride adsorption on MgO<sub>2</sub>/Ppy nanocomposite was confirmed by the positive values of  $\Delta S^\circ$  and  $\Delta H^\circ$  respectively. The spontaneous nature of fluoride adsorption on MgO<sub>2</sub>/Ppy nanocomposite was confirmed by the negative values of  $\Delta G^\circ$  at different temperatures from 303 K to 323 K [31].

### 3.9 Fluoride removal mechanism

The adsorbent MgO<sub>2</sub>/Ppy nanocomposite follows basic mechanism for the fluoride removal process, which depends on the



**Fig. 7** Graphical Plots for Adsorption Isotherm models a) Langmuir isotherm, b) Freundlich isotherm, c) Dubnin – Radushkevich

**Table 2** Thermodynamic parameters of the MgO<sub>2</sub>/Ppy nanocomposite

Temperature (K)	Thermodynamic parameters		
	$\Delta G^\circ$ (KJ mol <sup>-1</sup> )	$\Delta H^\circ$ (KJ mol <sup>-1</sup> )	$\Delta S^\circ$ (KJ mol <sup>-1</sup> K <sup>-1</sup> )
313	-0.81	4.6327	18.6301
323	-1.36		
333	-2.21		

solution pH medium. In acidic pH the hydroxyl groups of the adsorbent and protonated amine groups in Polypyrrole have electrostatic interaction with negatively charged fluoride ion. At neutral pH the ion exchange mechanism will follow by the adsorbent because of the hydroxyl group of the Magnesium moiety have exchange the hydroxyl ion with the fluoride ion in the solution. Finally the adsorbent MgO<sub>2</sub>/Ppy nanocomposite follows both ion exchange and electrostatic attraction mechanism in fluoride removal process.

### 3.10 Field study

The field condition applicability of the MgO<sub>2</sub>/Ppy nanocomposite was examined by collecting the fluoride enriched from the village (Vellaimalaipatti, Usilampatti Taluk, Madurai District (latitude 10°0 N and attitude 77°47 E)). The 0.1 g of the nano adsorbent and 50 ml of fluoride water sample were shaken with constant time at room temperature, and the results are given in Table 3. The fluoride ion concentration observed in the field water sample is 3.82 mg·L<sup>-1</sup>, which is higher than the permissible value of WHO recommendation. After treatment with MgO<sub>2</sub>/Ppy nanocomposite, the fluoride concentration comes below the permissible level in the field water. In field water the concentration of other ions are higher than the fluoride ion, the concentration of other ions also reduced is the interesting think. Hence, the adsorbent MgO<sub>2</sub>/Ppy nanocomposite can be effectively used for water purification purpose. The removal of fluoride by

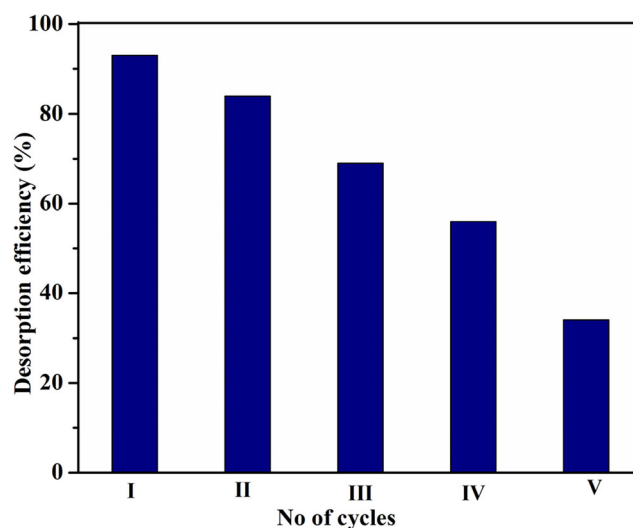
**Table 3** Field study parameters of the MgO<sub>2</sub>/Ppy nanocomposite

Water Quality Parameters	Before usage	After usage
F <sup>-</sup> (mg.L <sup>-1</sup> )	3.42	0.71
pH	7.3	6.9
Chloride (mg.L <sup>-1</sup> )	543	272
Sulphate (mg.L <sup>-1</sup> )	266	247
Nitrate (mg.L <sup>-1</sup> )	47	31
Bicarbonate (mg.L <sup>-1</sup> )	162	154
Hardness (mg.L <sup>-1</sup> )	693	371
Total Dissolved Solids(TDS) (mg.L <sup>-1</sup> )	456	323
Electrical Conductivity (mSm <sup>-1</sup> )	7.2	3.1

the MgO<sub>2</sub>/Ppy nano composite adsorbent was followed via the ion exchange mechanism. From the field study results shows that the adsorbent was removed 79% of fluoride. As well as other co-ions was also removed by this adsorbent through ion exchange mechanism. Since, the field water comes in the permissible water standard level of advised by WHO.

### 3.11 Regeneration studies

The fluoride adsorbed MgO<sub>2</sub>/Ppy nanocomposite was desorbed by using the regenerant dilute sodium hydroxide solution. About 0.1 g of the fluoride adsorbed MgO<sub>2</sub>/Ppy nanocomposite was treated with dilute sodium hydroxide solution (50 mL) with various concentrations ranging from 0.02 to 0.1 M for 1 h. From Fig. 8, at 0.1 M solution the maximum desorption of 92% was achieved. After regeneration, the nanocomposite was separated by filtration, and washed with DD water, and dried in hot air oven and a fresh fluoride solution was added before each run. The desorption efficiency of MgO<sub>2</sub>/Ppy nanocomposite was found to be 93.0, 84.0, 69.2, 56.0 and 44.1% respectively for five cycles.

**Fig. 8** Regeneration capacity studies of the MgO<sub>2</sub>/Ppy nano composite adsorbent



## 4 Conclusion

The conclusion of the work is the defluoridation capacity of MgO<sub>2</sub>/Ppy nanocomposite. The maximum fluoride adsorption was attained at 50 mins of conduct time and 20 mg of the MgO<sub>2</sub>/Ppy nanocomposite dose. The pH of the solution was raised from 3.0 to 11.0 than the defluoridation capacity of the MgO<sub>2</sub>/Ppy nanocomposite was drastically reduced. Except bicarbonate and sulphate ions only influences the adsorption capacity of the MgO<sub>2</sub>/Ppy nanocomposite. The Langmuir adsorption isotherm was well fitted than D-R and Freundlich isotherm models. The MgO<sub>2</sub>/Ppy nanocomposite possesses a higher DC (4328 mgF<sup>-</sup>/Kg) because of the MgO<sub>2</sub>/Ppy nanocomposite removes the fluoride ion by electrostatic adsorption and ion exchange mechanism. The thermodynamic parameters values indicate the fluoride removal is endothermic and spontaneous nature. The field trial results of MgO<sub>2</sub>/Ppy nanocomposite show that it can be effectively employed for defluoridation and it gives the ideas for the development household defluoridation technology unit in future.

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