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Enhanced adsorption capability of Congo red dye onto novel Polypyrrole/ZnO/$ZnCr_2O_4$ composite

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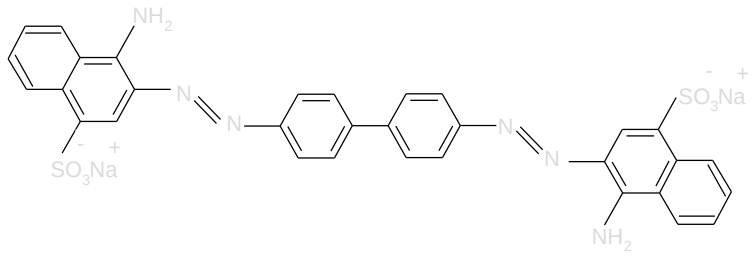
Abstract In this study, the polypyrrole/ZnO/$ZnCr_2O_4$composite as an efficient adsorbent was synthesized by two steps. At first, zinc oxide/zinc chromite (ZnO/$ZnCr_2O_4$) composite was synthesized using simple and facile co-precipitation method. Then, ZnO/$ZnCr_2O_4$composite was modified by polypyrrole (PPy). The adsorbent was characterized by X-ray diffraction (XRD), Fourier transform infrared (FT-IR), scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDXA). The PPy/ZnO/$ZnCr_2O_4$ compositeshowed excellent adsorption properties towards Congo red (CR) than ZnO and ZnO/$ZnCr_2O_4$ adsorbents. The adsorption studies have been carried out for contact time, different pH values, different temperatures, and adsorbent doses. The investigation of removal kinetics of CR indicates that the removal process obeys the rate of second-order kinetic equation. The results indicate that the Langmuir adsorption isotherm fitted the data better than the Freundlich.

Keywords Polypyrrole, ZnO/$ZnCr_2O_4$,Adsorption, Congo red, Composite

1. Introduction

Dye effluents from textile industries and photographic industries are becoming a serious environmental problem because of their toxicity, unacceptable color, high chemical oxygen demand content, and biological degradation [1].Congo red (CR) (Scheme 1) (sodium salt of benzidinediazobis-1-naphthylamine-4-sulfonic acid) is metabolized to benzidine, a known human carcinogen and exposure to this dye can cause some allergic responses [2]. The treatment of contaminated CR in wastewater is difficult because the dye is generally present in sodium salt form giving it very good water solubility. Also, the high stability of its structure makes it difficult to biodegrade and photodegrade [3]. Various treatment techniques and processes have been used to remove the pollutants from contaminated water. In this regard, adsorption is used as an excellent treatment method with many advantages such as low capital investment, abundant raw material source, simple design and operation and non-toxic properties [4].However, the adsorbents reported receive many drawbacks such as high cost of investment and operating, regeneration difficulty, and long time to achieve adsorption equilibrium, thus restricting the application employing adsorption method in dye removing in large scale. Therefore, investigations of new adsorbents are emergent to be conducted. Recently, many investigators focus on the conducting polymer polypyrrole (PPy) in various research fields due to its good electrical conductivity, relatively high air stability, low cost and useful properties for fabricating nano-structured material. The combination of polymers and metal oxides such as spinels used as adsorbents have received their extensive attention [5,6]. Zinc chromite ($ZnCr_2O_4$) has a normal spinel structure and in this mixed oxide,the Zn^{2+} and Cr^{3+} ions have a strong preference for the tetrahedral and the octahedral sites, respectively. The crystalline $ZnCr_2O_4$ spinel has many applications, such as catalysts [7,8], sensors for toxic gases [9,10] semiconductors [11] and catalysts [12-15]. To the best of our knowledge, this work is a novel research for

adsorption of Congo red dye on the surface of PPy/ZnO/$ZnCr_2O_4$ composite. Thus, the aim of this work is to study the influence of PPy on adsorption characteristics of ZnO/$ZnCr_2O_4$ composite.The synthesized composites were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscope (SEM) and energy dispersive X-ray analysis (EDXA). Batch adsorption experiments were conducted to investigate the effect of contact time, different pH values, different temperatures, and adsorbent doses. Two kinetic models were also analyzed for the removal of Congo red on PPy/ZnO/$ZnCr_2O_4$ composite.



Scheme 1: The chemical structure of Congo Red

2. Experimental

All the analytical chemicals $Cr(NO_3)_3.9H_2O$, $Zn(NO_3)_2.6H_2O$, $Zn(CH_3COO)_2.2H_2O$, sodium dodecylbenzenesulfonate (SDBS), Triton X-100, pyrrole, ammonium persulfate, sodium hydroxide and Congo red dye were purchased from Merck and used without further purification. The structural analysis of the samples was performed by powder X-ray Diffraction (Holland Philips Xpert, X-ray diffractometer with Cu-Kα radiation) and FT-IR analysis using a Fourier transmission infrared spectrometer (JASCO FTIR-4200, Japan) in KBr pellet, in the range of 4000-400 cm^{-1}. The morphology of the samples was characterized by scanning electron microscopy, SEM (VEGA3, TESCAN). The UV-Vis absorption spectra were recorded using a Shimadzu UV-2550 spectrophotometer.

2.1. Synthesis of the $ZnCr_2O_4$ sample

The procedure used for synthesis of the $ZnCr_2O_4$ reported previously [16]. In this synthesis, $Cr(NO_3)_3.9H_2O$ (6×10^{-3} mol), $Zn(NO_3)_2.6H_2O$ (3×10^{-3} mol), NaOH (0.040 mol), sodium dodecyl benzenesulfonate (SDBS) (5.74×10^{-4} mol) and 10 mL distilled water was used. Above chemicals stirring vigorously via magnetic stirrer for 30 min at 60 °C, the final product was washed with double distilled water and dried at room temperature. Then, the product was annealed at 700 ºC for 3 h.

2.2.Synthesis of the ZnO sample

The ZnO sample was prepared via precipitation method. In this method, 5.27g (0.024 mol) of $Zn(CH_3COO)_2.2H_2O$, 2.8 g (0.07 mol) of NaOH, 15 mL distilled water and 0.012 mol of Triton X-100 was used. Above chemicals vigorous stirring via magnetic stirrer for 120 min at room temperature.The product was washed with double distilled water several times and dried at room temperature. Then, the product was annealed at 500 ºC for 1 h.

2.3. Synthesis of the PPy/ZnO/$ZnCr_2O_4$ composite

The procedure used for the synthesis of the ZnO/$ZnCr_2O_4$followed by in-situ chemical polymerization of pyrrole that is similar to the previous reports[17]. In this procedure, 0.04 g (2×10^{-4} mol) $ZnCr_2O_4$ and 0.05 g (6×10^{-4} mol) ZnO was mixed with a 30 mL aqueous solution containing of 1.4×10^{-5} mol sodium dodecyl benzenesulfonate followed by sonication for 30 min and stirrer mechanically for 3h. After adding of 26.1 mL pyrrole monomer, the solution was continuously stirred for another 1 h. Then, 11.5 mL of the 0.1 M ammonium persulfate solution was added drop wise into the above solution. The polymerization process was conducted while stirring for 2h at room temperature. The product was magnetically separated and washed with deionized water, ethanol and then dried in an oven at 80 °C.

2.4. Batch adsorption experiments

The adsorption experiments by decolorization of Congo red dye solution were performed under the same conditions (60 mgL^{-1} initial concentration of Congo red dye solution, 0.5 gL^{-1} adsorbent dosage and t=25 °C). The suspension

was sampled at regular intervals and the adsorbent was removed byCentrifugation. Then, the degree of adsorption (X), as a function of time is given by $X=(C_\circ-C)/C_\circ$ where $C_\circ$ is the initial concentration of dye, and C the concentration of dye at time t. The disappearance of peak at λ = 498 nm was chosen for monitoring of dye adsorption for Congo red. For comparison, above experiments for the ZnO and$ZnO/ZnCr_2O_4$ samples were also performed.

3. Results and Discussion

3.1.Characterization of the samples

Fig. 1 (a-c) shows the XRD patterns of $ZnCr_2O_4$, ZnO and $PPy/ZnO/ZnCr_2O_4$samples after annealed at 700 °C for 3 h respectively. The XRD results shows that the $ZnCr_2O_4$ with cubic phase was obtained (JCPDS No. 22-1107), and the distinctive peaks at 18.45°, 30.35°, 35.75°, 37.35°, 43.45°, 53.93° , 57.45° and 63.21° matched well with cubic phase of $ZnFeCr_2O_4$(Fig.1(a)) [16]. The crystal phases corresponding to peaks at 31.8°, 34.4°, 36.3°, 47.5°, 68.0°, and 69.1° are corresponded to ZnO (JCPDS No. 36-1451) (Fig.1(b)). In the XRD spectrum of $PPy/ZnO/ZnCr_2O_4$, the peaks corresponding to the polypyrrole are not detected, indicating that polypyrrole was amorphous in $PPy/ZnO/ZnCr_2O_4$composite (Fig.1(c)).

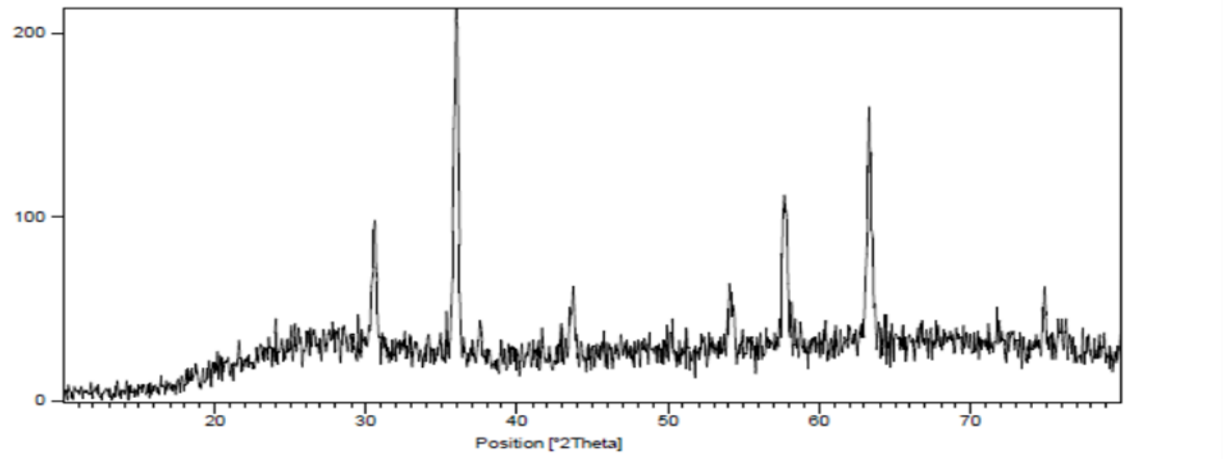


Fig.1 (a)

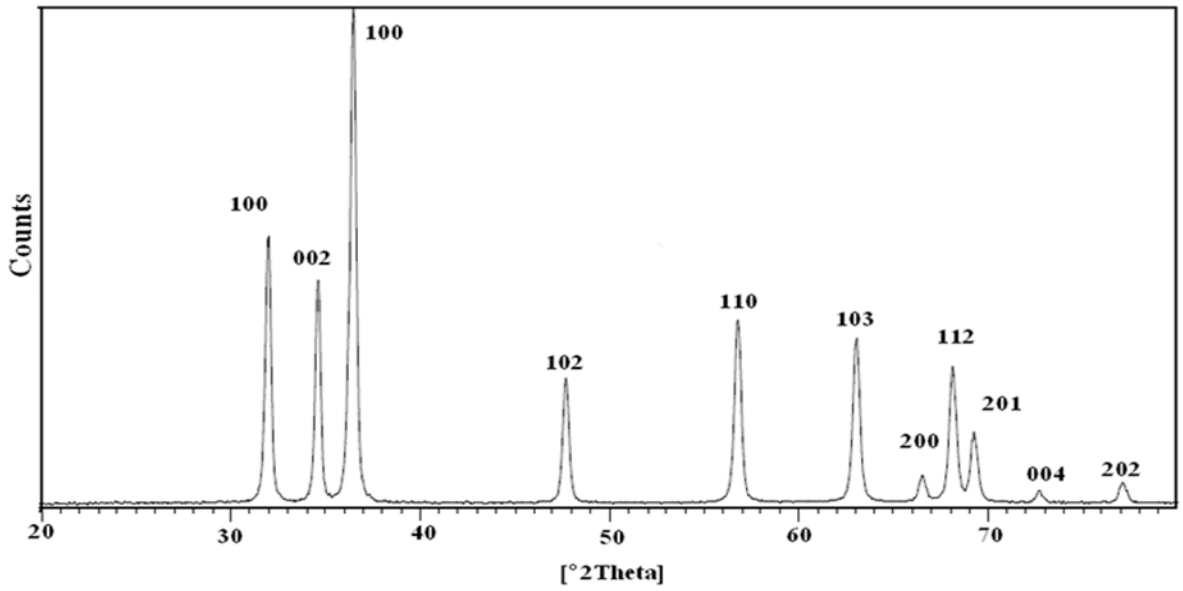


Fig.1(b)

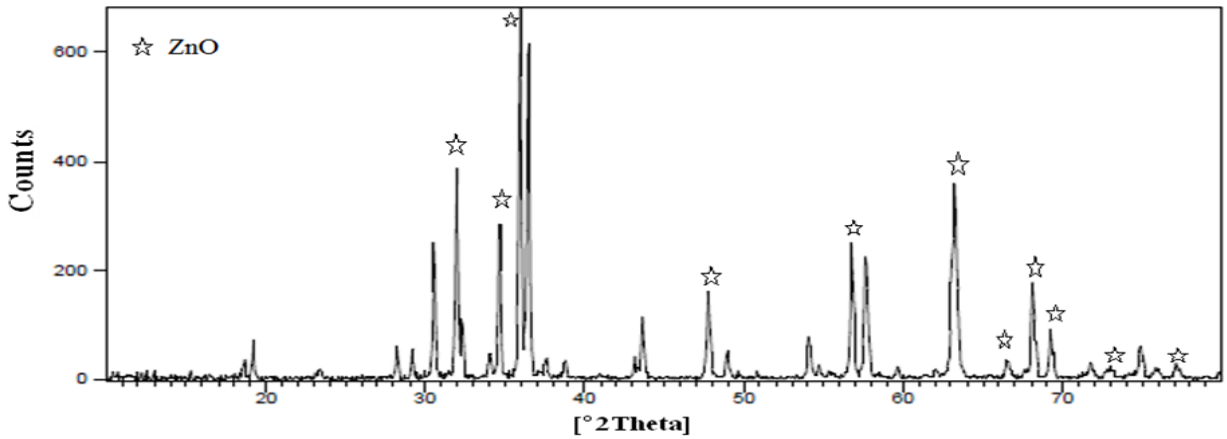


Fig.1(c)

Figure 1 (a-c): The XRD patterns of (a) $ZnCr_2O_4$, (b) $ZnO/ZnCr_2O_4$ and (c) /$PPy/ZnO/ZnCr_2O_4$.

The chemical structure of the $PPy/ZnO/ZnCr_2O_4$composite was confirmed by FT-IR analysis. In the FT-IR spectrum of ZnO, the band at 436 cm^{-1} was ascribed to Zn-O stretching vibrations [18]. In the FT-IR spectrum of $ZnCr_2O_4$, two characteristic peaks observed at around 513 and 625 cm^{-1} corresponds to octahedral-metal stretching and to intrinsic stretching vibrations of the metal at the tetrahedral site, respectively [16].These bands indicate the formation of spinel $ZnCr_2O_4$.The FT-IR spectrum of $PPy/ZnO/ZnCr_2O_4$composite,the band at 441 cm^{-1} confirmed the presence of ZnO in prepared composite [19]. Also, some shift as compared to PPy confirmed that the PPy had incorporated with ZnO and $ZnCr_2O_4$ successfully [20, 21]. From the results it can be inferred that the polymerization was successfully carried out.The morphology of the ZnO, $ZnO/ZnCr_2O_4$ and $PPy/ZnO/ZnCr_2O_4$is presented in Fig. 2 (a-c).

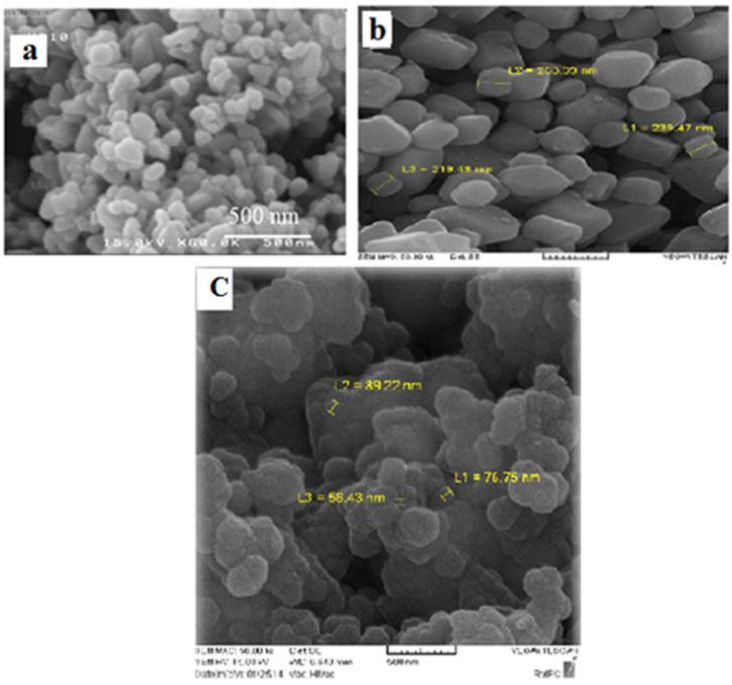


Figure 2 (a-c): The SEM images of (a) ZnO, (b) $ZnO/ZnCr_2O_4$ and (c) $PPy/ZnO/ZnCr_2O_4$

Fig. 2 (a) shows that the morphology of the ZnO is nanoparticle and particle size is of about (30-100 nm). Fig. 2b for the $ZnO/ZnCr_2O_4$ sample shows that the particles are quite polydispersed with a mean diameter of 213 nm. Fig. 2c shows a PPy layer coated on mixed $ZnO/ZnCr_2O_4$particles.The EDAX analysis of the $ZnO/ZnCr_2O_4$ and $PPy/ZnO/ZnCr_2O_4$samples sintered at 700 °C was performed along with its elemental analysis in order to check the purity of sample. The EDAX analysis revealed that the entire samples synthesized without any impurities (Fig 3(a) and (b)).

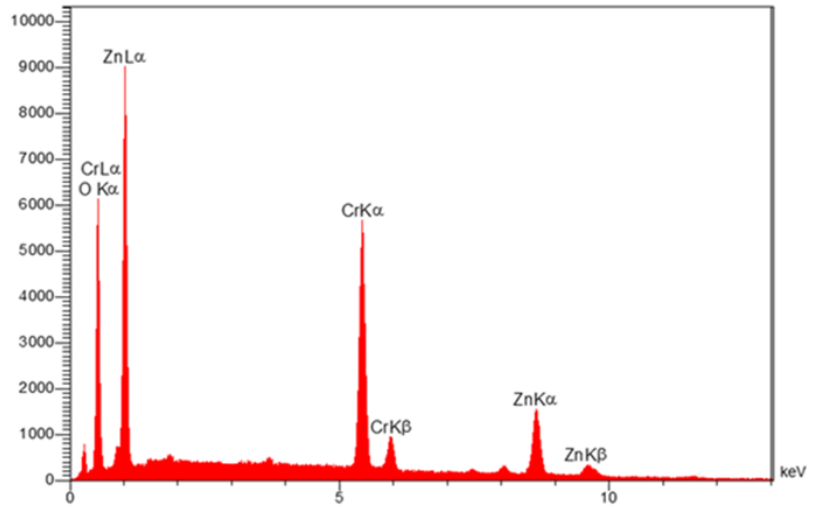


Figure 3(a): The EDAX spectrum of $ZnO/ZnCr_2O_4$

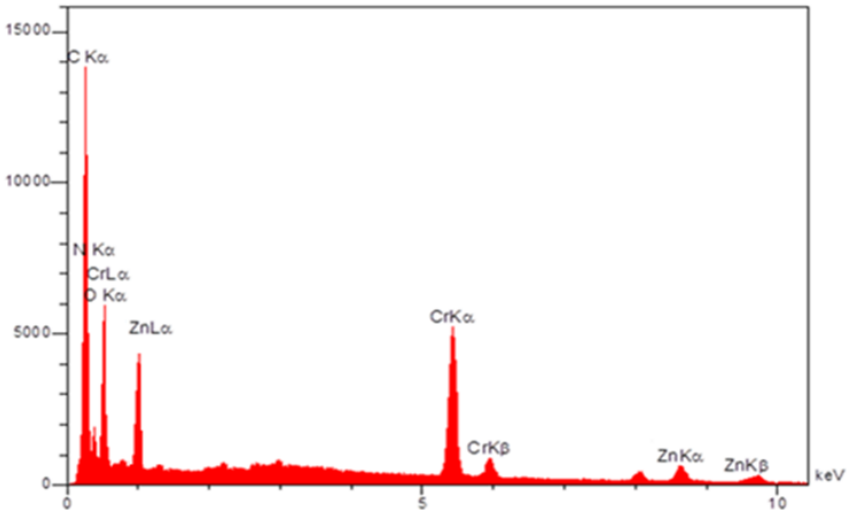


Figure 3(b): The EDAX spectrum of $PPy/ZnO/ZnCr_2O_4$

Based on the experimental results and analysis of the XRD, FTIR, SEM and EDAX it was found that the $PPy/ZnO/ZnCr_2O_4$composite was obtained.

3.2. The adsorption behavior of Congo red on the $PPy/ZnO/ZnCr_2O_4$

In order to investigate the adsorption behaviors of the $PPy/ZnO/ZnCr_2O_4$composite towards Congo red molecules, dark adsorption experiments were carried out. The amount of dye adsorbed per gram of adsorbent (mg/g) at time t (min) was calculated using the following equation [22]:

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (1)$$

Where q_t (mgg^{-1}) is the amount of adsorbed Congo red per gram of adsorbent at time t (min), C_0 is the initial concentration of Congo red in solution (mgL^{-1}), C_t is the concentration of dye (mgL^{-1}) at time t (min), V is the volume of the solution (L) and m is the mass of the adsorbent (g). The results of adsorption percentage versus time for Congo red dye on the surface of samples indicate that 28, 40, 78 (%) of Congo red dye was adsorbed on the ZnO,$ZnO/ZnCr_2O_4$ and $PPy/ZnO/ZnCr_2O_4$samples respectively. Fig. 4 represent the plots of the adsorption capacity versus time of the ZnO, $ZnO/ZnCr_2O_4$and $PPy/ZnO/ZnCr_2O_4$.

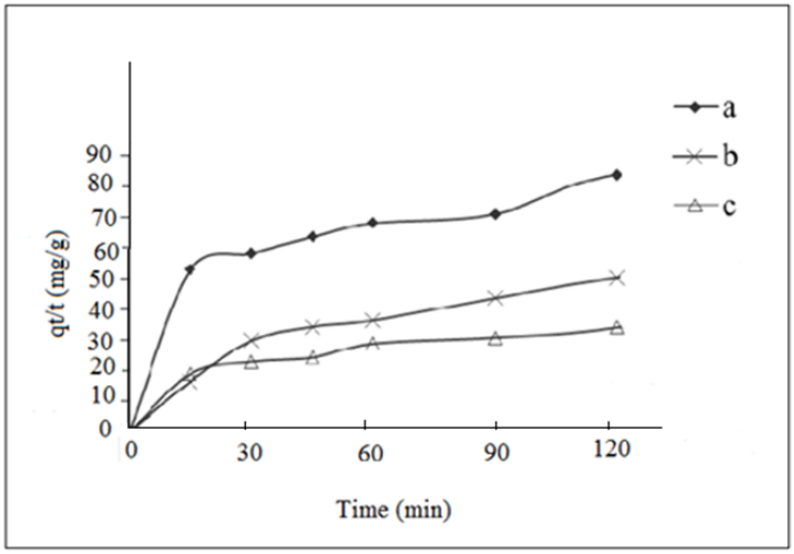


Figure 4: Adsorption capacity of (a) $PPy/ZnO/ZnCr_2O_4$, (b) $ZnO/ZnCr_2O_4$ and (c) ZnO

As shown in Figure 4, the adsorption capacity of samples was detected as $PPy/ZnO/ZnCr_2O_4$ (80 mgg^{-1}) >$ZnO/ZnCr_2O_4$ (42 mgg^{-1}) >ZnO (30 mgg^{-1}).

3.3. Effect of pH

The initial pH of dye solution play an important role for adsorption process [23]. The effect of pH is studied between 4 and 9 because at strong acidic medium, the solution of Congo red changes its color from red to dark blue and the original red color is different above pH 10. As shown in Fig.5, the maximum of removal efficiency on the surface of $PPy/ZnO/ZnCr_2O_4$sample is achieved in the acidic medium (74%) and reduced at the basic medium (48%).

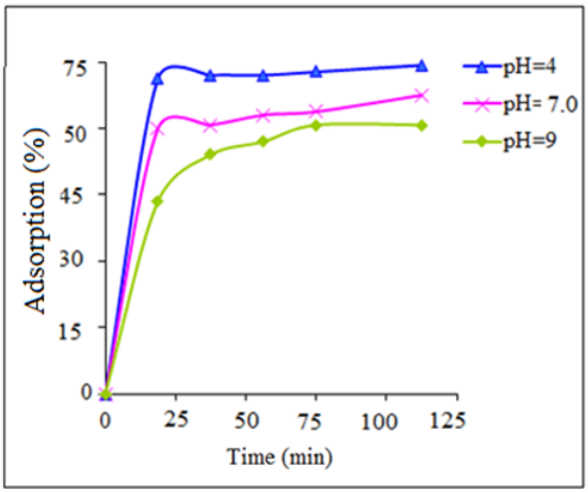


Figure 5: Effect of pH on adsorption of Congo red on the $PPy/ZnO/ZnCr_2O_4$sample

In the acidic medium, the solution of Congo red exists as cationic form [24] and the adsorption of cation favorite at pH>pH_{zp} [25]. When transfer from acidic to basic medium, due to the electrostatic repulsion the removal efficiency is reduced. Also, in the basic medium (pH = 10-12) there are competing between anionic dye and OH^- in the basic medium [26].

3.4. Adsorption kinetics

The study of adsorption kinetics provided valuable insight into the reaction pathways and the mechanism of the reaction [27]. Several kinetic models have been used to study the kinetics of the adsorption process: the pseudo-first-order and pseudo-second-order kinetic models.

3.5. Pseudo-first-order kinetic model

The kinetics of adsorption can be described using several models. A simple kinetic model is the pseudo-first-order equation [28]:

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \quad (2)$$

After definite integration by applying the initial conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, Eq. (2) becomes:

$$\ln (q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

Where q_e and q_t are the amounts of adsorbate adsorbed (mg/g) at equilibrium and at any instant of time t (min), respectively and k_1 is rate constant for pseudo-first-order adsorption (min^{-1}).The adsorption rate constant k_1 and equilibrium adsorption capacity $q_{e,cal}$, calculated from the slopes and intercepts of plots of log (q_e-q_t) versus time (Fig.6) along with correlation coefficients R^2 are listed in Table.1.As shown in Table.1, the experimental $q_{e,exp}$ values did not agree with the calculated ones obtained from the linear plots. The results indicated that the adsorption of Congo red dye onto PPy/ZnO/$ZnCr_2O_4$, ZnO/$ZnCr_2O_4$and ZnO did not follow the pseudo-first-order kinetic model and the reaction mechanism was not a first order reaction.

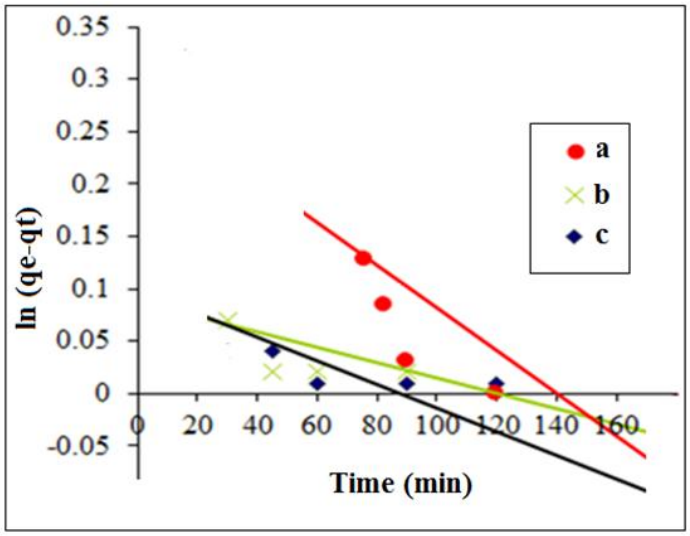


Figure 6: Plot ln(q_e-q_t) versus time (pseudo-first-order model) for the (a) ZnO/$ZnCr_2O_4$, (b) PPy/ZnO/$ZnCr_2O_4$and (c) ZnO samples

Table 1: Results of Kinetic Study

Sample	q_e^{exp}(mg/g)	Pseudo-first-order			Pseudo-second-order		
		k_1(min^{-1})	q_{e1}(mg/g)	R^2	k_2(g/mg min)	q_{e2}(mg/g)	R^2
ZnO/$ZnCr_2O_4$	42	0.0009	1.09	0.6216	0.014	40	0.9993
PPy/ZnO/$ZnCr_2O_4$	80	0.0024	1.39	0.8037	0.0014	79	0.9922
$ZnCr_2O_4$	30	0.0018	2.8	0.8433	0.5309	29	0.9997

3.6. Pseudo-second-order equation kinetic model

The pseudo-second-order kinetic model based on equilibrium adsorption can be represented in the form [29]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (4)$$

Where k_2 is the equilibrium rate constant of pseudo-second-order adsorption (g/mg min). The straight line plots of t/q_t versus time as shown in Fig.7 have been used to obtain the rate parameters. The values for q_e and k_2 along with the correlation coefficient (R^2) values are presented in Table.1. It can be found from Table.1 that the calculated q_e values agreed well with those of experimentally obtained q_e for the pseudo-seond-order model. Also the correlation coefficient values obtained by fitting the experimental data to Eq.(4) were close to 1.0.The calculated q_e values also agree very well with the experimental data in the case of pseudo-second- order kinetics and suggest that the rate-limiting step may be chemical sorption or chemisorption involving valency forces through sharing or exchange of electrons between the samples and dye ions [30].

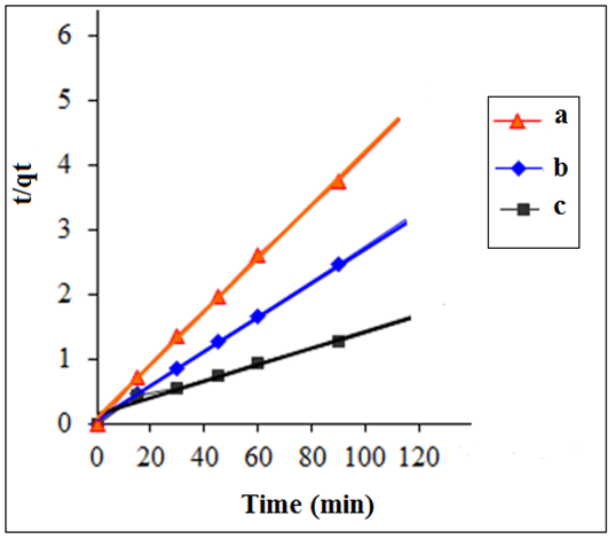


Figure 7: Plot of t/q_t versus time (pseudo-second-order model) for the (a) $ZnO/ZnCr_2O_4$, (b) $PPy/ZnO/ZnCr_2O_4$and (c) ZnO samples.

4. Conclusion

In our study, $PPy/ZnO/ZnCr_2O_4$ composite was synthesized by easy and effective precipitation method and used as adsorbent for Congo red removal from aqueous solution. The adsorption experiments indicated that the $PPy/ZnO/ZnCr_2O_4$composite adsorbent have great dye removal efficiency with respect to ZnO and $ZnO/ZnCr_2O_4$. Therefore, the low cost $PPy/ZnO/ZnCr_2O_4$composite is an efficient adsorbent for removal of anionic azo dyes in industrial wastewater treatment.

Acknowledgements

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