# Multifunctional 1D/2D polypyrrole nanotubes@pg-$C_3N_4$ binary nanocomposite for removal of mercury ($Hg^{2+}$) from wastewater: Characterization and mechanism interpretation


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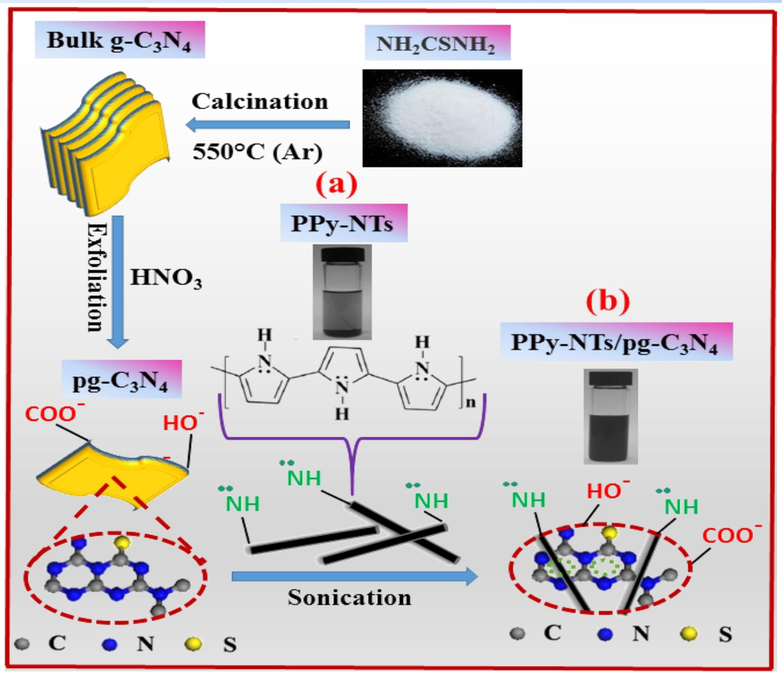
## Abstract


A facile one-step synthesis of 1-D PPy-NTs on the surface of 2-D p-g-$C_3N_4$ providing new hybrid nanocomposites was developed. Herein, the effect of 1-D and 2-D shape nanomaterials on the efficiency of the developed PPy-NTs-based nanocomposites for heavy metal removal was investigated. The prepared nanocomposites were used as cost-effective adsorbents to remove $Hg^{2+}$ heavy metal ions from wastewater. Different factors were studied such as pH, contact time, adsorbent dose, initial concentration of metal ions, and contact time. The adsorptive ability of the developed nanocomposite reached 1.5 ppb residual $Hg^{2+}$concentration, which is below the accepted limit for mercury (II) concentration in drinking water (2 ppb) according to the Environmental Protection Agency (EPA) in addition

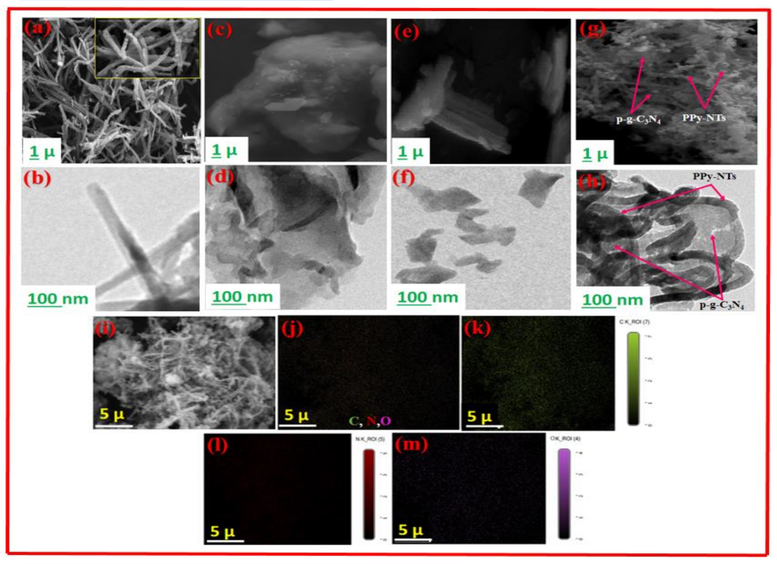

## Experimental

### Preparation of PPy-NTs/p-g-$C_3N_4$ hybrid nanocomposite

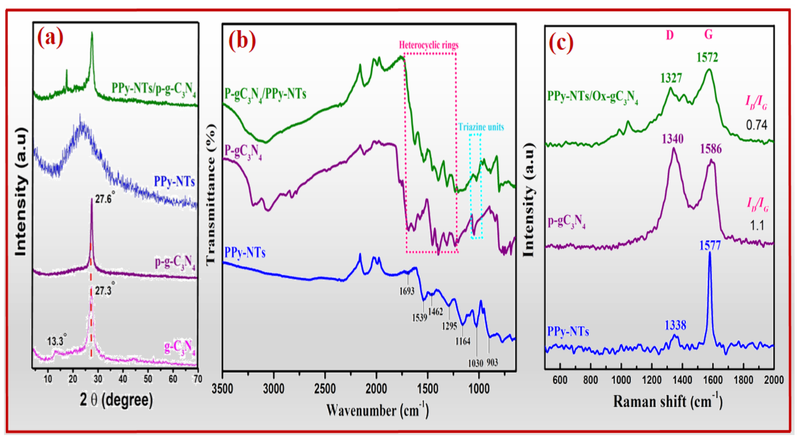



## Characterization Tools

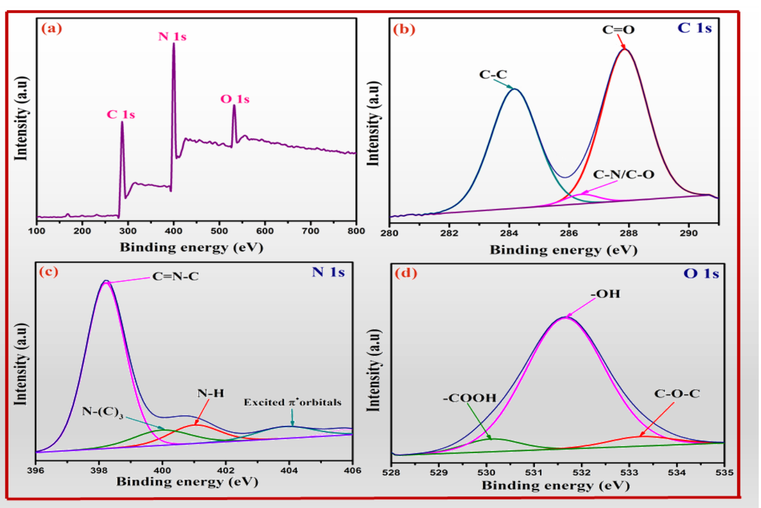
### TEM and SEM




### XRD, FT-IR, and Raman

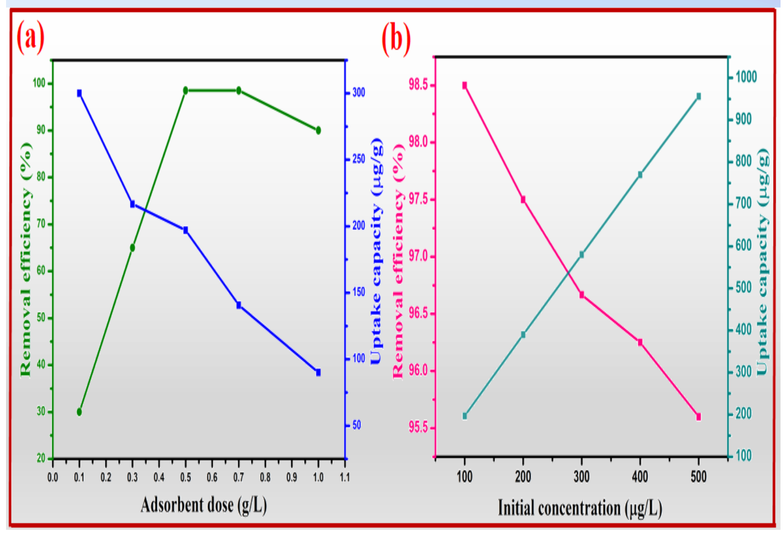



### XPS analysis




## Experimental

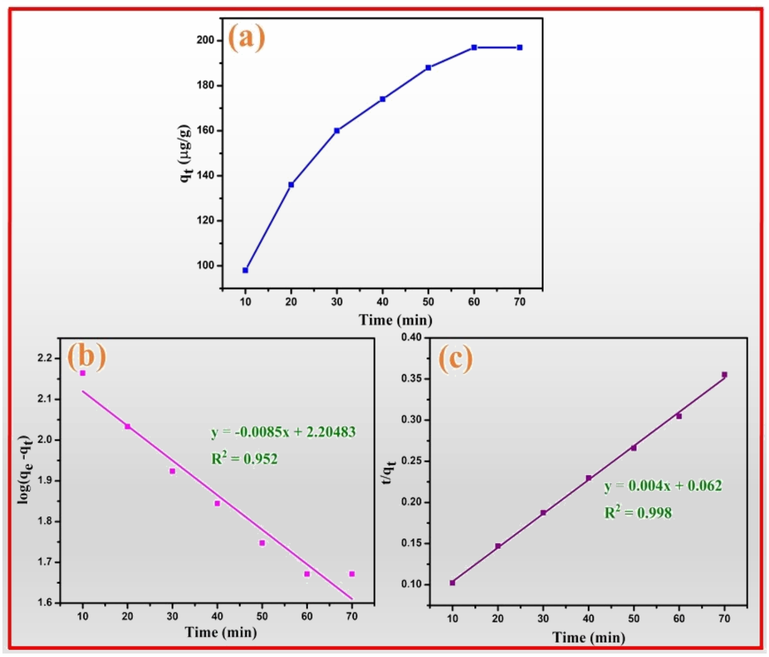
**Effect of contact time on the adsorption behavior of $Hg^{2+}$ heavy metal ions using pg-$C_3N_4$/PPy-NTs (a), Pseudo-first order (b), and Pseudo-second order (c) kinetic plots of $Hg^{2+}$ onto p-g-$C_3N_4$/PPy-NTs.**



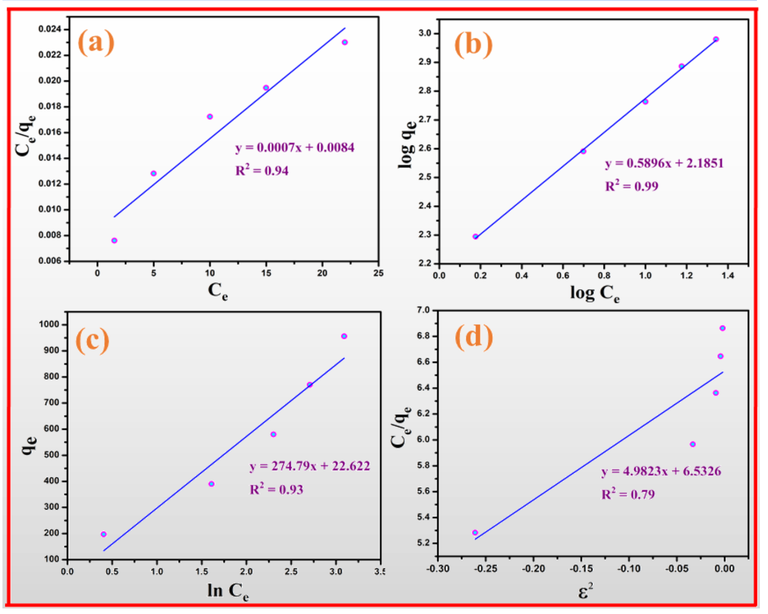

**The Adsorption kinetic parameters for adsorption of $Hg^{2+}$ onto pg-$C_3N_4$/PPy-NTs hybrid nanocomposite**

| Pseudo-first-order kinetics | | | Pseudo-second-order kinetics | | | |
|---|---|---|---|---|---|---|
| $K_1$ ($min^{-1}$) | $q_{e,cal}$ ($\mu g \cdot g^{-1}$) | $R^2$ | $k_2$ ($g \cdot mg^{-1} \cdot min^{-1}$) | $q_{e,cal}$ ($\mu g \cdot g^{-1}$) | $q_{e,exp}$ ($\mu g \cdot g^{-1}$) | $R^2$ |
| 0.0196 | 9.068 | **0.952** | 0.0026 | 243.9 | 197 | **0.998** |

**(a) Effect of adsorbent dosage on the removal efficiency and uptake capacity of $Hg^{2+}$ ions, (b) Adsorption capacity and removal efficiency % of $Hg^{2+}$ ions onto pg-$C_3N_4$/PPy-NTs adsorbent as a function of initial metal concentrations**



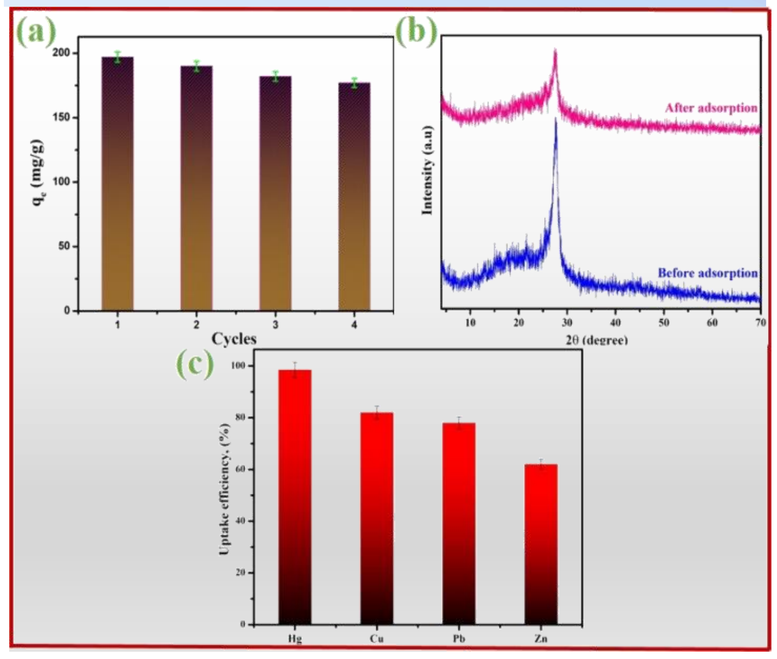

**The adsorption isotherm parameters for adsorption of $Hg^{2+}$ onto pg-$C_3N_4$/PPy-NTs hybrid nanocomposite.**



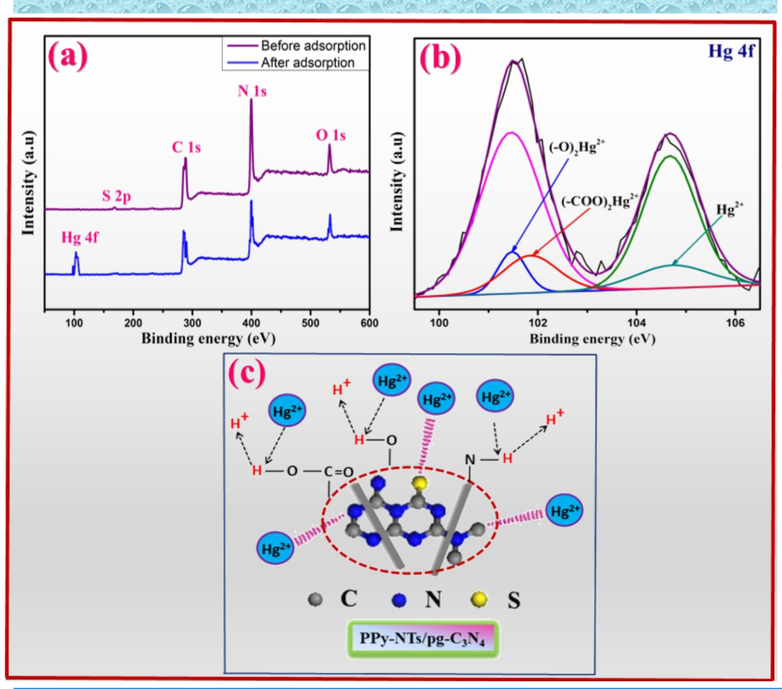

**Adsorption isotherm, (a) Langmuir, (b) Freundlich, (c) Temkin and (d) D-R models fitting $Hg^{2+}$ adsorption onto pg-$C_3N_4$/PPy-NTs adsorbent.**

| Langmuir | | | Freundlich | | | | Temkin | | | D-R | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $R^2$ | $K_L$ | $q_{max.}$ | $R^2$ | $K_f$ | n | 1/n | $R^2$ | A | B | $R^2$ | K | $q_D$ |
| 0.94 | 0.083 | 1428.5 | **0.999** | 0.34 | 1.6 | 0.59 | 0.93 | 1.08 | 274.7 | 0.79 | 4.98 | 685 |

**Fig. 9. (a) The regeneration of $Hg^{2+}$ from pg-$C_3N_4$/PPy-NTs after four successive adsorption/desorption cycles, (b) XRD pattern and SEM images of pg-$C_3N_4$/PPy-NTs before and after Hg2+ adsorption and (c) Impact of competing ions on Hg2+ions adsorption, with vertical error bars indicating the ± standard deviations (n = 3).**




## The mechanism of $Hg^{2+}$ speculation from wastewater




## Conclusion

In this study, a novel uniformly dispersed adsorbent of PPy-NTs/pg-$C_3N_4$ was synthesized via an effective and innovative approach for developing a hybrid nanocomposite with a high affinity toward the adsorption of toxic $Hg^{2+}$ heavy metal ions from wastewater. Such a rational design of this composite can solve the agglomeration problem of PPy-NTs in an aqueous medium due to its hydrophobic nature, decreasing its surface area and hindering the available active sites for $Hg^{2+}$ adsorption. The results indicate that the highly hydrophilic pg-$C_3N_4$ exfoliated sheets can help in the dispersion and stabilization of the PPy-NTs in an aqueous medium. Moreover, the pg-$C_3N_4$ exfoliated sheets are prepared using a facile method through the in-situ pyrolysis of urea under inert conditions, followed by protonation under reflux with nitric acid. he developed a nanocomposite that offered various accessible active sites for the adsorption of $Hg^{2+}$ with a removal efficiency of 98.5% with 197 mg $g^{-1}$ adsorption capacity. What is more, the adsorptive ability of the developed nanocomposite reached 1.5 ppb residual $Hg^{2+}$ concentration, which is below the accepted limit for mercury (II) concentration in drinking water (2 ppb) according to the Environmental Protection Agency (EPA). The adsorption of $Hg^{2+}$ on PPy-NTs/pg-$C_3N_4$ hybrid nanocomposite confirms the pseudo-second-order model and Freundlich isotherm which reveals that $Hg^{2+}$ heavy metal ions are chemically adsorbed on various adsorption site of secondary amine in PPy-NTs backbone and the oxygen surface functional groups of pg-$C_3N_4$. Most importantly, regeneration of the PPy-NTs/pg-$C_3N_4$ nanocomposite demonstrates a long lifetime after 2 successive desorption–reabsorption studies to reach the accepted concentration limit in drinking water. In mixed $Hg^{2+}$, $Zn^{2+}$, $Pb^{2+}$, and $Cu^{2+}$ ions systems, the selective $Hg^{2+}$ absorption by pg-$C_3N_4$ /PPy-NTs was maintained. Therefore, the developed PPy-NTs/ pg-$C_3N_4$ is a promising candidate for the selective removal of $Hg^{2+}$ from wastewater.

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