Supplementary Material

Magnetic Ni/PPy nanocomposite as effective reusable adsorbent for removal of arsenite and fluoride from contaminated water

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1. Experimental details

1.1. Characterizations

X-ray diffraction (XRD) patterns of the samples were recorded with D8 Advance diffractometer, Bruker, Germany, with Co K_{α} radiation ($\lambda = 0.179$ nm) with a scanning rate of $2\theta = 3^{\circ}$ per min. The morphology of the as prepared products was studied by field emission scanning electron microscopy (FESEM) on Carl Zeiss Supra 40 instrument at an accelerating voltage of 20 kV respectively. High resolution transmission electron microscopy (HRTEM) of the samples was performed using Phillips CM 200 with an acceleration voltage of 200 kV and digital images were recorded on a Gatan multipole charge-coupled device (CCD) camera. Room temperature magnetizations data were recorded using SQUID VSM DC magnetometer, Quantum design, USA. Raman analysis was performed at room temperature on a Renishaw invia Raman microscope equipped with an argon-ion laser at a wavelength of 514.5 nm. Fourier Transform Infrared spectroscopy (FTIR) and surface area measurement were carried out using a Perkin Elmer and Quantachrome autosorb iQ instruments respectively. Atomic absorption spectroscopy (AAS) study was done using Atomic Absorption Spectrophotometer (Model No. 240 FF) made in Varian, Netherlands. Orion Ion Meter, Thermo Fisher Scientific with ion selective electrode was used for the determination of fluoride.

2. Supplementary Figures



Fig. S1 FTIR spectra of (a) Ni nanoflower and Ni/PPy nanocomposite prepared using mass ratio of Ni: Py (b) 2:1, (c) 1:1and (d) 1:2.

Fig. S1 displays the FTIR spectra of Ni nanoflower and Ni/PPy nanocomposite prepared using 2:1, 1:1 and 1:2 weight ratio of Ni:Py. The absence of transmittance bands due to stretching vibrations (OH, C-H, C-O) and bending vibration (CH₂) of TEA confirms the formation of high purity Ni nanoflower.¹ The corresponding spectra of Ni/PPy nanostructures are also shown in Fig. S1. The peak at 672 cm⁻¹ is associated with the C-C out-of-plane ring deformation vibration or the C-H rocking vibration.² The transmittance bands corresponding to C-H out-of-plane deformation vibration and out-of plane ring deformation vibration of the ring are also observed at 907 cm⁻¹ and 780 cm⁻¹ respectively.³ A band at 1544 cm⁻¹ is attributed to the fundamental vibrations of the

pyrrole ring.⁴ The characteristic bands at around 1180 and 1038 cm⁻¹ in the spectra are associated with the C-N stretching and N-H in-plane deformation vibrations respectively.³ In addition, the FTIR spectra of Ni/PPy show the presence of a broad peak at around 1295 cm⁻¹, which is ascribed to =C-H in-plane deformation modes.² All these characteristic bands appearing due to PPy in Ni/PPy, observed more or less at the same position in PPy. This clearly indicates the absence of any chemical interaction between Ni and PPy in Ni/PPy nanostructures.^{2,5}



Fig. S2 Raman study of Ni/PPy nanocomposite prepared using mass ratio of Ni: Py (a) 1:2, (b) 1:1 and (c) 2:1

Raman spectroscopy (λ =514.5 nm) of Ni/PPy nanocomposites has also been carried out at room temperature and the corresponding findings are shown in Fig. S2 (Supplementary Material). The strong peaks at 1578 cm⁻¹ and 1380 cm⁻¹ in the nanocomposites correspond to the C=C stretching and ring stretching modes respectively.^{6,7} In addition, another peak at 1040 cm⁻¹ could be ascribed to the C-H deformation mode.⁸ Interestingly the presence of an additional peak at 945 cm⁻¹ is observed due to ring deformation asymmetry at the highest Ni/PPy ratio of 1:2. All these findings confirmed that the PPy exists in the oxidized state.^{6,8}



Fig. S3 Room temperature magnetic property of Ni/PPy nanocomposite prepared using mass ratio of Ni: Py (a) 2:1,(b) 1:1 and (c) 1:2 (inset shows the corresponding magnified image of the hysteresis loop).

It is well-known that the surface chemistry of magnetic particles greatly affects its properties.² Therefore, a comparative measurement of the field-dependent magnetic properties of Ni/PPy nanocomposites has been carried out at room-temperature and findings are displayed in Fig. S3. The appearance of hysteresis loop in the magnetization curves (inset of Fig. S3) confirmed the ferromagnetic behaviour of Ni/PPy. The magnetization data in Table S1 showed that the saturation magnetization (and coercitivity) values of Ni, Ni/PPy (2:1), Ni/PPy (1:1) and Ni/PPy (1:2) nanostructures are found to be 29.8 (259 Oe),⁹ 28.9 (170 Oe), 26.3 (165 Oe) and 24.2 (135 Oe) emu/g respectively. This result clearly indicates that the ferromagnetic behaviour of Ni is

retained even in the Ni/PPy nanocomposites. The saturation magnetization of Ni/PPy is reduced compared to pure nickel due to the coating of diamagnetic PPy on its surface. Alternatively, the decrease in Ni content could also reduce the saturation magnetization in Ni/PPy composite.^{10,11}



Fig. S4 Removal efficiency of (a) As (III) and (b) F⁻ by Ni/PPy (1:2, 1:1 and 1:2).



Fig. S5 Nitrogen adsorption-desorption isotherm of Ni/PPy (1:2)

3. Supplementary Tables

No	Ni:monomer (wt. ratio)	Saturation magnetization (emu/g)	Remnant Magnetization (emu/g)	Coercivity (Oe)
a.	2:1	28.9	0.305	170
b.	1:1	26.3	0.305	170
C.	1:2	24.2	0.305	135

Table S1. Magnetic property of the Ni/PPy nanocomposite

Table S2.Chemical analysis of real ground water of Nagaon, Assam, India

Contents in real water	Concentration (ppm)	Limit (DL-PL) (ppm)	After removal (ppm)
Sulphate	110	200400	95
Phosphate	4	-	4
Hydroxide	18	-	16
Sodium	77	20200	73
Potassium	25	20100	25
Calcium	55	200	55
Magnesium	47	150	47
Bicarbonate	100	1000	93
Nitrate	14	45-100	14
Iron	10.4	0.31.0	8.4
Dissolved solids	154	5002000	154
Turbidity	8	510	8
Arsenic	0.195	0.010NR	0.008
Fluoride	0	11.5	0

Contents in real water	Concentration (ppm)	Limit (DL-PL) (ppm)	After removal (ppm)
Sulphate	110	200400	95
Phosphate	4	-	4
Hydroxide	15	-	13
Sodium	75	20200	75
Potassium	25	20100	25
Calcium	55	200	55
Magnesium	49	150	49
Bicarbonate	98	1000	93
Nitrate	14	45-100	14
Iron	7.5	0.31.0	6.8
Dissolved solids	154	5002000	154
Turbidity	8	510	8
Arsenic	0.007	0.010NR	0
Fluoride	7	11.5	1.5

Table S3. Chemical analysis of real ground water of Karbiangling, Assam, India

References

1. R. K. Sahu, A. K. Ray, T. Mishra and L. C. Pathak, Cryst. Growth Des. 2008, 8, 3754-3760.

2. P. Xu, X. Han, C. Wang, D. Zhou, Z. Lv, A. Wen, X. Wang and B. Zhang, *J. Phys. Chem. B* 2008,**112**, 10443-10448.

- 3. N. V. Blinova, J. Stejskal, M. Trchova´, J. Prokes` and M. Omastova,´ *Eur. Polym. J.* 2007, **43**, 2331-2341.
- 4. T. Nguyen and A. Diaz, Adv. Mater. 1994, 6, 858-860.
- 5. L. Zhang and M. Wan, J. Phys. Chem. B 2003, 107, 6748-6753.
- 6. W. Zhang, X. Wen and S. Yang, Langmuir 2003,19, 4420-4426.
- 7. J. Ota and S. K. Srivastava, J. Phys. Chem. C 2007,111, 12260-12264.
- 8. S. J. Vigmond, V. Ghaemmaghami and M. Thompson, Can. J. Chem. 1995,18, 1711-1718.
- 9. S. Senapati, S. K. Srivastava, S. B. Singh and K. Biswas, *Cryst. Growth Des.* 2010,**10**, 4069-4075.
- 10. S. Senapati, S. K. Srivastava, S. B. Singh and H. N. Mishra, *J. Mater. Chem.* 2012, **22**, 6899-6906.
- 11. S. Senapati, S.K. Srivastava and S. B. Singh, Nanoscale 2012, 4, 6604-6612.