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Chromium(VI) removal from water by using polyaniline biocomposites with *Madhuca longifolia* and *Szygium cumini* leaves

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Biocomposites of polyaniline with *Madhuca longifolia* (PANI/ML*)* and S*zygium cumini* (PANI/SC) were synthesized, characterized and used for batch-wise adsorption of Cr(VI) from water. Optimum conditions for PANI/ML: 20 min contact time, adsorbent dose 0.3 g in 50 mL solution of Cr(VI), 50˚ C temperature and pH 2; and for PANI/SC: 80 min contact time, adsorbent dose 0.1 g in 50 mL solution of Cr(VI), 10˚ C temperature and pH 5. Langmuir isotherm shows that chemisorptive monolayer removal of Cr(VI) has occurred on the composite binding sites. 13.334 mg/g is the maximum adsorption capacity of PANI/ML, in case of PANI/SC it is 4 mg/g. ΔG° negative value confirms the feasibility and spontaneity of the adsorption process. Freundlich isotherm tells about heterogeneously distributed sites and physio-sorptive metal ion removal. For PANI/ML and PANI/SC the constant K_F values are 0.019 and 0.005, respectively. Results revealed that PANI/ML is a better ecofriendly biocomposite for Cr(VI) removal from water as compared to PANI/SC.

Keyword: Cr(VI), Polyaniline composites, ecofriendly, leaves, water.

INTRODUCTION

In Pakistan uncontrolled industrialization has become the main cause of environmental degradation. Industrial effluents which contain hazardous substances and heavy metals are disposed either into water bodies or onto open land directly or indirectly. Through different routes these hazardous substances enter and disturb the lifecycle and also cause diseases, e.g, cancer [1]. One of these toxic substances is chromium which is present in aqueous systems in trivalent and hexavalent form. Different industries, for example metal finishing, pigments, glass, inks, dyes, certain glues and ceramics use chromium [2]. Heavy metals are not biodegradable and bring high level toxicity to the environment [3].

The French chemist Vauquelin discovered chromium in 1798 [4]. Cr(VI) is more poisonous than Cr(III) [5]. Cr (VI) compounds are responsible for many clinical problems. Its retention and inhalation can cause asthma, nasal septum perforation, pneumonitis, bronchitis, liver and larynx inflammation, and bronchogenic carcinoma [6-8]. For Cr(VI) removal, adsorption on activated carbon is a very efficient process but it is very expensive [9]. In the last decades, metal ion adsorption by conducting polymers as PANI and polythiophene has been reported [10]. Among conducting polymers polyaniline (PANI) is very efficient. Abundant amine and imine groups in it can chelate metal ions [8]. In this research work, polyaniline composites with plant leaves of *Szygium cumini* (Jamun) PANI/SC, and *Madhuca longifolia (*Mahva*)* PANI/ML were prepared and used for Cr(VI) adsorption in batch mode.

EXPERIMENTAL WORK

Instruments used were: Digital balance, Chiller apparatus Caoran CAN-7000-B, FT-IR spectrophotometer, atomic absorption spectrophotometer (Perkin Elmer Aanalyst 100). Chemicals used were: aniline monomer, anhydrous ferric chloride, HCl (AnalaR), DMF (PRS Panreac), acetone (BDH). Aniline was purified by distillation before use. The middle fraction of the distillate was collected, kept under nitrogen atmosphere and stored in a refrigerator. Aniline polymerization was carried out as already reported [7].

Synthesis of PANI composites with Szygium cumini, Madhuca longifolia leaves

The composites were prepared in a similar way as already reported [11] and characterized by UV/Visible spectroscopy and FT-IR.

Preparation of stock solution and standards for adsorption studies of Cr (VI):

For a stock solution of 1000 ppm, 2.82 g of potassium dichromate was dissolved in 1000 ml of water and further standards were prepared by dilution.

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ADSORPTION STUDIES

The adsorption studies of Cr(VI) were carried out in batch mode separately for both composites as described earlier [7]. The percent removal of Cr(VI) ions was calculated by:

$$\text{Adsorption \%age} = [(C_{in}-C_{fin})/C_{in}] \times 100$$

where C_{in} is the initial concentration of Cr(VI), C_{fin} is Cr(VI) concentration after adsorption.

RESULTS AND DISCUSSION

UV/VISIBLE spectroscopic analysis

PANI and its composites were analyzed after dissolution in dimethyl formamide and their spectra were taken. The λ_{max} of PANI and its composites are given in Table 1. Absorption at λ_{max1} 330 nm is due to a $\pi - \pi^*$ transition of aniline in the benzenoid ring [11]. Absorption at 645 nm is due to an excitonic transition of benzenoid to quinonoid ring. Presence of two peaks in the UV/Vis spectra shows that two non equivalent rings, benzenoid and quinonoid, are present in the polymer chain.

FT-IR Characterization

FT-IR was used to characterize PANI and its composites (PANI/ML, PANI/SC) and relevant peaks are given in Table 2 [12]. By comparing the FT-IR spectra of PANI and its composites (PANI/ML, PANI/SC) it was observed that the band (due to amino group (N-H) [13] stretching frequency) for PANI at 3431 cm^{-1} is shifted to 3425 cm^{-1} in case of PANI/ML and PANI/SC. The absorption band at 1571 cm^{-1} is due to benzenoid to quinonoid rings nitrogen bond, because of benzenoid to quinonoid transition. In case of PANI/ML it is shifted to 1584 cm^{-1} and in case of PANI/SC - to 1575 cm^{-1}. Peaks due to secondary amine stretching [14] are shifted from 1293 cm^{-1} (PANI) to 1288 cm^{-1} (PANI/ML) and 1266 cm^{-1} (PANI/SC). Bands in the range of 1571-1116 cm^{-1} are due to the conductive nature of PANI.

CONDUCTIVITY MEASUREMENTS

The conductivity of PANI and its composites was measured by the Four Probe Method using Keithley 4200-SCS. The conductivity of polymers depends upon their size, type of monomer, doping level, shape, and interaction between filler molecules. Temperature dependent conductivity measurements were carried out with the samples at room temperature. Results in Table 3 show that PANI/ML is less conductive than PANI/SC. Its lower conductivity is due to the poorer connectivity between grinded leaves and polymer due to which its compactness and packing density decrease, because of the presence of chains of polymer not supported by leave particles, so conductivity also decreases [11].

Table 1. λ_{max} of PANI and its composites

Sample	λ_{max1} (nm)	Absorbance	λ_{max2} (nm)	Absorbance
PANI	330	0.376	645	.285
PANI/SC	330	0.373	635	.227
PANI/ML	325	0.327	645	.169

Table 2. FT-IR analysis of PANI and its composites

Vibrational Assignment	Reference absorption band (cm^{-1})	PANI (cm^{-1})	PANI/ML (cm^{-1})	PANI/SC (cm^{-1})
N-H Stretching	3426	3431	3425	3425
N=Q=N	1577	1571	1583	1575
N=B=N	1489	1493	1499	1499
-C=N Stretching	1295	1293	1288	1266
Aromatic C-N-C	1121	1116	1132	1132

Table 3. Conductivity, resistivity and thickness of PANI and its composites.

Sr. No.	Samples	Thickness (cm)	Resistivity (Ω)	Conductivity (S/cm)
1.	PANI	0.014	60.3613	16.5669×10^{-3}
2.	PANI/ML	0.0172	1.6495×10^{3}	606.2393×10^{-6}
3.	PANI/SC	0.0188	76.42753	1.3084×10^{-2}

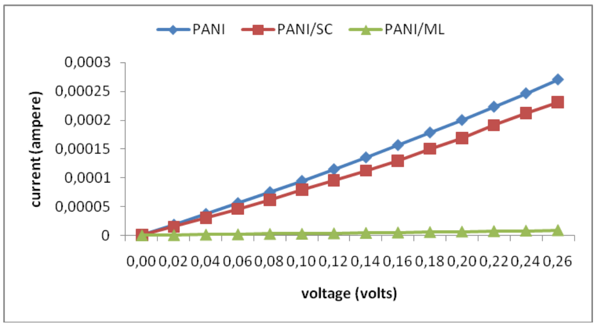

Fig.1. I-V Plots by PANI and its composites.

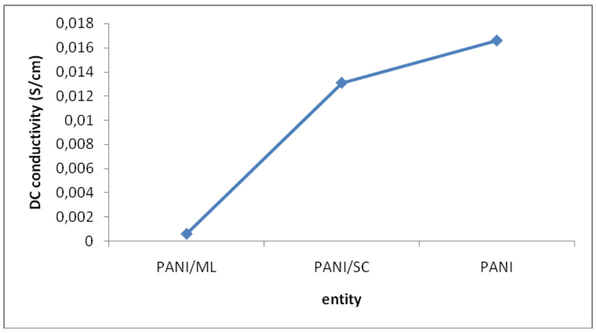

Fig.2. Comparison of conductivity of PANI and its composites.

BATCH ADSORPTION EXPERIMENTS

ADSORBENT DOSE

The effect of various adsorbent doses was studied for the percent removal of Cr(VI) metal. The results are given in Fig.3. The maximum percent removal of Cr (VI) was observed with 0.1 g of PANI/SC (89.52% removal) and 0.3 g of PANI/ML (91.03% removal). The results revealed that preventing the PANI/ML particles from aggregation and exposing Cr(VI) towards available active sites for adsorption showed greater efficiency in its removal. In case of PANI/ML adsorption firstly increases and then decreases because of adsorbent particles coagulation, due to which the number of sites available for adsorption decreases [12].

CONTACT TIME

Adsorption phenomenon is time dependent. The effect of different time intervals on the percent removal of Cr (VI) by PANI/ML and PANI/SC was observed. Results are shown in Fig.4. The maximum percent removal value was 82 % for PANI/SC composite for 80 min, and 88.236 % for PANI/ML composite for 20 min. The reduced time interval for maximum removal of Cr(VI) using PANI/ML composite showed that it has more adsorption sites which are available for adsorption of metal ions. After the maximum removal of Cr (VI), the adsorption decreased with increase in contact time because all available sites were occupied [13]. PANI/ML was more appropriate for removal of Cr (VI) than PANI/SC.

METAL SOLUTION pH

The results of the pH study are shown in Fig.5. Solution pH is responsible for the type and ionic state of functional groups present on the sorbing material and the ionic state of chromium. Cr(VI) is converted to Cr(III) in acidic medium, which is further converted to $Cr(OH)^{2+}$ and $Cr(OH)_2^{+}$, that can interact with -NH, N=Q=N and N=B=N functional groups of PANI composites [14-18]. The Cr(VI) adsorption mechanism on the composites may be an exchange between the Cl^- and $Cr_2O_7^-$ anions [19,21]. The maximum percent removal value was 88.666 % for PANI/SC composite at pH 5 and 91.03 % for PANI/ML composite at pH 2. PANI/ML was more appropriate for removal of Cr(VI) than PANI/SC.

TEMPERATURE

The adsorption of Cr (VI) was studied at various temperatures ranging from 10 to 100° C on PANI/ML and PANI/SC (Fig.6). The maximum percent removal of Cr(VI) was observed at 10 °C using PANI/SC and at 50 ℃ using PANI/ML composite. The percent removal values were 85.655 and 87.161% for PANI/SC and PANI/ML composites, respectively. The results showed that PANI/ML was more appropriate for removal of Cr(VI) than PANI/SC.

ADSORPTION ISOTHERMS

The Langmuir and Freundlich isotherms for PANI/ML and PANI/SC are shown in Tables 4 and 5, respectively.

Table 4. Langmuir isothermal parameters

Adsorbent	Slope	Intercept	R^2	q_m (mg/g)	b (L/mg)	ΔG° (KJ/mol)	R_L
PANI/ML	13.27	0.075	0.912	13.334	0.005	-13.129	0.7
PANI/SC	13.99	0.250	0.979	4.0	0.017	-10.096	0.5

Table 5. Freundlich isothermal parameters

Adsorbent	Slope	Intercept	R^2	K_F	n
PANI/ML	1.730	1.710	0.853	0.019	0.578
PANI/SC	1.749	2.272	0.862	0.005	0.571

Langmuir isotherm indicated that monolayer chemisorptive removal of Cr(VI) ions has occurred on the homogeneously distributed composites' binding sites [22-24]. It is predominant over the Freundlich model. This means that chemisorption is predominant over physisorption, as indicated by the greater R^2 value of Langmuir than Freundlich. Maximum adsorption capacity (q_m) values for

PANI/ML and PANI/SC are 13.34 and 4 mg/g, respectively.

The negative sign of ΔG^o showed that the adsorption process is feasible and spontaneous. Results revealed that PANI/ML shows better adsorption than PANI/SC, where 'n' and 'K_F' are Freundlich isotherm constants. 'K_F' value was 0.019 and 0.005 for PANI/ML and PANI/SC, respectively. For Cr(VI) ions the value of 'n' was 0.578 for PANI/SC and 0.571 for PANI/JL. Separation factor R_L value is between 0 and 1, indicating the favorability of this process [23]. At higher values of 'n' the affinity and heterogeneity of adsorbent sites will be greater.

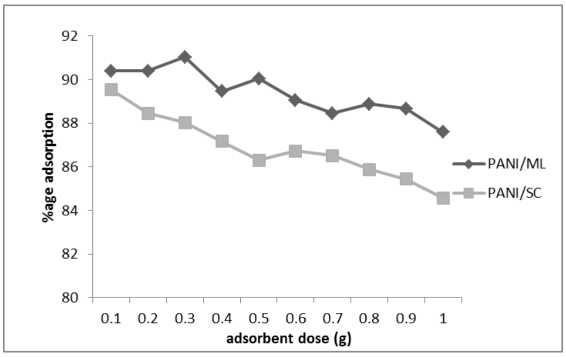

Fig. 3. Comparative graph of PANI/ML and PANI/SC showing the effect of adsorbent dose on the % adsorption of Cr(VI).

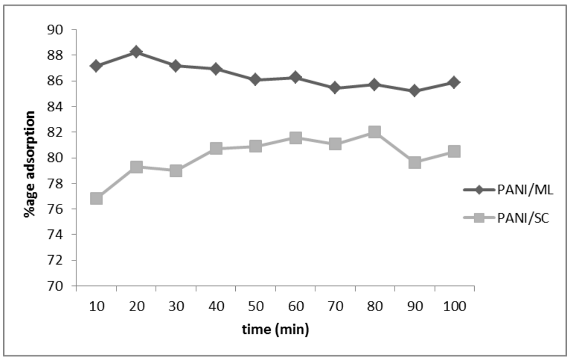

Fig. 4. Comparative graph of PANI/ML and PANI/SC showing the effect of contact time on the % adsorption of Cr(VI).

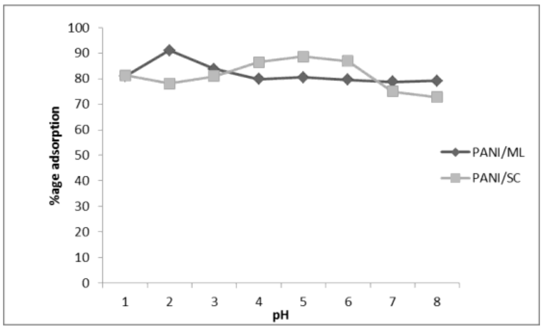

Fig. 5. Comparative graph of PANI/ML and PANI/SC showing effect of pH on the % adsorption of Cr(VI).

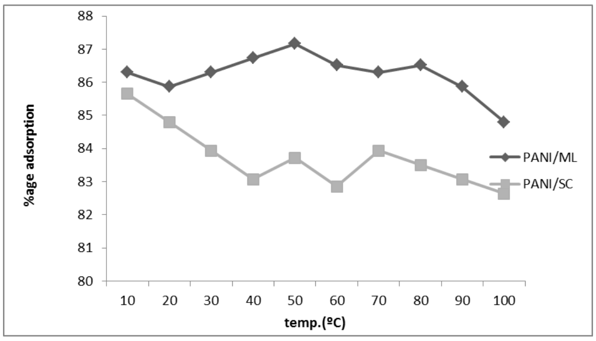

Fig. 6. Comparative graph of PANI/ML and PANI/SC showing the effect of temperature on the % adsorption of Cr(VI).

CONCLUSIONS

Polyaniline composites PANI/ML and PANI/SC were synthesized, characterized and used as adsorbents for Cr(VI) removal from water. It was observed that PANI composite formation enhanced the adsorption capacity due to morphology modification and prevention of polyaniline particles aggregation. The batch experiments showed that Langmuir adsorption isothermal model is better fitted during adsorption of Cr(VI), which suggested that chemisorption occurred during removal of Cr(VI). The negative value of ΔG^o confirmed the spontaneity and feasibility of the adsorption process. The observed trend of adsorption is

PANI/ML > PANI/SC.

Results revealed that polyaniline composites with *Syzygium cumini* (PANI/SC), and *Madhuca longifolia* (PANI/ML) are good adsorbents for removal of Cr(VI).

REFERENCES

1. S.A. Khan, Riaz-ur-Rehman, M. Ali Khan, *Waste Manag.*, **15,** 271 (1995).
2. C. Namasivayam, R.T. Yamuna, *Chemosphere*, **30**, 561 (1995).
3. R.K. Gupta, R.A. Singh, S.S. Dubey, *Sep. Purif. Tech.*, 38, 225 (2004)
4. A.K. Shanker, C.Cervantes, H. Loza-Tavera, S. Avudainayagam, *Env. Int.*, **31**, 739 (2005).
5. M.R. Samani, S.M. Borghei, A.Olad, M.J. Chaichi, *J. Hazard. Mat.*, **184**, 248 (2010).
6. J. Kotas, Z. Stasicka, *Env. Poll.*, **107**, 263 (2000).
7. F.Kanwal, R.Rehman, J. Anwar , M. Saeed, *J. Chem. Soc. Pak.*, **34**,1134 (2012).
8. Q. Li, L. Sun, Y. Zhang, Y. Qian, J. Zhai, *Desalination*, **266**, 188 (2011).
9. E. Malkoc, Y. Nuhoglu, M. Dundar, *J. Hazard. Mat.,B*, **138**, 142 (2006).
10. A.G Yavuz, E. Dincturk-Atalay, A.Uygun, F. Gode, E. Aslan, *Desalination*, **279**, 325, (2011).

11. F.Kanwal, A. Batool, S. Rasool, S. Naseem, R. Rehman, *Asian J. Chem.*, **26**, 7519 (2014).
12. K.Y. Xu, X. Zheng, C.L. Li and W.L. She, *Phys. Rev*., **71**, 066604 (2005).
13. J.B. Pendry, A.J. Holden, W.J. Stewart, I. Youngs, *Phys. Rev. Lett*., **76**, 4773 (1996).
14. L. Ai, J. Jiang, R. Zhang, *Syn Mat*, **160**, 762 (2010).
15. A.Olad, A. Rashidzadeh, *Iranian J. Chem. Eng.*, **5**, 45 (2008).
16. O.V.Dalgov, D.A.Kirzh, E.G.Maksimov, *Rev. Mod. Phys.*, **53**, 81, (1981).
17. P.A.Kumar, S.Chakraborty, M.Ray, *J. Chem. Eng.*, **141**, 130 (2008).
18. J.Anwar, U.Shafique, W.Zaman, M.Salman, Z.Hussain, M.Saleem, N.Shahid, S.Mahboob, S.Ghafoor, M.Akram, R.Rehman, N. Jamil, *Green Chem. Lett. Revs.*, **3**, 239 (2010).
19. Y.Zhang, Q.Li, L.Sun, R.Tang, J.Zhai, *J. Hazard. Mat.*, **175**, 404 (2010).
20. F.Kanwal, R. Rehman, J. Anwar, T. Mahmud, *EJEAFChe*. **10**, 2972, (2011).
21. R.Rehman, J. Anwar, T. Mahmud, *J. Chem. Soc. Pak.*, **34**, 460 (2012).
22. Li. X, M. Zhong, *J. Sep. Sci.*, **31**, 2839, (2008).
23. F. Kanwal, R.Rehman, J. Anwar and T. Mahmud, *J. Chil. Chem. Soc*., **57**, 1058 (2012).
24. J. Anwar, U. Shafique, M. Salman, W. Zaman, S. Anwar, *J. Hazard. Mat.*, **171**, 797 (2009).

ОТСТРАНЯВАНЕ НА ХРОМ (VI) ОТ ВОДИ С ИЗПОЛЗВАНЕТО НА ПОЛИАНИЛИНОВИ БИОКОМПОЗИТИ С ЛИСТА ОТ *Madhuca longifolia* И *Szygium cumini*

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(Резюме)

Синтезирани са биокомпозити от полианилин с листа от *Madhuca longifolia* (PANI/ML) и S*zygium cumini* (PANI/SC). Те са охарактеризирани и използвани за периодична адсорбция на Cr(VI) от вода. Оптималните условия за PANI/ML са: контактно време 20 мин., доза адсорбент 0.3 г в 50 mL разтвор на Cr(VI), 50˚ C и pH 2. За PANI/SC: контактно време 80 мин., доза адсорбент 0.1 г в 50 mL разтвор на Cr(VI), 10˚ C и pH 5. С помощта на изотермата на Лангмюир е показано, че отстраняването на хрома става чрез мономолекулярна хемисорбция върху активните центрове на адсорбента. Максималният адсорбционен капацитет на PANI/ML е 13.334 mg/g, докато за PANI/SC той е 4 mg/g. Отрицателната стойност на ΔG° потвърждава надеждността и спонтанността на адсорбционния процес. Изотермата на Freundlich свидетелства за хетерогенно разположени активни центрове и физичното отстраняване на металните йони. Стойностите на K_F за PANI/ML и PANI/SC са съответно 0.019 и 0.005. Резултатите показват, че PANI/ML е екологично по-добър биокомпозит за отстраняването на Cr(VI) от води спрямо биокомпозита PANI/SC.