Synthesis of novel polyaniline composites with *Eriobotrya japonica* leaves for removal of Methyl Red dye from wastewater

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Polyaniline (PANI) and its biocomposite with *Eriobotrya japonica* (PANI/EJ) leaves were synthesized using chemical oxidative polymerization, characterized by FTIR and UV/Vis spectrophotometry, and used for adsorption studies of Methyl red (MR) dye. Optimum conditions for PANI: 30 min contact time, 20°C temperature, adsorbent dose 0.8 g in 25 mL solution of MR dye and pH 1; and for PANI/EJ: 35 min contact time, 20°C temperature, adsorbent dose 1.0 g in 25 mL solution of MR dye and pH 2. Langmuir isotherm depicts that monolayer chemisorption of MR dye occurred on PANI and its composite binding sites. The maximum adsorption capacity of PANI is 2.407 mg/g while for PANI/EJ it is 3.842 mg/g. ΔG^o negative value indicates the feasibility and spontaneity of the adsorption. Freundlich isotherm explains the physio-sorption and heterogeneity of the adsorption. The K_F values of PANI and PANI/EJ are 0.366 and 0.641, respectively. Results revealed that PANI/EJ is a better eco-friendly biocomposite for removal of Methyl red dye from water as compared to PANI.

Keywords: Polyaniline composite, *Eriobotrya japonica* leaves, Methyl red dye, adsorption.

INTRODUCTION

Environmental degradation in Pakistan is mainly caused by the rapid industrialisation including dyes and inorganic waste material in wastewater. Dyes have been used for colouring in various industries, paper, textile, soap, cosmetic, etc. The release of coloured waste water is hazardous for the environment and it poses a threat of bioaccumulation which in turn may damage human food chain [1]. Azo dyes are the main contributor to the water pollution as they are persistent, and they are the most commonly used colorants in the industries [2]. They have a nitrogen-to-nitrogen double bond backbone: R—N=N—R' [3]. Azo dyes directly influence human health by triggering allergic reactions or cancer [4].

Methyl Red is an anionic azo dye which is commonly used in paper and textile industry [5]. It acts as an eye, throat and skin irritant [6]. It is, thus, necessary to remove dye from industrial waste water and to decolourise it. Several processes can be used to remove MR dye from industrial wastewater. Xylene can be used as an extractant to remove it, but it is an expensive [7]. Other processes include photo-catalytic degradation, coagulation and electro Fenton's and hypochlorite treatment but they are not cost effective [6, 8-10].

In the past two decades, conducting polymers have been increasingly used for their adsorption capability and polyaniline (PANI) is the most efficient among them. Biomass from different plants has also been used for adsorption but it is not as efficient [11]. In this research work, PANI and its biocomposite with leaves of *Eriobotrya japonica* (PANI/EJ) were synthesized and used for batch mode adsorption of MR dye.

EXPERIMENTAL

Instruments used were: digital balance, FT-IR spectrophotometer, UV/Visible spectrophotometer (721 Visible Spectrophotometer). Chemicals used were: aniline, $FeCl_3$, HCl, DMF, acetone and ethanol. Aniline was used after distillation. 10 g of freshly purified aniline was taken in a three-necked flask which was placed in an ice bath on a stirrer and temperature was maintained at 0 °C. Whole of the process was performed in an inert environment using nitrogen. Solution of hydrated ferric chloride (0.75M) was prepared and added to aniline in the flask with vigorous shaking. Mixture was continuously stirred at 0°C for 24 h. The end of the reaction was indicated by the formation of a dark green precipitate in the solution.

The purification of the prepared precipitates was carried out by filtration through a pyrex sintered glass crucible and vacuum pump apparatus. The precipitates were then washed with distilled water followed by acetone and methanol until the filtrate became completely neutral. The residue was then dried in an oven at 60°C for 48 h. This process was performed twice till the required amount was obtained [11-13].

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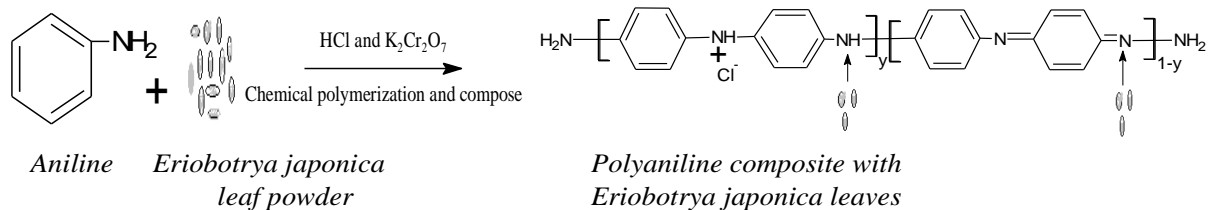E-mail: grinorganic@yahoo.com

Aniline   Eriobotrya japonica   Polyaniline composite with
              leaf powder   Eriobotrya japonica leaves

Fig.1. Schematic presentation of the synthesis of polyaniline composite.

Synthesis of PANI composite with Eriobotrya japonica leaves

Polymerization was carried out in a similar way as reported earlier using 2 g of powdered leaves in the reaction mixture. Fig. 1 shows the chemical reaction schematically. The product was characterized by UV/Vis and FT-IR spectrophotometry [14-16].

Preparation of stock solution and standards for adsorption studies of MR dye

For the stock solution of 1000 ppm, 2.69 g of Methyl red was dissolved in 1000 ml of water and it was diluted for preparing further standards.

Adsorption studies

The adsorption studies of MR dye were carried out in batch mode for both PANI and its composite. The removal of MR dye was calculated by eq. 1:

$$\text{Adsorption \%age} = [(C_{in}-C_{fin})/C_{in}] \times 100 \quad (1)$$

where C_{in} is the initial concentration of MR dye while C_{fin} is the final concentration after adsorption has taken place.

RESULTS AND DISCUSSION

UV/Vis spectroscopic analysis

UV/Vis spectra of PANI and PANI/EJ were taken after dissolving them in dimethyl formamide. The λ_{max} of PANI and its composite are given in Table 1 and graphically shown in Fig. 2. Absorption at $\lambda_{max}1$ 280 nm is due to a $\pi - \pi^*$ transition of aniline in the benzenoid ring [17]. Absorption at 525 nm is attributed to transition of benzenoid ring into quinonoid ring.

Table 1. λ_{max} of PANI and PANI/EJ

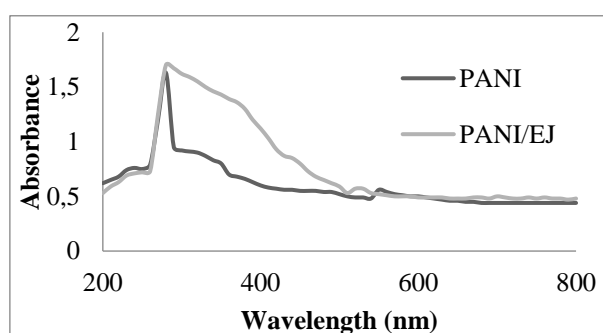| Sample	λ_{max1} (nm)	Absorbance 1	λ_{max2} (nm)	Absorbance 2
PANI	280	1.632	525	0.572
PANI/EJ	290	1.67	550	0.558

Fig. 2. Comparative UV-Vis spectra of PANI and PANI/EJ

FT-IR characterization

FT-IR was used to characterize PANI and its composite (PANI/EJ) and relevant peaks are compared in Fig. 3 [18]. By comparing the FT-IR spectra of PANI and its composite (PANI/EJ) it was observed that the band (due to amino group (N-H) stretching frequency [19]) for PANI at 3295 cm^{-1} is shifted to 3205 cm^{-1} in case of PANI/EJ. The absorption band at 1577 cm^{-1} is due to benzenoid to quinoid rings nitrogen bond. In case of PANI/EJ it is shifted to 1698 cm^{-1}. Peaks due to secondary amine stretching [20] are shifted from 1226 cm^{-1} (PANI) to 1288 cm^{-1} (PANI/EJ). Bands in the range of 1571-1116 cm^{-1} are due to the conductive nature of PANI.
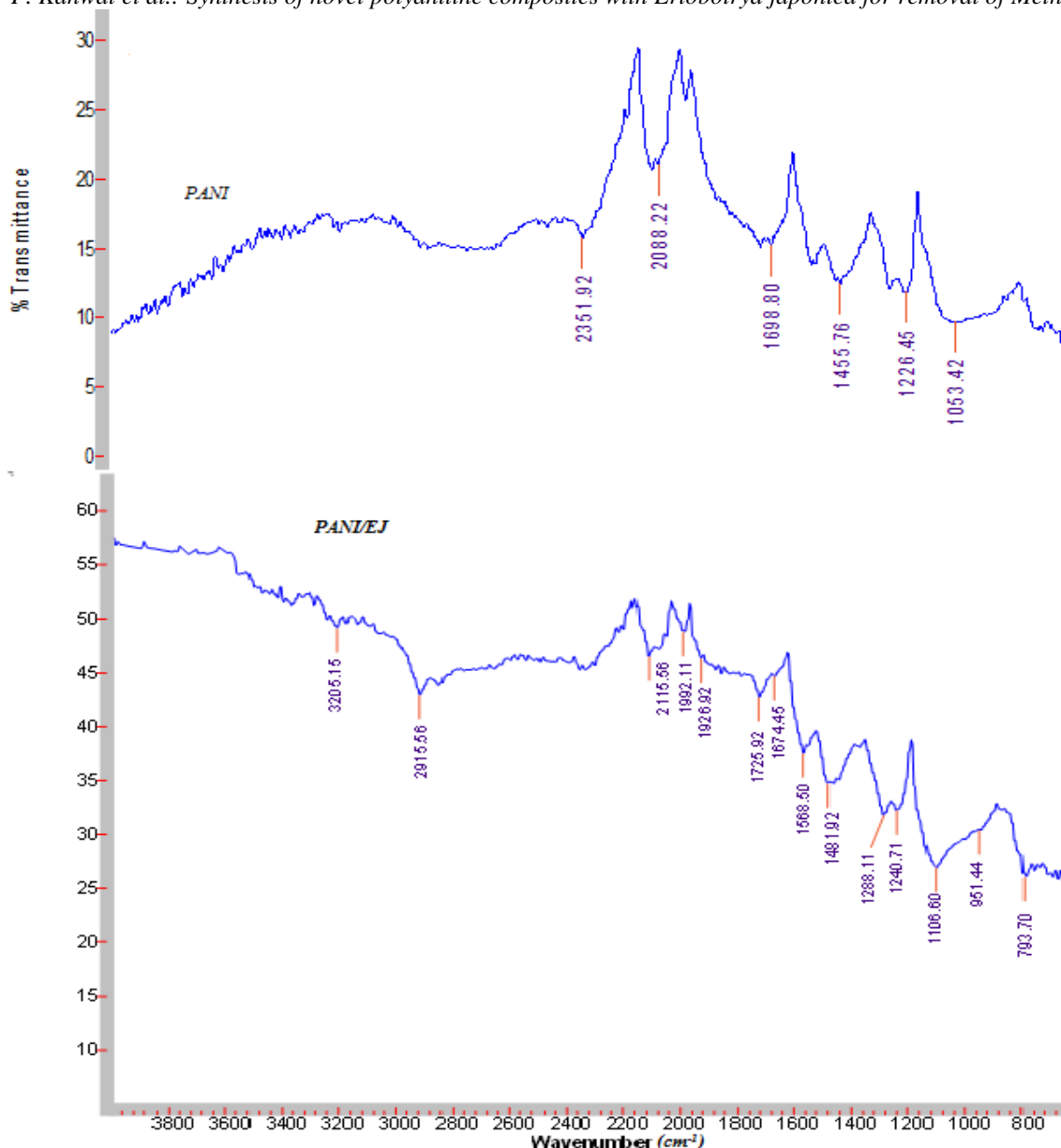
Fig. 3. Comparative FT-IR spectra of PANI and PANI/EJ.

BATCH ADSORPTION EXPERIMENTS

Adsorbent dose

The effect of various adsorbent doses is shown in Fig. 4. The maximum removal of Methyl Red was observed with 0.8 g of PANI (84.44% removal) and 1.0 g of PANI/EJ (94.60% removal). The results revealed that preventing the PANI/EJ particles from aggregation and exposing MR dye towards available active sites for adsorption showed greater efficiency in its removal. In case of PANI adsorption firstly increases and then decreases because of adsorbent particles coagulation, due to which the number of sites available for adsorption decreases [18].

Contact time

Adsorption phenomenon is time dependent. The effect of different time intervals is shown in Fig. 5 for removal of MR dye by PANI and PANI/EJ composite. The maximum removal value was 89.52 % for PANI for 30 min, and 95.24% for PANI/EJ composite for 35 min. The increased time interval for maximum removal of MR dye using PANI/EJ composite showed that it has less adsorption sites which are available for adsorption of metal ions. There is more contact time for PANI/EJ which allows more adsorbate-adsorbent interaction, thus increased adsorption. After the maximum removal of MR dye, the adsorption decreased with increase in contact time because all available sites were

occupied. PANI/EJ was more appropriate for removal of Methyl red dye than PANI.

Solution pH

The results of the pH study are shown in Fig. 6. Solution pH corresponds to the functionality of adsorbent and dye in the solution. As Methyl red is an acidic dye, hydrogen bonding, π-π interaction and electrostatic forces between the dye and the functional group on PANI surface occur in the acidic medium. The maximum removal value was 95.56 % for PANI composite at pH 1 and 99.68 % for PANI/EJ composite at pH 2. PANI/EJ was more appropriate for removal of MR dye than PANI [14].

Table 2. Langmuir Isotherm parameters

Adsorbent	PANI	PANI/EJ
Slope	4.5545	1.2961
Intercept	0.4154	0.2603
R^2	0.8382	0.9707
q_m (mg/g)	2.407	3.842
b (L/mg)	0.091	0.201
R_L	0.1208	0.0585
ΔG^o(KJ/mol)	-5.933	-3.975

Table 3. Freundlich Isotherm parameters

Adsorbent	PANI	PANI/EJ
Slope	1.0337	0.7462
Intercept	0.4366	0.1931
R^2	0.6124	0.9739
K_f	0.366	0.641
n	0.967	1.34
1/n	1.0337	0.7462

Adsorption Isotherm

The Langmuir and Freundlich isotherm parameters for PANI and PANI/EJ are shown in Tables 2 and 3, respectively.

Langmuir isotherm indicated that monolayer chemisorptive removal of MR dye has occurred on the homogeneously distributed composites' binding sites [11-13]. It is predominant over the Freundlich model. This means that chemisorption is predominant over physio-sorption, as indicated by the greater R^2 value of Langmuir than Freundlich. Maximum adsorption capacity (q_m) values for PANI and PANI/EJ are 2.407 and 3.482 mg/g, respectively. Table 4 shows examples of other PANI composites previously used for dyes removal on lab scale.

Table 4. Other reported PANI composites used for contaminants removal on a lab scale.

Dyes	Composite	Removal capacity (mg/g)	Reference
Tartrazine	Chitosan/PANI	584.0	[21]
Crystal violet	PANI / *Tectona grandis* saw dust	263.2	[22]
Methyl orange	ZnO/PANI	240.84	[23]
Congo red	PANI/lignocellulose	1672.5	[24]
Congo red	Polyaniline/carboxymethyl cellulose/TiO_2	119.9	[25]
Green SF dye	Heulandite/PANI	44.6	[26]

The negative sign of ΔG^o showed that the adsorption process is feasible and spontaneous. Results revealed that PANI/EJ shows better adsorption than PANI, where 'n' and 'K_F' are Freundlich isotherm constants. 'K_F' value was 0.366 and 0.641 for PANI and PANI/EJ, respectively. For

MR dye the value of 'n' was 0.697 for PANI and 1.340 for PANI/EJ. Separation factor R_L value is between 0 and 1, indicating the favourability of this process [15]. At higher values of 'n' the affinity and heterogeneity of adsorbent sites will be greater.
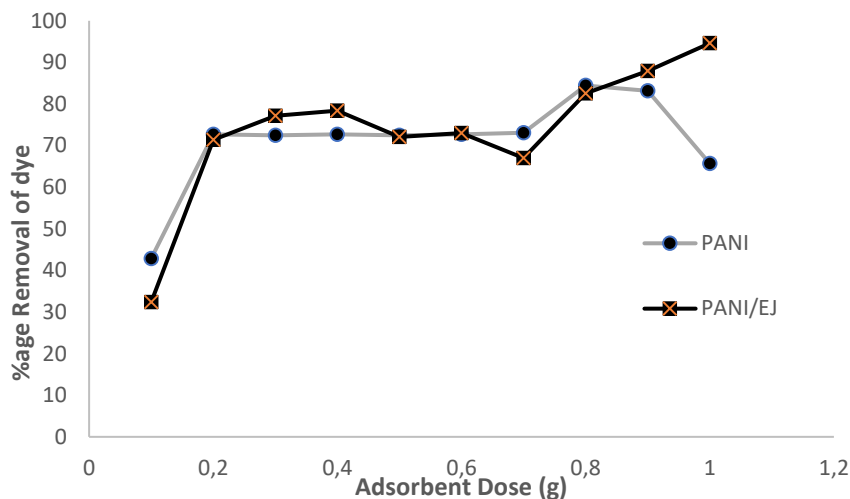
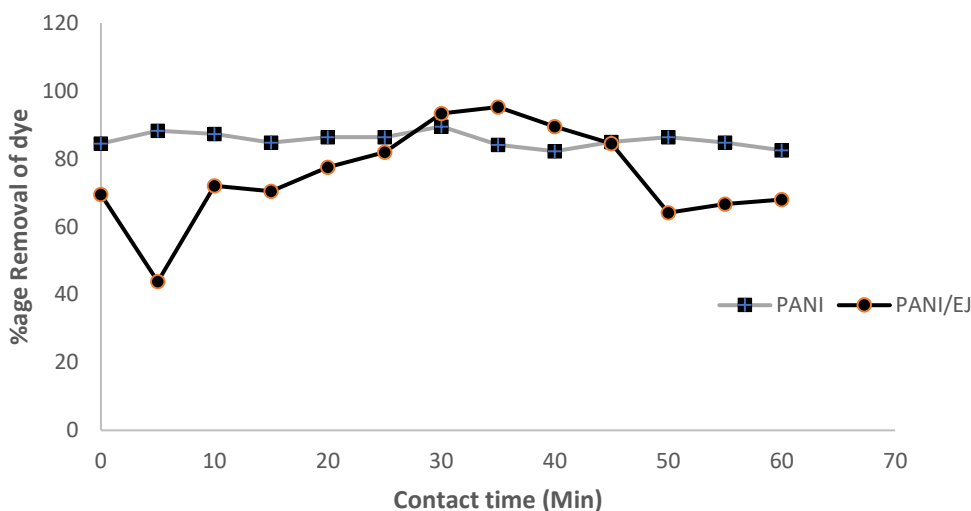**Fig.4.** Comparative graph showing the effect of adsorbent dose on % absorbance of MR dye on PANI and PANI/EJ

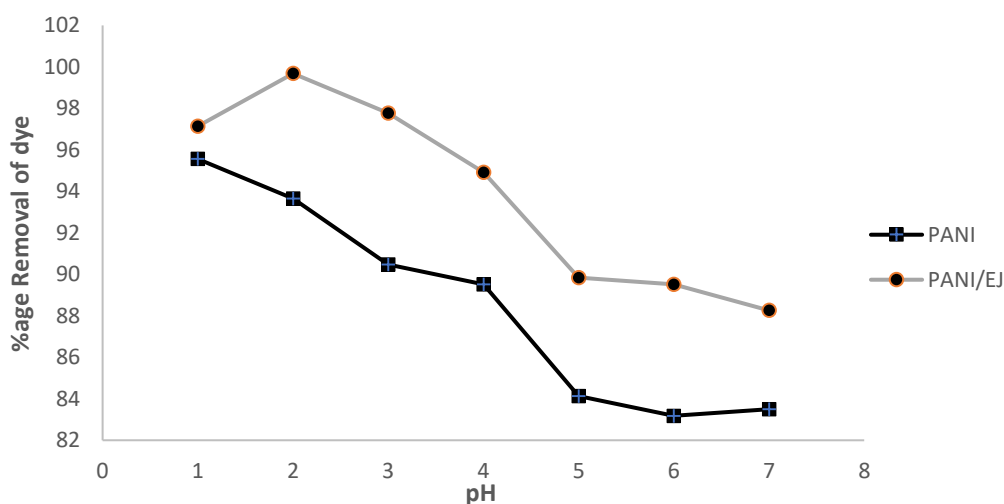**Fig. 5.** Comparative graph showing the effect of contact time on the % absorption of MR dye by PANI and PANI/EJ

Fig.6. Comparative graph showing the effect of pH on the % adsorption of MR dye on PANI and PANI/EJ

CONCLUSION

Polyaniline composites PANI and PANI/EJ were synthesized, characterized and used as adsorbents for MR dye removal from water. It was observed that PANI composite formation enhanced the adsorption capacity due to morphology modification and

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prevention of polyaniline particles aggregation. The batch experiments showed that Langmuir adsorption isothermal model is better fitted during adsorption of MR dye, which suggested that chemisorption occurred during removal. The negative value of ΔG^o confirmed the spontaneity and feasibility of the adsorption process. The observed trend of adsorption is:

PANI/EJ > PANI

Results revealed that polyaniline composite with *Eriobotrya japonica* leaves (PANI/EJ) is a good adsorbent for removal of Methyl Red dye.

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