STUDENT PROJECT PROPOSAL SSN INTERNAL FUNDING (2017 – 2018)

Project Title

Removal of heavy metal ions and azo dyes from aqueous solution using low molecular weight polymers

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Under guidance of Dr. A. Murugesan

OVERVIEW

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- 2. Objective
- 3. Scope of the study
- 4. Conclusion
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Introduction

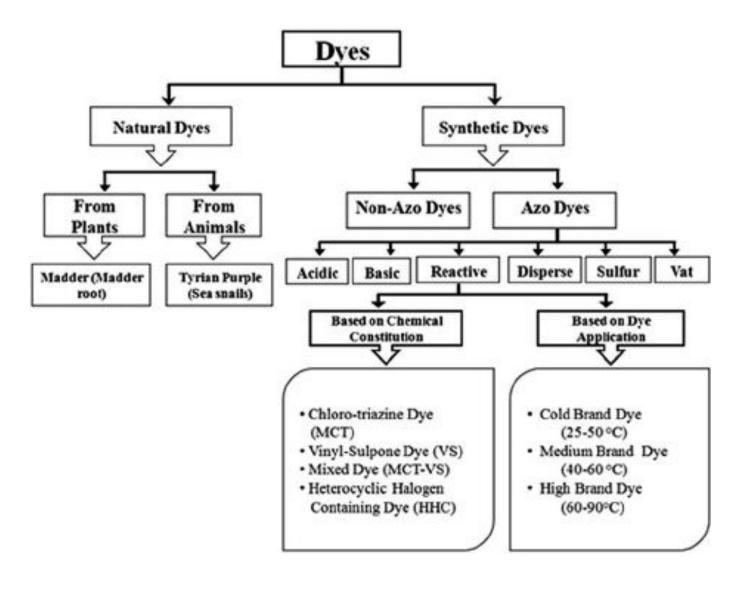






Huffington Post (2013)





1. Anila ajmal et al., RSC. Adv. (2014)



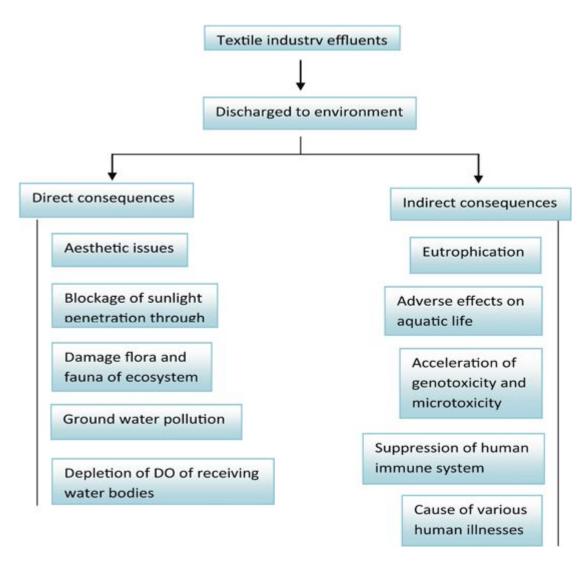


Ashleighwhite (2017)

THOMAS STEGE BOJER (2016)

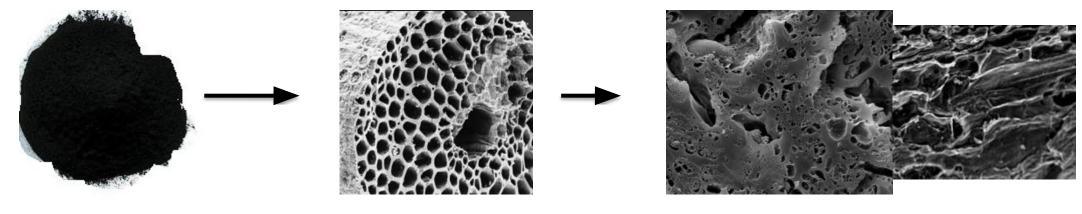






2. Khan S., Malik A. Environmental and Health Effects of Textile Industry Wastewater. In: Malik A., Grohmann E., Akhtar R. (eds) Environmental Deterioration and Human Health. Springer, Dordrecht (2014) 55-71





Porous structure of A. carbon- Porous in nature and High thermal stability

After Adsorption

Alternative for commercial AC: rice husk, Psidium guajava, sweet potato, peanut hull, saw dust neem bark, coconut shell, olive stone, cashew nut shell and corncob were used without affecting its porous and thermal properties. Later Zeolites introduced for the adsorption of pollutants and NANO materials.

4. Murugesan, Environ. Prog. Sustain. Energy. 33(2013) 844-854

Activated carbon (AC)

- 5. Ayhan AbdullahCeyhana ÖmerŞahinb OrhanBaytara CaferSaka, J. **Anal. Appl.** Pyrolysis.104 (2013)378-383
- 6. Yusef Omidi-Khaniabadi, Ali Jafari, Heshmatollah Nourmoradi, Fatemeh Taheri and Seddigheh Saeedi.
- J. Adv. Environ. Health. Res. 3(2013) 120-129 7. Sadegh, H., Ali, G.A.M., Gupta, V.K. et al. J Nanostruct Chem (2017) 7: 1



Limitations

- High Cost
- Methods of preparing AC and nano adsorbent is a factor that affects the adsorption.
- Limited surface area and stability of the active sites.
- Lower regeneration capacity



Polymer Adsorbents

High performance

High porosity

Intermolecular force of attraction

More repeating unit and More binding sites

Regeneration, recycling and reusability

Thermal and mechanical stability

Hradil J. (2008) Adsorption Properties of Polymer Adsorbents. In: Mota J.P., Lyubchik S. (eds) Recent Advances in Adsorption Processes for Environmental Protection and Security. NATO Science for Peace and Security Series C: Environmental Security. Springer, Dordrecht



Comparison of adsorbents and adsorption capacities for the dye removal

Adsorbents	Dye adsorbate	Adsorption Capacity (mg/g)	References
Activated carbon (wood apple)	Malachite green	80.645	(a)
Coconut	Methylene Blue(MB)	15.59	(b)
MWCNTs	MB	95.3	(7)
Oxidized MWCNTs	Bromothymol blue	55	(7)
Co ₃ O ₄ /SiO ₂ nanocomposi te	MB	53.87	(7)
Polyvinyl alcohol	MB	123.3	(7)
Polyaniline zirconium (IV) silicophosphate (PANI-ZSP)	MB	12.00	(8)
Polyacrylamide/ $Ni_{0.02}Zn_{0.}$ 98O nanocomposite	Malachite Green, Rhodamine B		(7)
Tryptycene based polymer	MB	204.9	(9)
IPP	MB	166.8	Present work



Objectives:

- Synthesis and characterization of low molecular weight polymers
- Purification of waste water containing azo dyes and heavy metal ions using polymer
- Optimization of cost of effluent water treatment
- Application of the adsorbed polymers in different fields like films, polymer composite, flexible printed circuits, hard disks, digital camera, solar cells etc.
- Regeneration of the adsorbed polymers



Scope of the study

To synthesize Imide porous polymer (IPP) by solution polycondensation.

To select the Basic dye Methylene Blue (MB) for adsorption study.

To study the effect of solution pH, adsorbent dosage, contact time and initial dye concentration for maximum removal of the dye using IPP adsorbent.

Adsorption isotherms - to calculate the adsorption capacity of the adsorbent for the removal of MB in their aqueous form, using the **Langmuir and Freundlich** adsorption isotherms.

To evaluate the **thermodynamic parameters** (ΔG , ΔS and ΔH), and to find out the feasibility of the adsorption process (exothermic or endothermic).

To evaluate the Adsorption Kinetics, to find first order, second order and Elovich model. Besides Intraparticle diffusion of the adsorbent (IPP)

Desorption studies - to elucidate the nature of the desorption process and to recycle the spent adsorbent

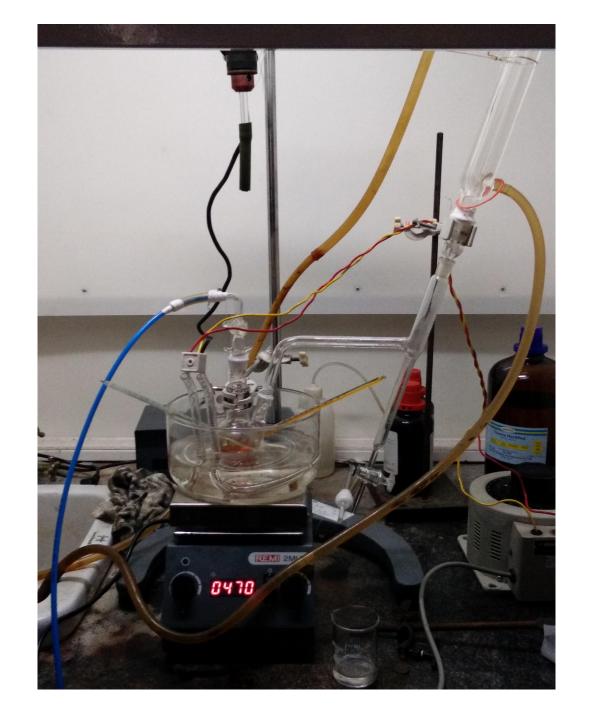


Proposed System and Innovation:

- This project is proposed to develop the synthesis of effective polymers with imide and amide functional moieties that can be used for the adsorption of dyes.
- Adsorbed polymers can be regenerated again and used for the preparation of polymer composite materials.
- The adsorbed polymers can be reused again in other fields like polymer composite, flexible printed circuits, hard disks, digital camera, solar cells etc.

Synthesis:

Solution Polycondensation:

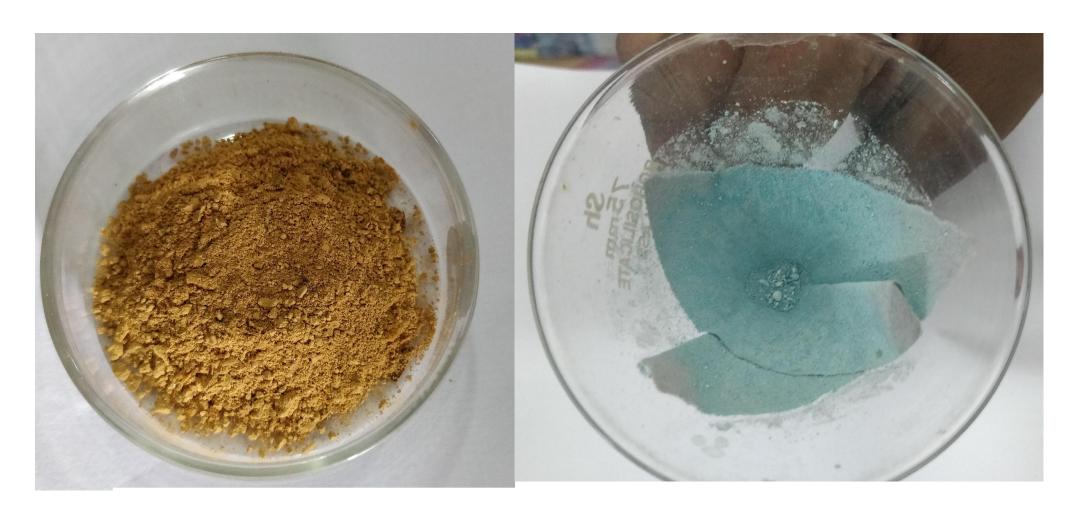


Synthesis of Polymer polyimide (Adsorbent):

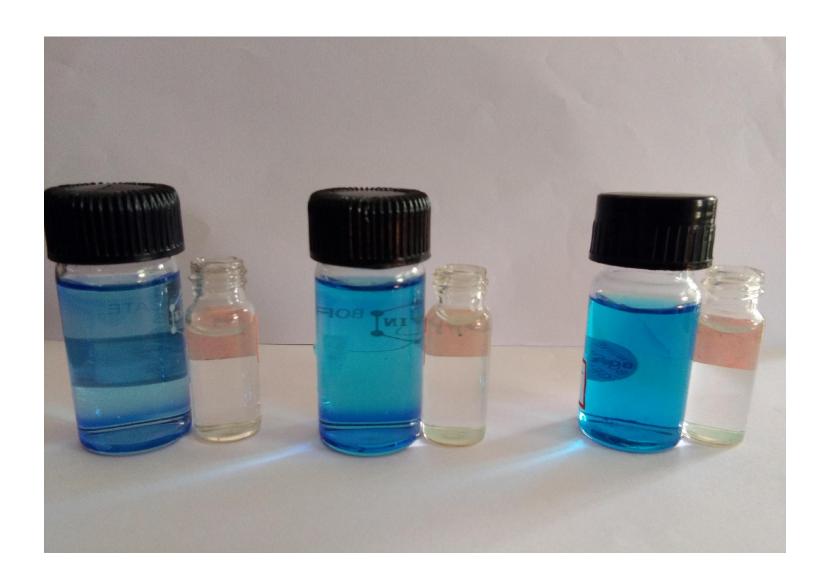
Methylene Blue:

$$\begin{array}{c} CH_3 \\ N \\ CH_3 \\ N \end{array}$$

Implementation:



Before and After adsorption:

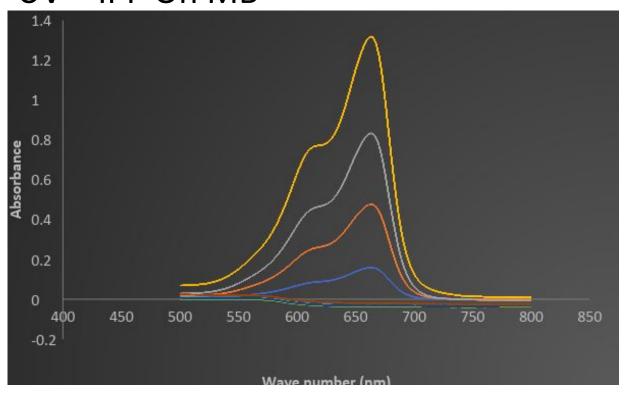


DYE-POLYMER INTERACTIONS:

$$\begin{array}{c} CH_3 \\ N \\ CH_3 \\ N^+ \\ CH_3 \\ \end{array}$$

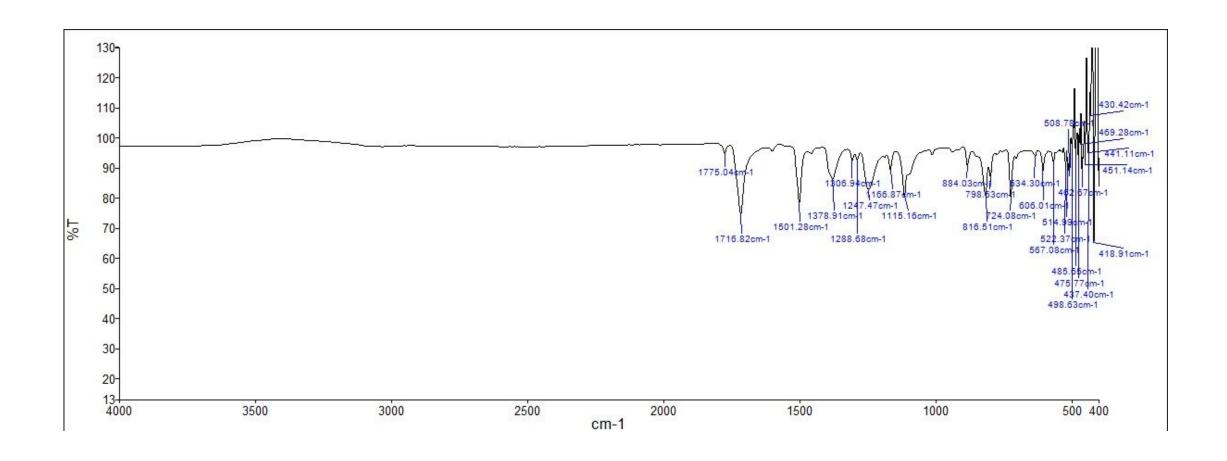
Characterization

UV – IPP On MB

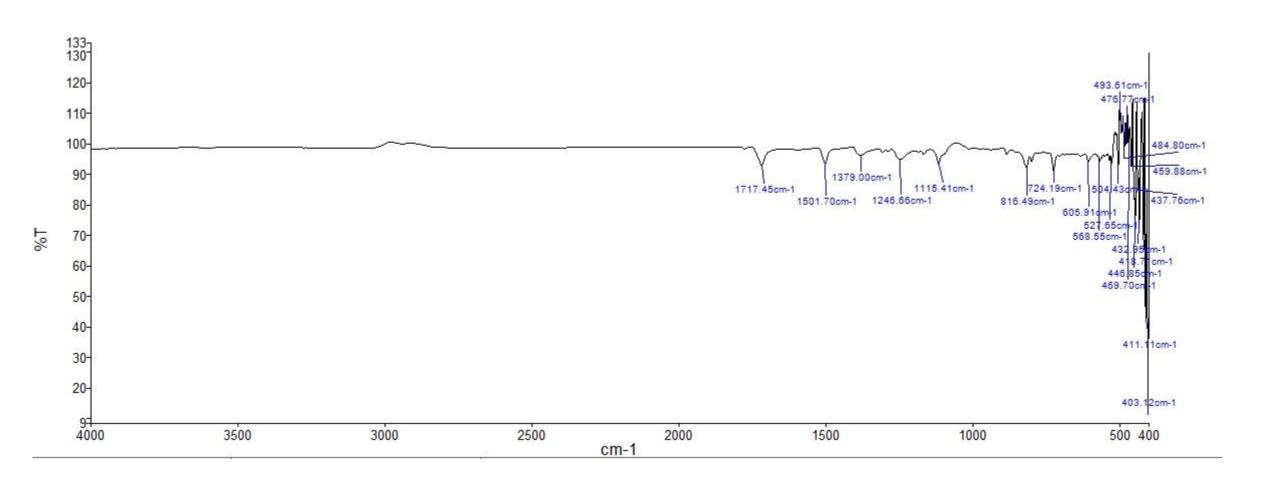




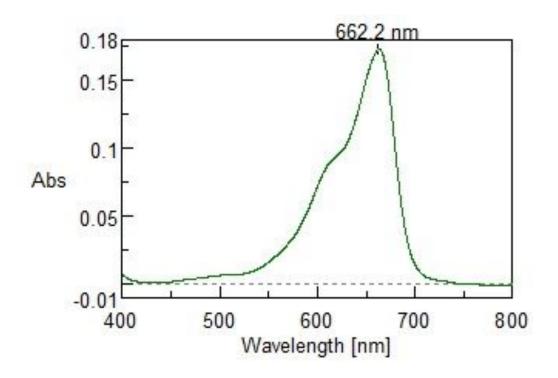
IR: To find Functional group PI-(I):

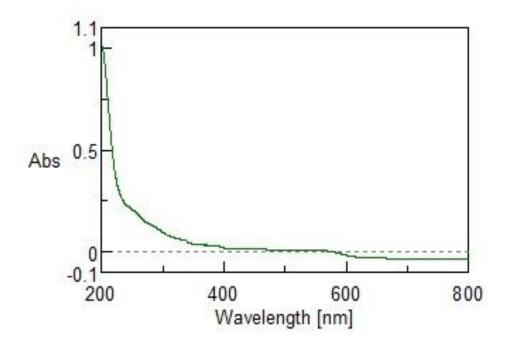


IR: PI-(I)-MB:

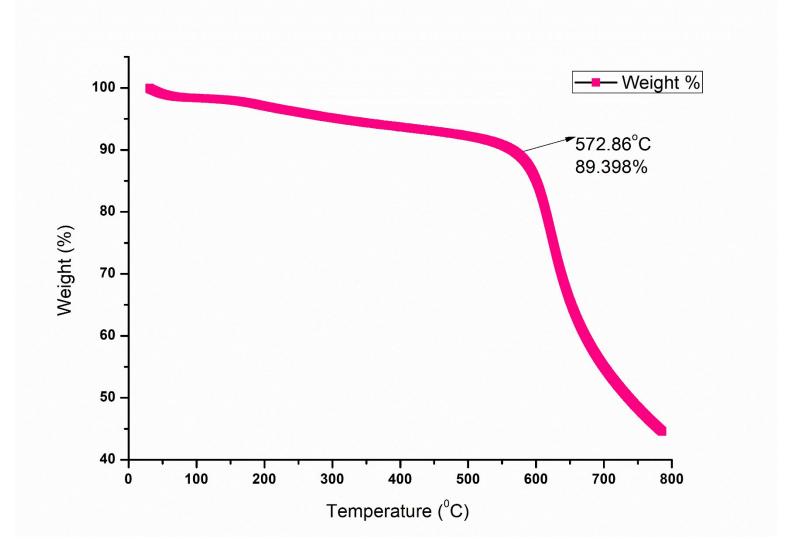


UV Analysis for MB & After



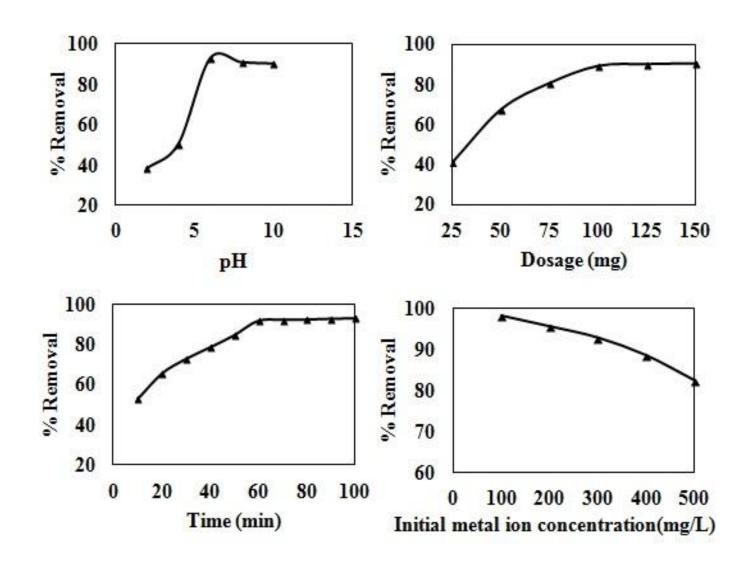


TGA Analysis of IPP

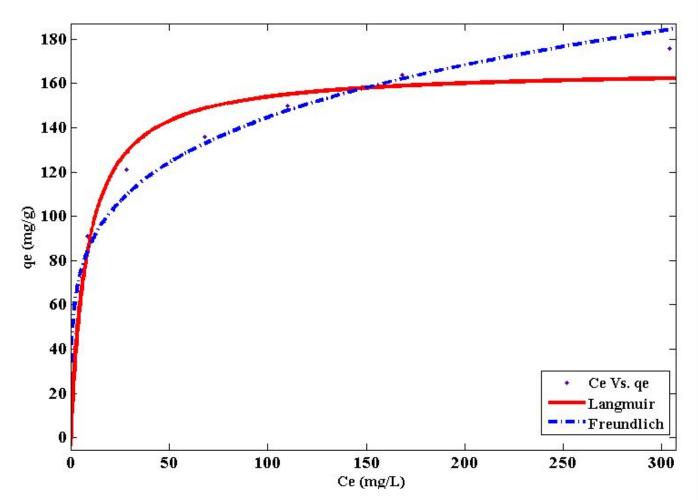




Performance as an adsorbent



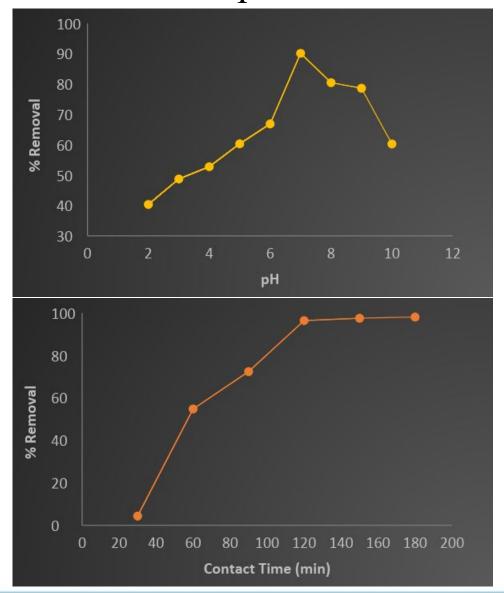
Adsorption Isotherms

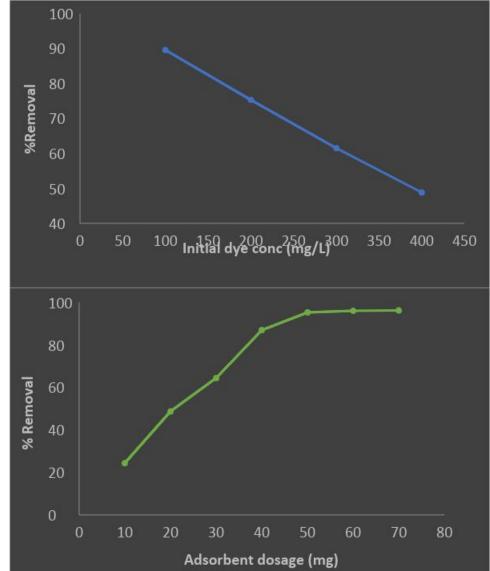


Parameters	MB
q_{m}	166.8
K_L	0.121
R_L	0.02-0.08
\mathbb{R}^2	0.9566
SSE	525.7
RMSE	10.25
K_{F}	52.86
n	4.575
\mathbb{R}^2	0.9477
SSE	633.6
RMSE	11.26
	$q_{ m m}$ $K_{ m L}$ $R_{ m L}$ R^2 SSE $RMSE$ $K_{ m F}$ n R^2 SSE



Batch adsorption studies

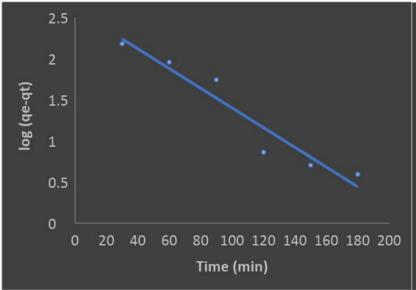


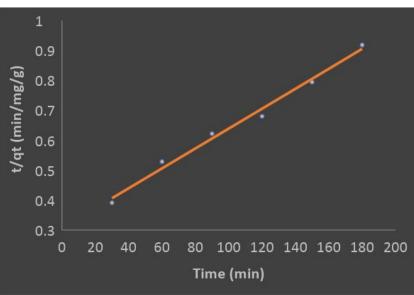


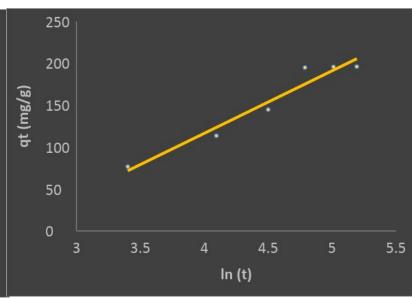


Kinetic model	Parameters	MB Initial Concentration (200 mg/L)	
		MB	
Pseudo-first order kinetic model	k _{ad} (min ⁻¹)	0.012	
$\ln(\mathbf{q}_{e} - \mathbf{q}_{t}) = \ln \mathbf{q}_{e} - \mathbf{k}_{ad} t$	q _{e,} cal (mg/g)	394.9	
	\mathbb{R}^2	0.9258	
$\frac{\overset{\text{Pseudo-second order kinetic model}}{\overset{\text{t}}{\textbf{q}_{t}}} = \frac{\overset{\text{I}}{\textbf{1}}}{\overset{\text{I}}{\textbf{k}_{2}}\overset{\text{I}}{\textbf{q}_{e}}} + \frac{\overset{\text{I}}{\textbf{q}_{e}}}{\overset{\text{I}}{\textbf{q}_{e}}} \overset{\text{I}}{\textbf{t}}$	k ₂ (g mg ⁻¹ min ⁻¹)	2.4266×10 ⁻⁵	
$\frac{\mathbf{q}_{t}}{\mathbf{q}_{t}} = \frac{\mathbf{k}_{2}\mathbf{q}_{e}^{2}}{\mathbf{k}_{2}\mathbf{q}_{e}^{2}} + \frac{\mathbf{q}_{e}}{\mathbf{q}_{e}}\mathbf{t}$	q _e ,cal (mg/g)	203	
	q _{e,} exp (mg/g)	198	
	\mathbb{R}^2	0.9834	
$\mathbf{q_t} = \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\beta} \ln(\mathbf{t})$	α (mg/g.min)	1.0144	
	β (g/mg)	0.01419	
$\mathbf{q_t} = \mathbf{k_p} \mathbf{t}^{1/2} + \mathbf{C}$	\mathbb{R}^2	0.9460	
Intraparticle diffusion kinetic model	$k_p (mg/g.min^{1/2})$	15.823	
	C	7.0232	

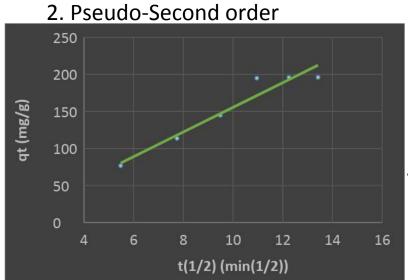
Kinetics







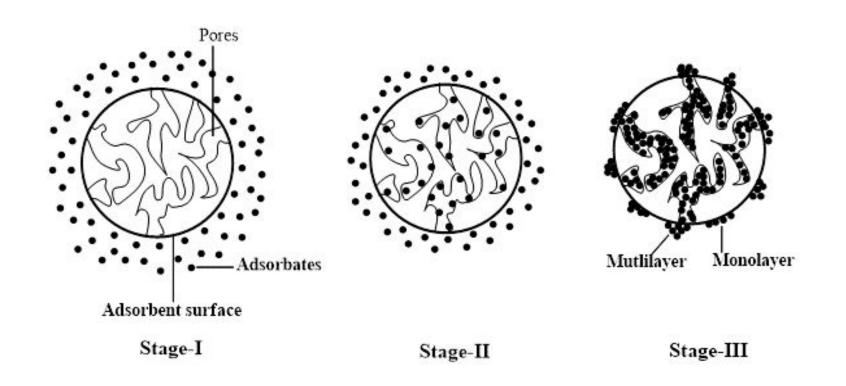
1. Pseudo-First order



3. Elovich Kinetic model

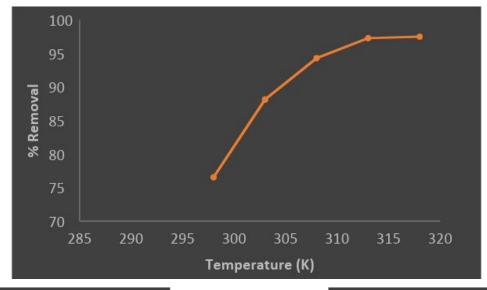
4. Intra particle diffusion

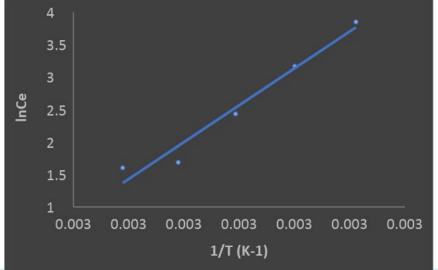


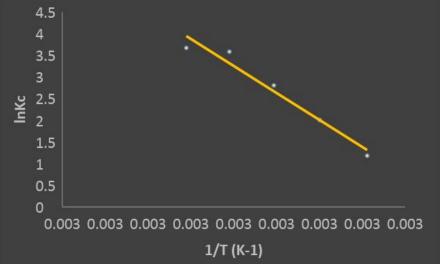


The diffusion adsorption mechanism of PAC-metal ions system

Thermodynamics







Thermodynamic parameters for the adsorption of MB on PPI

Parameters	Temperature (°C)	MB
R ²		0.966
ΔH(kJmol)		93.734
ΔS (J/mol)		0.327
-∆G (kJ/mol)	298	3.714
	303	5.349
	308	6.984
	313	8.619
	318	10.254



Reusability of the Dye adsorbed waste:

• To make different polymer composite for various electro optical applications.



Further work:

- To present in international Conferences.
- To publish under Stringers journal.

REFERENCE

Bingol et al (2004) investigated the removal of Cr(VI) ions from an aqueous solution, using surfactant-modified yeast.

Duran et al (2008) prepared Poly(vinyl pyridine-poly ethylene glycol methacrylate-ethylene glycol dimethacrylate) beads for heavy metal removal. They have been good heavy metal adsorbers, and have great potential for applications involving environmental protection.

Ji et al (2007) synthesized and characterized a new chelating resin containing bis[2-(2-benzothiazolylthioethyl)sulfoxide]. The adsorption capacities of the resin for Hg²⁺, Ag⁺, Cu²⁺, Zn²⁺, Pb²⁺, Mn²⁺, Ni²⁺, Cd²⁺ and Fe³⁺ ions have been investigated.

Ahamed et al (2008) synthesized carboxymethylpoly(urethane-acrylate) resin, which has been used as an adsorbent for the removal of Cu(II), Ni(II) and Cr(VI) ions. The resultant polymeric resin showed high efficiency for the removal of heavy metal ion adsorption.

Pan et al (2009) reviewed polymer-based hybrid adsorbents for inorganic pollutants removal from contaminated waters.

Arsalani et al (2009) synthesized new amine-containing resins based on polyacrylonitrile and the adsorption behaviour of the resins has been studied for Ni(II) ion.

