

REVIEW PAPER

## ***Parthenium hysterophorus*: Novel adsorbent for the removal of heavy metals and dyes**

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**ABSTRACT:** Heavy metals and dyes are major contributors in contamination of water streams. These contaminants enter into our eco- system, thus posing a significant threat to public health, ecological equilibrium and environment. Thus a combined discharge of these contaminants results in water pollution with high chemical oxygen demand, biological oxygen demand, color, particulate matter, suspended particles and odor. The mounting pollution of the water bodies has attracted attention of the researchers towards the development of novel techniques and materials for water pollution. The paper describes the use of such a material *Parthenium hysterophorus*, a weed, explored for water purification. The potential of the weed has been tested for several heavy metals and dyes as described in this paper. As per literature the weed is capable of showing adsorption tendency up to 90% in certain cases for some heavy metals and dyes. Powdered weed, activated carbon, ash etc. of *Parthenium* have been employed for the removal process.

**KEYWORDS:** Adsorption; Dye; Heavy metal; Isotherms; *Parthenium hysterophorus*; Wastewater

### **INTRODUCTION**

Nowadays, water pollution has become a global issue. Heavy metals and dyes are the major contributors towards the contamination of water streams. Effluent released from metal plating, mining, radiator, battery manufacturing, fertilizer and fungicide manufacturing is the main source of heavy metal contamination (Kadirvelu *et al.*, 2002; Rengaraj *et al.*, 2003; Saifuddin and Kumaran, 2005; Barakat, 2011; Marzouk *et al.*, 2013; Kyzas and Kostoglou, 2014; Karbassi and Pazoki, 2015). Similarly effluent released from textile manufacturing, dye manufacturing, paper-pulp mills, and tannery industry pours dye contaminants into the water streams (Zawahry and Kamel, 2004; Allen and Koumanova, 2005; Rajamohan, 2009; Kanawade and Gaikwad, 2011; Soni *et al.*, 2012; Saltabas *et al.*, 2012; Gupta *et al.*, 2015).

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Some of the heavy metals like, Lead, Cadmium, Chromium, Zinc, Nickel, and Mercury are the most toxic heavy metals which can cause reduced growth and development, nervous system damage, development of autoimmunity, rheumatoid arthritis, kidney failure, skin and eyes allergies, respiratory irritation etc., in addition to being carcinogenic (Abas *et al.*, 2013; Sanghamitra *et al.*, 2012; Barakat, 2011; Hadi and Bano, 2009; Babel and Kurniawan, 2004; Park and Jung, 2001). Several classes of dyes such as basic, acidic, reactive, direct, azo, mordant, sulfur and vat dyes are the important classes used extensively by the textile, paper and leather industries which are the major pollutants (Bhatnagar and Minocha, 2006; Klemola, 2008; Pramanik *et al.*, 2011; Sivashankar *et al.*, 2013; Topsakal *et al.*, 2013). Many physical and chemical processes like flocculation-coagulation (Moghaddam *et al.*, 2010; Gupta *et al.*, 2012), flotation (Matis and Mavros, 1991; Shakir *et al.*, 2010; Princa *et al.*, 2015), precipitation

(Charentanvarak, 1999; Becker *et al.*, 2012; Fu *et al.*, 2012; Golbaz *et al.*, 2014), electro kinetic coagulation (Parga *et al.*, 2005; Mansoorian *et al.*, 2014; Rincon and Motta, 2014), ion exchange (Tiravanti *et al.*, 1997; Rengaraj *et al.*, 2001; Tor *et al.*, 2005), membrane filtration (Rashidi *et al.*, 2014; Ahmad *et al.*, 2002; Kozłowski and Walkowiak, 2002), electro chemical destruction (Juttner *et al.*, 2000; Gomes *et al.*, 2011; Rocha *et al.*, 2011), irradiation-ozonation (Glaze *et al.*, 1987; Martins *et al.*, 2006; Dong *et al.*, 2007; Tehrani *et al.*, 2010), photo degradation (Gupta *et al.*, 2011, 2012; Saleh and Gupta, 2012a), electro deposition (Elsherief, 2003; Ras and Ghizellaoui, 2012; Llanos *et al.*, 2013), ultra-filtration with resins (Ghosh and Bhattacharya, 2006), reverse osmosis (Kadirvelu *et al.*, 2002; Ipek, 2005; Mohsen *et al.*, 2007; George *et al.*, 2015), adsorption with activated carbon and nano composites (Sharma and Forster, 1996; Jain *et al.*, 2003; Saleh *et al.*, 2011; Saleh and Gupta, 2012b; Gupta *et al.*, 2011, 2013; Marzouk *et al.*, 2013) have already been investigated for the removal of toxic heavy metals and dyes. The major drawback associated with all these techniques is the high cost of application, complicated procedures, sludge generation, generation of by-products with long retention time (Gautam *et al.*, 2014). Among the mentioned methods, adsorption using activated carbon has been reported to be one of the most versatile, dynamic and superior technique to quarantine the heavy metals and colorants (Sharma and Forster, 1996; Khalkhali and Omidvari, 2004; Marzouk *et al.*, 2013; Sivakumar, 2015), but the high cost of regeneration and limited application for large scale has motivated the researchers to develop biologically originated/ environmental friendly, economically feasible and technologically sound alternatives, with same efficiency as commercial activated carbon (Gupta and Ali, 2001; Gupta and Nayak, 2012; Gupta *et al.*, 1998, 2005, 2011, 2012; Mittal *et al.*, 2009, 2010).

#### *Parthenium hysterophorus* a novel adsorbent

*Parthenium hysterophorus* is often found in the open lands, developing residential colonies, near railway tracks, at the roadsides, at highways, near drainage lines and sewage plants, at the dumping grounds etc. Due to its high fecundity or growth rate, adaptability in various environmental conditions and ability to dominate various types of natural habitat it spreads all over to cover a larger area. Unfortunately the weed entered in India as a contaminant in wheat

grains brought from USA in 1954 (Under Public Law 480) (Singh *et al.*, 2008; Javaid and Riaz, 2012; Bhojar *et al.*, 2014). Congress grass, White top, Santa maria, Gajarghas are some of the regional names of weed (Patel, 2011; Saini *et al.*, 2014; Khaket *et al.*, 2015). *Parthenium* weed shows many adverse effects on agriculture, biodiversity, animal health and human health. The pollens of *Parthenium hysterophorus* induce the health issues such as burning sensation in respiratory track and allergies on skin, eyes, nose, and mouth. (Aneja *et al.*, 1991; Qureshi *et al.*, 2014). The weed is also dangerous to animals with respect to tainting of milk and meat (Parashar *et al.*, 2009; Patel, 2011; Kushwaha and Maurya, 2012).

After various unsuccessful attempts and strategies to remove the weed by physical, chemical and biological measures leading to only a temporary solution, researchers found out a novel way to use of this weed as a “biosorbent” in dried form, for removal of hazardous heavy metals, toxic dyes and colorants from waste water. *Parthenium* has been used in several forms, such as powdered biomass of plant parts or whole weed, ash or activated carbon and acid activated biomass for the extinction of the said contaminants which in detail have been incorporated in this review.

Several adsorption studies carried out utilizing *Parthenium*, the noxious weed (Roy and Shaik, 2013) have been discussed at length in this research paper. The paper mainly focuses on highlighting the studies carried out using *Parthenium hysterophorus*, as a non-living biomass as a low cost, environmental friendly biosorbent for the removal of heavy metals and dyes pollution. Research on isothermal analysis including Langmuir and Freundlich also are a part of the manuscript.

#### *Parthenium hysterophorus* for removal of heavy metals

Kadirvelu *et al.*, 2002; carried out studies on activated carbon prepared from *Parthenium* for the elimination of Nickel, Ni(II) from aqueous solution. Authors reported that with increased in pH from 2 to 10, the metal ion removal was also found to increase. Based on the kinetics data authors fixed one of the crucial parameters i.e. stirring time to 6 hr. Rate constant calculation suggested that adsorption was a first order reaction. Adsorption followed Langmuir and Freundlich isothermal models.

Removal of mercury Hg(II) using *Parthenium* carbon was also demonstrated by Kadirvelu *et al.*, 2002.

Authors concluded that adsorption was assisted by acidic pH in comparison to basic due to formation of  $\text{Hg}(\text{OH})_2$ . Linear relation between amount of mercury adsorbed and agitation time validate the Lagergrens equation and thus confirming first order kinetics.

Cadmium Cd(II) was removed from waste water by using dried *Parthenium* adsorbent (Ajmal *et al.*, 2006). Impact of various limiting parameters were studied by authors which suggested that acidic pH was most favorable. Kinetics obeyed second order rate equation. Langmuir and Freundlich adsorption isotherm fitted well for the adsorption data. Adsorption was endothermic and spontaneous.

Acid activated charred biomass of *Parthenium* was used for elimination of Nickel, Ni(II) from stimulated water matrix (Lata *et al.*, 2008c). Adsorption was pH sensitive and pH 5.0 was found to be optimum for the process. Rate constant calculation suggested that adsorption was second order reaction. FTIR spectra of adsorbent, showed the presence of alcoholic and carbonyl functional groups. Authors proposed that these functional groups probably played the role of "active sites" for Nickel adsorption.

Effective adsorption of Cr(VI) from the aqueous solution by using ash of *Parthenium hysterophorus* has also been investigated in the study (Singh *et al.*, 2008). Adsorption was found inversely proportional to pH, particle size and adsorbate concentration, whereas directly proportional to temperature. Langmuir and Freundlich adsorption isotherms could also be well correlated with the results. Linear hike of chromium adsorption with time suggested the compliance of first order kinetics.

The dried powder of *Parthenium* was utilized (Khan, 2008) for Cd(II) adsorption. The physicochemical parameters were closely monitored, pH of solution was found crucial. Adsorption increased with increased initial concentration and dosage of adsorbent. Adsorption was endothermic and spontaneous in nature. Regression coefficient of 1.0 for pseudo second order equation implied second order kinetics. The desorption experiments carried out in continuation with 0.1M HCl showed 82.0% recovery.

Mineral acid activated *Parthenium* adsorbent was utilized to quarantine the toxic pollutant p-cresol (Singh *et al.*, 2008). Superiority of adsorbent was established by parallel experimentation on commercial activated carbon. Process variables in batch operation were altered and impact on adsorption was studied by

authors. pH showed vital role in adsorption process, and ideal value is 6.0. *Parthenium* adsorbent followed Freundlich, Redlich-Peterson, and Fritz-Schlunder isotherms, whereas commercial activated carbon followed Radke-Prausnitz and Fritz-Schl under isotherms. Both adsorbents showed first order kinetics model. Authors demonstrated an eco-friendly way for pollution control.

The biosorption of Nickel, Ni(II) using ash of *Parthenium hysterophorus* was studied by Singh *et al.*, 2009. At low initial concentration and at high pH the adsorption increased drastically from 67% to 97%. Metal ion removal was favorable at pH 11.0, thus variation in mentioned process parameters greatly affected biosorption. Adsorption followed Lagergren's kinetic equation.

Apte *et al.*, 2011; studied the utilization of dried powder of leaves and stem of *Parthenium hysterophorus* for the reduction of excess of chlorides. The efficiency of biosorption was dependent upon the pH, Initial chloride concentration and contact time. The authors demonstrated that with an increased chloride concentration biosorption decreased and the equilibrium contact time was 120 min.

The potential of adsorbent prepared from dried *Parthenium hysterophorus* weed for the removal of hexavalent chromium was studied by Venugopal and Mohanty, (2011). Authors varied various process parameters to estimate the mechanism of adsorption. Authors suggested that adsorption took place in three steps i) Bulk diffusion ii) film diffusion iii) surface adsorption and found that it followed pseudo- second order kinetics. Authors proposed that pore diffusion and film diffusion were the rate determining steps with the help of Weber and Morris model. The FTIR graphs of adsorbent before and after adsorption were recorded to estimate the functional groups responsible for biosorption. The shifting of FTIR frequencies from 3400 to 3450  $1/\text{cm}$  and 1424 to 1245  $1/\text{cm}$  with varying intensities proved the presence of carboxyl, amine, alkane and amide groups as chromium binding sites.

Singh, *et al.*, (2015) demonstrated the elimination of Chromium (VI) using dried carbon slurry and ash of *Parthenium hysterophorus* with a special emphasis on intra particle diffusion phenomenon. Various batch experiments with varying process parameters were explored by authors for the studied adsorbent, to demonstrate the presence of Intra particle diffusion as key limiting step. Crank Nicholson's equation and finite

difference approximations were utilized by authors to elaborate the diffusion process. Langmuir and Freundlich adsorption isotherms were best fitted for *Parthenium* ash and carbon slurry respectively. Kinetics followed Lagergrens equation. The linear rise of amount of solute adsorbed with half power of contact time conform the presence of intra particle diffusion. Table 1 summarizes several adsorbents which have been used for removal of heavy metals.

*Parthenium hysterophorus* for dye removal

The removal of methylene blue, malachite green, Rhodamine B, Procion orange, Acid violet 17 dyes and Chromium(VI), Mercury(II), Iron(II), Nitrates metal ions with carbonized *parthenium* treated with sulfuric acid and ammonium per sulphate was studied by Sivaraj and Subburam, (2002). With an increase in the contact time, the removal capacity increased. Physico-chemical properties of *parthenium* carbon were thoroughly determined by authors. Lata *et al.*, (2008a) used mineral acid activated *parthenium* carbon to remove

Rhodamines B dye from synthetically prepared dye solution. The influence on adsorption efficiency due to factors like agitation time, pH, adsorbate concentration and quantity of adsorbent was studied. The optimum pH was 7.0 and contact time 60 mins. for adsorption to occur. The particle size of adsorbent material was in the range of 0.3 -1.0 mm. The Linearity plot of pseudo second order rate equation and the value of regression coefficient suggested the second order kinetics for adsorption. Sum of error square (SSE) equation was utilized to verify the kinetic model. FTIR spectra of untreated adsorbent showed 3385.9 1/cm, 1708.5 1/cm and 1037.4 1/cm frequencies which were shifted to 3448.1 1/cm, 1891.2 1/cm and 1083.4 1/cm respectively in dye bound adsorbent. Authors proposed that the inflection in the FTIR frequencies, in exhausted adsorbent were due to binding of hydroxyl, carbonyl and carbon-oxygen functional groups in dye molecules. Similarly the SEM image of unused adsorbent showed porous surface morphology which in turn changed to rough in nature due to dye

Table 1: *Parthenium hysterophorus* for removal of heavy metals

Heavy metal	Experimental adsorbent	Outcomes	Important observations	References
Nickel(II)	Activated carbon of whole weed	Maximum adsorption capacity 54.35 mg/g at pH 5.0 and 20°C	The successful recovery was proposed for Ni(II) with Hydrochloric acid as eluent	Kadirvelu <i>et al.</i> , (2002)
Mercury(II)	Activated carbon of whole weed	Maximum adsorption capacity 10mg/g at pH 5.0 and 30°C	Adsorption was highly pH sensitive.	Kadirvelu <i>et al.</i> , (2002)
Cadmium(II)	Dried powder of whole weed	Maximum adsorption percentage 99.7% at pH range 3-4.	Desorption with 0.1M Hydrochloric acid was well established.	Ajmal <i>et al.</i> , (2006)
Nickel(II)	Sulphuric acid treated Parthenium carbon	Maximum adsorption capacity 17.24 mg/g	Pseudo second order kinetic equation fitted well with adsorption data.	Lata <i>et al.</i> , (2008)
Chromium(VI)	Ash of whole weed	Maximum removal 63.97% at pH 2.0	Average rate constant was $7 \times 10^{-2}$ 1/min	Singh <i>et al.</i> , (2008)
Cadmium(II)	Dried powdered biomass of whole weed	Maximum removal percentage was 99.16%	Efficient Breakthrough capacity of 280 mL of Cd(II) was established by column technique.	Khan, (2008)
Nickel(II)	Ash of whole weed	Rate constant of adsorption was found to be $6.82 \times 10^{-2}$ /min at 25°C	Adsorption was exothermic in nature.	Singh <i>et al.</i> , (2009)
Chlorides(I)	Dried powder of leaves and stem of weed	30-34% Chloride removal was achieved at lab scale.	The adsorption was greatly affected by pH. The optimum pH is 7 to 7.5.	Apte <i>et al.</i> , (2011)
Chromium(VI)	Dried powder of whole weed	Maximum biosorption capacity 24.5 mg/g	Adsorption was found to be spontaneous and exothermic in nature.	Venugopal and Mohanty, (2011)
Chromium(VI)	Ash of whole weed	Rate constant 0.0568 1/min.	Adsorption obeyed first order kinetics.	Singh, <i>et al.</i> , (2015)

adsorption. Presence of bulky and shiny particles on the surface of exhausted adsorbent supported the observation.

Elimination of malachite green dye from aqueous solution using mineral acids activated *parthenium* biosorbent was demonstrated (Lata *et al.*, 2008b). Adsorption was higher, at lower dye concentration and higher dosage of adsorbent. Equilibration time of 90 min. was observed to be ideal for all studied concentrations.

A comparative adsorption of acid blue 92 dye by using ashes of three different biosorbents namely cow dung, mango stone, *Parthenium* leaves with commercial activated carbon was studied. (Purai and Rattan, 2010) pH and initial dye concentration were monitored. Ash of *Parthenium* leaves and commercial activated carbon showed higher adsorption at acidic pH, whereas cow dung and mango stone ash exhibited satisfactory adsorption at neutral and basic pH respectively. A great agreement in the regression value (0.99) for Langmuir adsorption isotherm was observed. Sequestration of safranin dye from aqueous solution with the help of

dried, powdered *parthenium* was evaluated by Shrivastava, (2010). Authors demonstrated that optimum contact time of 40 min was suitable for all studied concentrations. Nearly constant value of rate constant implied that adsorption proceeded via second order dynamics.

A significant utilization of *Parthenium* weed for preparation of activated carbon by physical and chemical activation techniques was established (Sivaraj *et al.*, 2010). Physical activation by heating (400-800°C), chemical activation by zinc chloride and various acids was demonstrated by the authors. The yield of activated carbon and various characterization parameters like pH, conductivity, specific gravity, bulk density, porosity, moisture, volatile matter, ash, surface area, metal content, soluble matters were thoroughly evaluated. Scanning electron microscopy (SEM) imaging was employed for surface characterization analysis which conform the amorphous and porous nature of zinc chloride activated carbon. The amorphous nature of adsorbent was in turn responsible for high surface area and high adsorption

Table 2: *Parthenium hysterophorus* for removal of dyes

Dye	Experimental Adsorbent	Outcomes	Important observations	References
Methylene blue, Malachite green, Rhodamine B, Procion orange, Acid violet 17	Sulfuric acid and ammonium per sulphate treated carbonized weed.	Affinity order of <i>Parthenium</i> carbon is Methylene blue > Malachitegreen> Rhodamine B > Acid Violet 17>Procion orange	Retention time of 90 min. was reported to be sufficient for total elimination	Sivaraj and Subburam, (2002)
Rhodamine B	Sulphuric acid treated weed carbon	Maximum adsorption capacity 18.52 mg/g	The maximum dye removal was 99.2% at pH 7.0	Lata <i>et al.</i> , (2008a)
Malachite green	Phosphoric acid, sulfuric acid treated weed biomass and commercial activated carbon.	Commercial activated carbon showed 2.01 and 2.63 times more adsorption capacity than phosphoric acid treated and Sulphuric acid treated adsorbent.	Langmuir isotherm well expressed the adsorption data.	Lata <i>et al.</i> , (2008b)
Acid blue 92	Ash of leaves of the weed.	Maximum biosorption capacity 4.84 mg/g	Adsorption was highly pH sensitive	Purai and Rattan, (2010)
Safranin	Dried, powdered weed.	Maximum adsorption capacity 89.3 mg/g.	Adsorption followed Langmuir isotherm model.	Shrivastava, (2010)
Methylene blue	Charred biomass of weed.	Maximum dye removal 99.9%	Recovery was highly pH sensitive.	Chatterjee <i>et al.</i> , (2012)
Methylene blue	Dried powder of untreated weed.	Maximum adsorption capacity 23.8 mg/g	Ideal pH for adsorption was 8.0	Mulugeta and Lelisa, (2014)

Table 3: Various forms of adsorbents prepared from *Parthenium hysterophorus*

Adsorbent	Activated carbon of whole weed	Dried powder of whole weed	Acid activated adsorbent	Ash of whole weed
Adsorbates: (Heavy metals/ dyes removed)	Nickel(II), Mercury(II)	Cadmium(II), Chloride, Chromium(II), Safranin, Methylene blue	Nickel(II), Methylene blue, Malachite green, Rhodamine B, Procion orange, Acid violet 17	Chromium(II), Chromium(VI), Nickel(II), Acid blue 92 dye, Methylene blue
References:	Lata <i>et al.</i> , (2008c) Kadirvelu <i>et al.</i> , (2002)	Ajmal <i>et al.</i> , (2006) Khan, (2008) Apte <i>et al.</i> , (2011) Venugopal and Mohanty, (2011) Shrivastava, (2010) Mulugeta and Lelisa, (2014)	Lata <i>et al.</i> , (2008a, 2008b) Sivaraj and Subburam, (2002)	Singh <i>et al.</i> , (2008, 2009) Purai and Rattan, (2010) Chatterjee <i>et al.</i> , (2012), Singh <i>et al.</i> , (2015)

efficiency. Authors concluded that the zinc chloride impregnated carbon exhibited a maximum surface area of 1089.26 m<sup>2</sup>/g. Thus authors suggested the various alternatives to commercial activated carbon.

The ability of mineral acid and zinc chloride activated charred *parthenium* biomass adsorbent for the sequestration of methylene blue dye was studied by Chatterjee *et al.*, (2012). The response surface methodology and ANOVA statistical tool was utilized to set the process parameters. Study demonstrated that 25 mg/L initial dye concentration, 35°C process temperature, 0.22 g adsorbent dosages and pH 7.0 were the optimum conditions for adsorption to occur. Based on the intra particle diffusion phenomenon the authors suggested that adsorption fitted well in second order kinetics. Physicochemical parameters of charred *parthenium* were thoroughly estimated. Scanning electron microscopy imaging was used to establish the topography of adsorbent material, which showed the porous nature of adsorbent. This porous nature was in turn responsible for high adsorptive capacity. FTIR spectra of charred and spent charred *parthenium* was also recorded which showed the presence of hydroxyl, carbon- carbon, carbon-hydrogen bonding in both adsorbent. FTIR frequencies corresponds to nitro compounds at 1570 1/cm, 1560 1/cm were exclusively found in spent charred charcoal due to adsorption of methylene blue dye.

Finely ground, raw / untreated *Parthenium hysterophorus* weed was used as biosorbent for elimination of cationic methylene blue dye (Mulugeta and Lelisa, 2014). Physico-chemical parameters for adsorption were monitor carefully. Dye removal was higher at the beginning and with time it diminished

due to loss of available active site of adsorption. High pH was found favorable for adsorption due to enhanced protonation at adsorbent surface. Langmuir isotherm equation well explained the adsorption phenomenon.

*Parthenium hysterophorus* was used for the bio synthesis of titanium nano-particles by Khan and Fulekar, (2015). Authors successfully demonstrated the photo degradation of dye Reactive red 31 with this bio synthesized nano-particles in presence of solar radiation. Impact of varying substrate concentration against photo degradation was studied by authors. Dye degradation was checked using UV-VIS Spectroscopic tool by continues absorbance measurement. Thus the authors demonstrated a novel way to utilize *parthenium* weed. Table 2 summarizes the use of the adsorbent for the removal of dyes.

Table 3 shows the use of several categories of the adsorbents prepared from *Parthenium* for the removal of heavy metals and dyes.

## CONCLUSION

The novelty of the biosorbent lies in its eco-friendliness, economic significance and comparable efficiency with commercial activated carbon. Thus the review explores a diverse way of utilization of this plant in the form of an emerging novel adsorbent for the removal of dyes and heavy metals from waste water.

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## CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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