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# Development of a green and sustainable clean up system from grape pomace for heavy metal remediation

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ABSTRACT

Bio-based adsorbents from grape pomace used in waste water clean-up activities are demonstrated in the present study. An application of thermal treatment to the oven dried and grinded grape pomace resulted in the development of a porous carbonaceous biosorbent having selective surface sites favourable for binding of metal ion adsorbates. While the electrostatic nature of adsorbent-adsorbate interactions were indicative from pH and FTIR studies, "Weber and Moris" plots helped to estimate the nature of the adsorbate transfer process which is interplay of film and particle diffusion. The maximum adsorption capacity was determined from Langmuir plot and reveals the higher uptake of $Pb^{2+}$ in comparison to $Cd^{2+}$. The relationship of the divalent cationic properties of the selected adsorbates in aqueous media is reflected. Effect of various operating parameters along with equilibrium, kinetic and thermodynamic studies reveal the efficacy of the GPMAC with an adsorption capacity comparable to other reported adsorbents. The developed adsorbent was tested under a real metal fabricating industrial effluent where despite the presence of competing pollutants and a high COD, greater than 89% metal removals was achieved. Also high regeneration capacity of GPMAC for reuse has established the practicality of the developed system. The experimental results reveal that the winery wastes have the potential for cost effective and eco-friendly wastewater treatment. Also, developing an effective, low cost adsorbent from winery solid waste like grape pomace is a new promising strategy and sustainable solution towards its efficient waste valorisation.



## 1. Introduction

The success of the adsorption process in waste water remediation mainly hinges on the precise surface properties of the activated carbons like a high degree of porosity, extensive internal surface area and favourable surface chemistry [1,2]. Commercial activated carbons usually prepared from coal and petroleum products are mostly used as adsorbents but are costly making the waste water treatment process expensive. Thus while the economic criteria is a major hindrance for the wide spread usage of the adsorption technology, the process has some distinct advantages over other water treatment technologies that are used till date. The characteristics that make it stand apart are its environmental friendliness with no usage of harmful chemicals or generation of toxic sludge. The growing awareness of using green technologies and processes under the Green Chemistry principles has resulted in the search for cheap, sustainable solution in the form of low cost eco-friendly adsorbents for waste water treatment [3]. Ever since the inception of the biorefinery concept under the Green Chemistry, the wastes generated from the agro-food sector due to their mass scale production, with no economic value has been targeted as efficient substrates for their valorisation to low cost high quality adsorbents for use in water clean-up activities.

In this context, it is worth mentioning that the grape pomace generated as a waste by-product from the wineries is an interesting and inexpensive medium for the development of activated carbons. Constituting about 20% of the input grape in a typical winery, the pomace has an estimated annual generation of 14.5 million tons in Europe [4]. Such solid wastes have practically

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no utility except for its use as a cattle feed or as a fertilizer; but prolonged use as a fertilizer has resulted in germination problems due to the toxicity associated with the high levels of polyphenols in the waste matrices [5,6]. Considering grapes to be the world's largest fruit crop with maximum production in the European countries of France, Spain and Portugal and considering the large scale generation of the grape pomace from the wineries of such countries, the pomace may be effectively utilised as a cheap alternative source for the preparation of adsorbent materials. The compositional analysis of grape pomace reveals its organic nature having a rich mixture of dietary fiber, protein, sugars, polyphenols and a low mineralogical content [7,8]. The high amount of organic components makes the grape pomace a suitable precursor for preparing activated carbons with specific surface features via different physical and chemical methods. An initial study carried out on the oven dried, grinded grape pomace revealed the presence of various oxygen rich functionalities of hydroxyl, carboxyl and carbonyl groups but had a non porous morphology. The adsorption studies revealed uptake capacities for model lead metal ions but its performance was lower as compared to literature studies. The dried pomace also released coloured polyphenolic compounds leading to increase of COD which is undesirable for water cleanup. Thus while the rich polyphenolic matrix is a boon for effective valorisation of grape pomace as a functional food, the same polyphenols are a major deterrent for its use in water cleanup activities.

The main objective of the present study was thus to carry out modifications in the preparation of the activated carbons from the oven dried grape pomace and further assesses its performance via various characterisation and batch adsorption studies. It is essential to either destroy or mask the polyphenolic functionalities and further incorporate sufficient surface porosity thereby necessitating the purpose of modification. With regard to the batch studies, the adsorptive potential of the modified bio-sorbent from grape pomace was not only assessed in detail but also the likely factors that affected its optimum capacity was determined. Finally, but most importantly, the performance of the developed biosorbent was assessed on a real metal fabricating industrial effluent. The model pollutants selected in this study (lead and cadmium) is a potential threat to the environment leading to adverse health effects when present in even trace amounts [9]. The drinking water guidelines for lead recommended by the World Health Organisation (WHO), the American Water Works association (AWWA) and the Bureau of Indian Standards (BIS) is 0.05 mg/L while for cadmium both WHO and AWWA recommended 0.005 mg/L [9,10]. Various bio-based adsorbents prepared from coir pith [11,12], rice husk [13,14], wheat bran [15,16], mango peel [17] and orange peel [18,19] have successfully demonstrated significant removals of lead and cadmium metal ions from aqueous medium. The wider availability of grape pomace as a waste product of wineries especially in the Mediterranean region and the rich organic characteristics make it a suitable low cost precursor for adsorbent development. Also, there is scarce literature on the use of grape pomace as a viable substrate for adsorbent development. The present study highlights the novelty of the development of low cost activated carbon from the solid residue of wine industries viz. grape pomace via thermal treatment methods. The activated carbon demonstrated well-developed porosity, higher surface area and selective surface binding sites which make them potentially attractive for use as biosorbents for wastewater remediation. The use of grape pomace as effective biosorbents can solve the problem of solid waste management associated with the disposal of such solid organic wastes of wine industries. Another important aspect with regard to the novelty is that the developed biosorbent showed good metal uptake capacities both at lower and higher adsorbate concentrations in aqueous medium.

## 2. Materials and methods

### 2.1. Collection and storage of grape pomace

The red grape pomace (GP), *V. vinifera* L. cv. *Cabernet,* was collected after the red vinification from the Experimental winery Mas Friars, the centre linked to the Faculty of Oenology of Universitat Rovira I Virgilli (URV) at Tarragona, Spain. The pressed pomace was received having a moisture content of 76%. The GP samples were oven dried in a conventional oven maintained at $100 \pm 5\,^{\circ}C$ for 24 h at atmospheric pressure. Dried GP samples were milled in a food processing grinder and finally stored in polythene bags.

### 2.2. Chemicals and reagents

All reagents (analytical grade lead nitrate, cadmium nitrate, zinc nitrate, nickel chloride, NaOH, $H_2SO_4$, and $HNO_3$) were purchased from Sigma Aldrich. A 1000 mg/L metal ion stock solution was prepared; standards and samples at required concentration range were prepared by appropriate dilution of the stock solution. Prior use, all glassware was cleaned with dilute nitric acid and repeatedly washed with deionized water. Deionised water was prepared using a Millipore (Milford, MA, USA) water purification system.

### 2.3. Equipment for characterization of adsorbent and adsorbate

pH studies were conducted on a pH meter (Model Cyberscan 510,Singapore). The concentration of the model metal ions used in the study was determined on an atomic absorption spectrophotometer model Z-7000 (Hitachi, Japan) at a wavelength of 283.3 nm for $Pb^{2+}$ and 228.8 nm for $Cd^{2+}$. The total polyphenols content in the waste waters were determined spectrophotometrically at 760 nm using the Folin test [20]. Spectrophotometric measurements were taken on a Perkin Elmer UV/Vis Spectrometer (Perkin Elmer, Lambda 35). Gallic acid served as the standard for the Folin test for preparing calibration curve ranging from 5 to 250 mg/L assay solution. The COD of the wastewaters was determined by digestion of the water samples in a COD digester at 150 °C for 2 h followed by photometric determination (Hannah Instruments).

Elemental analysis of the adsorbent was carried out on an Elementar Vario ELHI CHNS analyzer. The infrared spectra of adsorbents were recorded in KBr discs on an infrared spectrophotometer (Model Perkin Elmer-1600 Series). LEO 435 VP (Leo Elektronenmikroskopie GmbH, Germany) scanning electron microscopy was used for scanning the adsorbent surface. The surface area of the adsorbent was measured on micromeritics ASAP 2010 (UK). The mesopores and micropore volumes were determined from $N_2$ gas adsorption isotherm at 77 K on micromeritics ASAP 2010 (UK) and mercury porosimeter (Pascal 440; M/s Spektron Instrument Inc., India). The total pore volume was obtained from the density measurement of mercury by Mercury porosimeter and density of helium by Automatic Gas pycnometer (Ultrapyc 1200e, Quantachrome Instruments, India).

For $pH_{pzc}$ determination, a series of 10 solutions of 0.1 M $NaNO_3$ were prepared each maintained at a constant pH. pH was adjusted in the range of 1–10 by adding 1 M NaOH or 1M$HNO_3$. 0.2 g of the adsorbent was added to these solutions and agitated at 100 rpm for 24 h. The final pH of each of the solution was measured and $pH_{pzc}$ determined from the plot of $pH_{drift}$ versus $pH_{initial}$.

Basic and acidic surface functional groups were determined by titration with HCl and NaOH respectively (Boehm method). Samples of 0.2 g of the adsorbent were kept in contact with 20 mL of 0.05N acidic and basic solution. The containers were