Adsorption of Paraquat by Treated and Untreated Rice Husks Studied by Flow Injection-Analysis

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Abstract

A flow injection analysis (FIA) was used for studies on the adsorption of paraquat on three types of rice husks, namely untreated- (RH), activated carbon derived from sodium hydroxide-treated (NAC) and phosphoric acid-treated (HPC) rice husks. They were studied under different experimental conditions of pH, adsorbent quantity, contact time and paraquat concentration. Equilibrium adsorption was reached within 5 minutes of contact with paraquat solution and maximum paraquat adsorption occured at pH > 6. The HPC exhibited the highest removal efficiency (~100 %) as compared to the NAC and RH adsorbent material. This high efficiency is probably due to the highly porous structure of the phosphoric acid-treated material. Modeling of the adsorption equilibrium suggested that the adsorption of paraquat fitted a Freundlich isotherm. The studies indicate that rice husks based materials can be used effectively for the removal of paraquat from water bodies.

Keywords: Flow-injection analysis, paraquat adsorption, rice husks.

Introduction

Since their introduction to the market-place in 1962, paraquat (1,1'-dimethyl-4,4'-bipyridinium) has enjoyed huge commercial success mainly for controlling terrestrial and aquatic weeds. Despite its many favourable characteristics such as rapid action, biodegradable in soil matrices, there is world-wide concern regarding the widespread use of this herbicide[1-4]. Countries such as Sweden and Finland have completely banned its use due to its high toxicity, while in Hungary and USA its use is very much restricted. Due to its toxicity, strict limits have been imposed in many countries where the allowed limit in drinking water ranges from 0.3-200 ppb[1]. Pollution of the water with paraquat is effected by their use in the control of terrestrial and aquatic weeds, leaching and run-off from agricultural lands.

Adsorption on activated carbon has long been recognized to be one of the most effective methods for the removal of pesticides from aqueous solution. In a continuing search for low–cost adsorbents, various lignocellulosic materials or agriculture wastes such as coconut shell, rice husks, saw dust, and wheat straw were used[5-7]. These materials were pyrolysed or carbonized in an inert atmosphere in order to remove volatile organic constituents, leaving behind a highly porous carbonaceous residue, followed by either chemicals, steam or gas activation.

Activated carbons have been prepared from the above materials by application of both physical and chemical activations. Activation and pyrolysis of rice husks with $ZnCl_2$, H_3PO_4 or CO_2 have been used for the adsorption of methylene blue[8] and benzene[9]. Separate and sequential application of physical activation with steam and chemical activation with H_3PO_4 were also reported[10,11]. Hu and Srinivasan[12] employed simultaneous activation by using $ZnCl_2$ and CO_2 to produce activated carbon from coconut shells and palm seeds. The adsorption of phenolic compounds and 2,4-dichlorophenoxyacetic acid (2,4-D) on rice husk and activated carbon, respectively have also been reported[13, 14].

Many analytical methods had been reported on the determination of paraquat. This includes high performance liquid chromatography (HPLC), gas chromatography with nitrogen phosphorus detector, immunoassay, capillary electrophoresis, potentiometry and spectrophotometry[1,3,4,15]. Of these methods, spectrophotometry is still popular as the instrument involved is relatively cheap. The basis of the analytical determination is based on the measurement of absorbance of coloured complex formed between alkaline paraquat solutions in the presence of reagents such as dithionate, ascorbic acid and glucose. The absorbance measurements, however, pose considerable handling difficulties due to the unstability nature of the complex due to rapid oxidation by atmospheric oxygen resulting in fading colour, often resulting in poor reproducibility in the determination[15]. This unstability problem had been considerably minimized by operating under flow injection analysis (FIA) conditions[15]. In this work, we utilized the FIA for the monitoring of paraquat adsorption activities by adsorbents derived from rice husks. The rapidity of the determination (sample throughput of ~50 samples/ hour), adequate sensitivity, plus the high reproducibility nature of the FIA approach made the technique suitable for such studies.

Material and Methods

Raw materials: Golden brown, atmospheric dried and fresh rice husks (RH) were used as the raw material to produce activated carbon. The rice husk was obtained from a rice mill in Seberang Perai, Malaysia. Typical composition of the rice husks used is 16 % silica, 14 % lignin, 36 % cellulose, 22 % hemicellulose, 3 % extractive materials and 9 % moisture[16].