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Preliminary investigation of mixed adsorbents for the removal of copper and methylene blue from aqueous solutions

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HIGHLIGHTS

- Multi-adsorbent systems containing tea waste and dolomite have been tested.
- The effects of contact time, solution pH and adsorption isotherms were investigated.
- The adsorption processes of Cu ad MB were favourable at the investigated conditions.
- Adsorption capacities of DO and TW:DO for Cu and MB were 237.7 and 150.4 g g^{-1}.
- The chemical adsorption was the main control process for the TW and DO materials.

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ABSTRACT

With most recent studies being focused on the development of advanced chemical adsorbents, this paper investigates the possibility of using two natural low-cost materials for selective adsorption. Multi-adsorbent systems containing tea waste (TW) and dolomite (DO) have been tested for their effectiveness in the removal of copper and methylene blue from aqueous solutions. The effects of contact time, solution pH and adsorption isotherms on the sorption behaviour were investigated. The Langmuir and Freundlich isotherms adequately described the adsorption of copper ions and methylene blue by both materials in different systems. The highest adsorption capacities for Cu and MB were calculated as 237.7 mg/g at pH 4.5 and 150.4 mg/g at pH 7 for DO and TW:DO respectively. Tea waste and dolomite were characterised by Fourier transform infrared spectroscopy, scanning electron microscopy and Energy dispersive X-ray analysis. The removal of Cu and MB by dolomite was mainly via surface complexation while physisorption was responsible for most of the Cu and MB adsorption onto tea waste. Identifying the fundamental mechanisms and behaviour is a key to the development of practical multi-adsorbent packed columns.

1. Introduction

Dyes (very frequently methylene blue and methyl orange) and heavy metals (copper, cadmium and nickel mostly from the organo-metallic dyes) are dangerous pollutants found in large quantities in wastewaters from textile and paper industries. It is known that heavy metals are toxic and non-biodegradable [1,2]. Heavy metals have many environmental issues such as animal and plant death, reduced rates of reproduction and the decrease of ecosystem diversity [3] while dyes are difficult to treat as the colour tends to hold strong even after the conventional removal processes [4]. There are more than 100,000 commercially available dyes with over 700,000 tons produced annually [5]. The presence of some of these dyes even in very small amounts i.e. <1 mg dm^{-3} is undesirable [6,7]. Dye-Heavy metal loaded wastewaters are highly coloured, have a fluctuating pH and regularly contain large amounts of suspended oils. Dyes and heavy metals find their way into the environment, primarily dissolved or suspended in water everyday [8] and create serious damage to the environment by changing the biological life balance in rivers and lakes [9,10]. Adsorption is a well-established and powerful practice for the removal of dyes and heavy metal pollutants from wastewaters. For these reasons, thousands of investigations have used uncountable adsorbents to remove heavy metals [11] or dyes [12]. Most of these studies focus

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on single-component aqueous solutions and recently, more research papers have been published dealing with the adsorption of dyes and metals in multi-component aqueous systems [6]. Also, composite adsorbents have been established to adsorb dyes and heavy metals from wastewater such as chitosan/montmorillonite composites [13–15] and fly ash/activated carbon [16]. In previous studies, composite materials were used to selectively adsorb a particular pollutant. Ho and co-workers proved that amino functionalised silica solids can selectively adsorb dye anthraquinone blue in the presence of methylene blue, while, from the same dye mixture, carboxy-functionalised materials adsorb methylene blue selectively [17]. Prediction of multicomponent adsorption is still one of the most challenging problems in the adsorption field [18]. There is little data available to provide more understanding about the interactions between adsorbents and developing design models for such practical systems is very important [19]. This is the case for many composite materials as well as adsorption processes with multi-adsorbate and multi-adsorbent systems. Dolomite, with a structure of alternative layers of calcite and magnesite, is a potential inexpensive and readily available adsorbent [20]. Many studies showed that dolomite and charred dolomite have the potential to act as adsorbents for reactive dyes and heavy metals [21]. Tea, processed leaves from *Camellia sinensis* species, is the second most common drink being consumed after water with an average daily consumption of 20 billion cups. The manufacturers of tea products face a problem in disposing of the spent tea leaves after the extraction [22,23]. The feasibility of using the richly available solid waste, spent tea leaves, for the removal of heavy metals and dyes has also been extensively investigated [24]. A good understanding of the effect of adsorbent-adsorbent interactions on selective adsorption is essential as a foundation for selecting the best adsorbent and employing it in an optimal way. Hence, the aim of this research is to clarify the chemical and physical interferences between the two materials, namely tea waste and dolomite, when used for the removal of copper and methylene blue from aqueous solutions. In this paper, the term adsorption will refer to biosorption onto tea waste (TW) and adsorption onto dolomite (DO). Copper ions and methylene blue dye adsorption onto tea waste and dolomite using different factors, such as reaction contact time and pH of solution as well as initial metal and dye concentration on selective adsorption was examined. Recognising the fundamental mechanisms and behaviour would be useful for practical multi-adsorbent packed columns.

2. Materials and methods

2.1. Adsorbents and adsorbates

The two low cost materials used in this experiment were tea waste (TW) biosorbent and dolomite (DO) adsorbent. Fine dolomite ($d_P < 50\ \mu m$) was supplied by Killwaughter Chemical Company, UK. The typical chemical composition of the dolomite in the deposit was 44% $MgCO_3$ and 53% $CaCO_3$ (obtained by XRD analysis) [25]. The tea waste biosorbent was collected from Queen's University cafeteria; it was washed several times with hot water and dried in a conventional oven at 110 °C. The two adsorbents were comprehensively characterised in previous investigations [26,27]. Copper(II) and Methylene Blue (MB) stock solutions were prepared by dissolving known amounts of $CuSO_4{\cdot}5H_2O$ and MB in deionised water. The stock solutions were then diluted to get various initial concentrations. All chemicals were purchased from Sigma Aldrich UK.

2.2. Adsorption experiment

To investigate the influence of pH on Cu(II) and MB adsorption onto TW and DO, six sets of experiments were prepared: Cu(II) or MB with TW biosorbent; Cu(II) or MB with DO adsorbent and Cu(II) or MB with a mixture of 1:1 TW:DO (w/w%). Samples of 25 cm^3 of adsorbate solutions with $C_o = 120$ and 100 mg/dm^3 of Cu and MB, respectively, were adjusted to different pH values: 2–11. The same procedures were performed to study the effect of contact time and adsorption isotherms. The initial concentrations of Cu(II) for the contact time studies was 200 mg/dm^3 and for MB it was 120 mg/dm^3. For the adsorption isotherm studies, a concentration of: $C_o = 10–100\ mg/dm^3$ for Cu(II) and $C_o = 10–75\ mg/dm^3$ for MB were used. An adsorbent dose of 1 g/dm^3 was used for all experiments at room temperature (~20 °C) and a contact time of 4 days to ensure reaching the equilibrium. There were no pH adjustments for contact time and isotherm experiments, so the experimental processes are more environmental friendly. The concentrations of Cu(II) and MB were analysed using an ICP–OES Thermo Scientific IRIS and UV/Vis spectrophotometer (Perkin Elmer LAMBDA 25, UK), respectively. The amount of Cu(II) and MB adsorbed per unit mass of adsorbent q in (mg/g) and removal percentage were calculated using Eqs. (1) and (2):

$$\text{The percentage removal} = \left[1 - \frac{C_e}{C_o}\right] \times 100\% \tag{1}$$

$$q = \left[\frac{C_o - C_e}{M}\right] \times V \tag{2}$$

Where C_o and C_e (mg/L) are the concentration of adsorbate at initial and equilibrium, respectively, M is the mass of adsorbent (g) and V is the volume (dm^3).

2.3. Infrared and SEM measurement

The FT-IR analyses for TW and DO surfaces before and after Cu(II) and MB adsorption were carried out on a Perkin Elmer Spectrum 100 within the range of 400–4000 cm^{-1}. For the SEM analysis and Energy dispersive X-ray (EDX) analysis, TW and DO samples were coated with carbon and vacuumed (5–10 min) for electron reflection prior to analysis on a JEOL-JSM 6400 scanning microscope.

3. Results and discussion

3.1. Effect of contact time

Fig. S1(a) and (b) are the plots of Cu(II) and MB removal against time for TW and DO materials, respectively. It can been seen that Cu(II) and MB were almost completely removed by dolomite and tea waste after 6 h at room temperature (20 °C). The adsorption of Cu(II) and MB dye was fast in the initial stage due to the large number of available binding sites, resulting in a concentration gradient [28]. The removal rate gradually declined with time until equilibrium was achieved. The maximum removal efficiencies of copper ions and MB onto TW and DO were approx. 90% at pH of 5–7. The adsorption capacities of Cu(II) and MB were reduced when the two materials were mixed together; this reduction was more significant in the case of Cu(II). The adsorption capacity of the mixed adsorbent (TW:DO) was reduced to approx. 45% and 85% for Cu and MB, respectively. This reduction is attributed to the change in the sorbent and solution properties such as pH_{PZC} and $pH_{equilibrium}$ [29]. However, results indicate that these pollutants can still be efficiently removed with high selectivity onto the mixed adsorbents.

3.2. Kinetics modelling

The adsorption mechanism can be investigated using various adsorption kinetics models. The pseudo first- [30] and pseudo