

Fabrication of a Smartphone-Based Spectrophotometer and Its Application in Monitoring Concentrations of Organic Dyes

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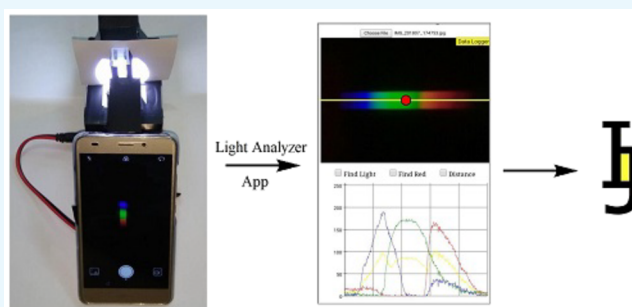


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Supporting Information

ABSTRACT: In this study, an in-house constructed paper-based spectrophotometer is presented and demonstrated for detecting three organic dyes, namely, methylene blue, malachite green, and rhodamine B, and monitoring the efficiency of their removal from a wastewater sample with Sistan sand as a costless adsorbent. The compact design and light weight of this simple spectrophotometer delivered portability, with materials costing less than a dollar. Spectral analysis of the captured images was performed using free downloadable software from the Google Play store. The main experimental parameters affecting the efficiency of dye adsorption including pH, sorbent dosage, initial dye concentration, and contact time were investigated and optimized using the Taguchi design experimental method. Validation experiments were performed using a standard commercial bench-top spectrophotometer, and results were compared in terms of analytical performance, speed, and cost of analysis. The smartphone-based spectrophotometer was able to measure accurately, as confirmed using the commercial spectrophotometer, with enhanced sensitivity for methylene blue and rhodamine B. The combination of the high spectral accuracy of the paper-based spectrophotometer, together with sand as a readily accessible sorbent, enabled us to develop a powerful yet simple approach and tool for the removal and monitoring of dyes within wastewater samples, which is potentially available to everybody who owns a smartphone.



1. INTRODUCTION

Since the first cell phone by Motorola was sold over three decades ago, it is estimated that around 17.37 billion mobile phones are now in use worldwide, with nearly 1.54 billion smartphones sold in 2017 alone.^{1,2} This staggering volume has inevitably resulted in falling prices year on year. Concurrently, the capabilities of smartphone technology have rapidly increased in terms of computational power, connectivity, and camera and imaging capability, with exceptionally high pixel counts. These devices are now essentially minicomputers containing a substantial internal memory and high quality cameras and compatible with an increasing variety of readily available sensors, thereby providing opportunities to gain application as advanced analytical sensing. Over the last decade, smartphone imaging has been increasingly applied across a variety of scientific domains and several applications that deal with analytical sensing have been reported in the literature.³ Established concepts and designs for “smartphone spectrometers” have been widely explored by researchers over the past few years.⁴ A smartphone spectrometer can present a simple, portable, and accessible alternative to the traditional costly commercial bench-top spectrophotometers. Interest in smartphone spectrometers was evidenced by the number of journal articles in the literature reporting on such devices, which was increased five times from 2015 to 2017.⁵

For example, smartphone sensors have been applied within the field of biomedical monitoring, including for the detection of specific nucleic acid sequences and biomarker protein.⁶ In 2014, Nemiroski *et al.* described an electrochemical sensor based upon a smartphone for the detection of important biomarkers, such as Na^+ and blood glucose in biological liquids. Detection ranges for these analytes were reported as low as 10^{-4} M and 50 mg dL^{-1} for Na^+ and blood glucose, respectively.⁷ A similar absorbance-based device was developed by Coskun *et al.* in 2013 for the detection of allergen contamination in food.⁸ A smartphone fluorescence analyzer was reported by Bueno *et al.* in 2016 to detect ochratoxin in beer samples. Ochratoxin is fluorescent at 460 nm, which can be readily recorded using a modern smartphone camera.⁹ A smartphone-based spectrophotometer was also used to measure Fe^{2+} in medicinal samples by Long *et al.*² In another report, a similar spectrophotometer was applied to monitor the pH of river water over the range of pH 6–8.¹⁰ Recently, the

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Table 1. Analytical Figures of Merit for Determination of Dyes by Smartphone-Based and Commercial Spectrophotometers

dye	dynamic range of the calibration curve ^a (mg L ⁻¹)		LOD ^b (mg L ⁻¹)		RSD ^c (%)	
	paper-based SP ^d	commercial SP	paper-based SP	commercial SP	paper-based SP	commercial SP
RhB	0.7–10.0	0.5–10.0	0.307	0.056	6.366	4.136
MG	1.0–15.0	0.5–15.0	0.390	0.097	3.536	2.457
MB	1.0–16.0	0.6–15.0	0.747	0.212	5.560	3.064

^a $R^2 \geq 0.98$. ^bLOD was based on a $3S_b/m$ criterion for 10 blank measurements. ^cRSD, relative standard deviation, for five replicate measurements of 6, 12, and 15 mg L⁻¹ of RhB, MG, and MB, respectively. ^dSP, spectrophotometer.

“spectrophone”, which is an improved smartphone-based spectrophotometer, was invented by de Oliveira *et al.*⁴

Although the above efforts have all shown elements of success and versatility and have all been created using a smartphone to collect and process data, most of these recent examples required the use of extra parts or peripheral devices, which were assembled on the smartphone, which in many cases were rather complex and not amenable to low-cost production.¹¹

The use of smartphone spectrometers to monitor adsorption processes, such as dye removal from wastewater, has not been presented previously. Therefore, in this current work, the authors have tried to investigate the suitability of a very simple paper-based smartphone spectrometer for such an application. This practical demonstration could have direct impact for such activities within resource-limited locations and indeed remote locations and at-site monitoring. Therefore, herein, we report upon the possibility of monitoring the removal of rhodamine B (RhB), malachite green (MG), and methylene blue (MB) dyes from environmental samples by relying on a smartphone spectrometer made simply from paper and a piece of a DVD disk as its light dispersing element. Ambient light was used as the light source, so the need for additional optical components, or indeed an additional power supply, was both eliminated. The three test dyes were selected because of their absorbance spectra, which spanned the three primary colors of light, i.e., red, green, and blue (RGB). In a previous work, the authors have already demonstrated that Sistan sand can be employed as a very efficient and low-cost adsorbent for the uptake and removal of organic dyes;¹² hence, it was applied herein once again as the sorbent. The Taguchi experimental design was employed to set conditions for optimization of the various factors affecting this process.

2. RESULTS AND DISCUSSION

2.1. Analytical Performance. To obtain quantitative information, calibration curves for both smartphone-based and commercial spectrophotometers were constructed; values of their respective analytical figures of merits are presented in Table 1. As can be seen, the calibration curves were obtained, and their dynamic linear ranges were very similar. However, in terms of limit of detection and precision, while values are of the same order, due to higher noise associated with manual measurements and visual detection using the simple smartphone spectrometer, the performance of the commercial spectrophotometer was notably better.

It should also be mentioned here that each run using the paper-based spectrophotometer took almost 1 min, in comparison to less than 5 s for the commercial spectrophotometer. However, the above performance should be viewed with regard to the absolute minimal cost of preparing the

smartphone-based spectrometer, compared to the commercial system.

2.2. Removal of Dyes by Sistan Sand. One aim of this research was to provide a handheld device available to everyone to be able to determine the organic dye content in wastewater samples (as a demonstrable application) as well to monitor their removal via a simple and available method. The harmful effects of these dyes on the human health and environment are discussed in many papers.^{13,14} Also, the necessity of the removal of dye compounds from aqueous environments by adsorption has been extensively studied.^{15,16} Desert sand is readily available in most parts of the world, and the authors have already demonstrated Sistan sand utility as a sorbent and how to successfully apply this.¹² To be able to efficiently remove dyes from the water samples, various factors affecting adsorption of MB, MG, and RhB on sand were optimized using an experimental design. Four factors in four levels were selected (Table S1). To confirm data obtained by Taguchi modeling, a batch technique was also employed. In a 50 mL flask, 25 mL of dye solution (with particulate concentration, as referred in Table S2) was added and its pH was adjusted using 0.1 M NaOH or 0.1 M HCl to the desired value. The adsorbent (sand) was added, and the mixture was shaking for a pre-set time. The supernatant liquid was taken and centrifuged for 5 min at 5000 rpm, and the concentration of the residual dye was measured and determined using an external calibration curve. All experiments were performed by both the paper-based spectrophotometer and commercial spectrophotometer in triplicate, and averages of the results were compared. These revealed that optimum removal conditions were of course the same for both paper-based and commercial spectrophotometers (Table S3). Under optimum conditions, adsorption capacities of the sorbent were calculated to be 0.1900, 0.5460, and 0.6975 (mg g⁻¹) for RhB, MG, and MB, respectively.

2.3. Application to a Real Sample. To evaluate the performance of the paper-based spectrometer with real sample matrices, the method was applied to the analysis of a wastewater sample. No MB, MG, and RhB were detected in this native sample; however, to investigate the effect of the sample matrix on removal efficiency, the same sample was spiked with the target analytes at different concentrations. The results, which are shown in Table 2, indicate that the

Table 2. Results Obtained for Removal of MB, MG, and RhB from Wastewater

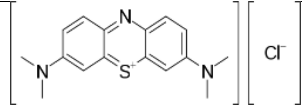
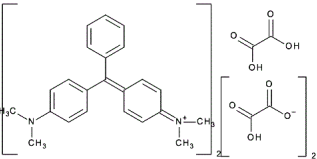
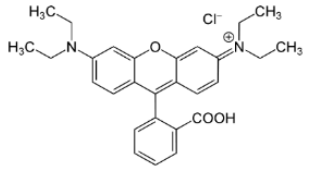
dye	added (mg L ⁻¹)	removal percent (%)	RSD (%) (n = 3)
MG	12	97	6.1
MB	15	95	6.4
RhB	6	90	5.7

Table 3. Application of Smartphone Spectrometers for Colorimetric Detection of Different Analytes in the Water Sample

analyte(s) determined	dynamic linear range (mg L ⁻¹)	LOD (mg L ⁻¹)	RSD (%)	ref
methylene blue	0.5–10	0.5	NM ^a	17
chlorine and nitrite	1.00–4.00 and 0.05–1.20, respectively	5.0×10^{-2} and 8.6×10^{-3} , respectively	8.75	18
calcium	0.06–1.50	0.02	2.71	19
Fe(II)	NM	2.0×10^{-2}	≤0.30	4
penicillamine	5.0–40.0	0.990	1.890	20
carbamazepine, ciprofloxacin, and norfloxacin	5.00–60.0	3.0, 10, and 1.0, respectively	6.120–7.420	21
iron(III)	0.50–10.0	0.10	0.90	22
rhodamine B, malachite green, and methylene blue	0.70–10.00, 1.00–15.00, and 1.00–16.00, respectively	0.307, 0.390, and 0.747, respectively	3.536–6.366	this study

^aNM, not mentioned

Table 4. Chemical and Physical Characteristics of Studied Dyes

Dye	Chemical structure	MW (g mol ⁻¹)	λ_{max} (nm)
Methylene Blue		319.86	667
Malachite green oxalate		927.01	618
Rhodamine B		479.02	554

developed method using the fabricated spectrophotometer can successfully be applied for such purposes. As can be seen, under optimum conditions, the removal percent between 90 and 97% was obtained for dyes spiked in sewage samples. These data were verified by the bench-top spectrometer applying Student's *t* test.

3. CONCLUSIONS

In this study, a simple, handheld, lens-free, and highly portable smartphone paper-based spectrometer was fabricated, equipped with a piece of DVD as the diffraction grating and a mini light-emitting diode (LED) as the source. As a possible application, the precise determination of three organic dyes, MG, MB, and RhB, covering the three main colors of RGB was performed in aqueous media. Detection limits down to 1 mg L⁻¹ were achieved. This handheld, lightweight spectrometer can be fabricated in minutes and can be used as a very precise and accurate device for dye detection. Furthermore, the device can be applied to monitor dye removal, in this case, using costless desert sand as an efficient sorbent. In comparison to a commercial instrument, the readout of this device revealed similar or better analytical features. Ease of operation and

portability of this very promising analytical tool were also positive features, providing such capability to everyone to use it in a wide field of applications.

The method itself has advantages such as being ultralow cost and capable of at-site analysis. Moreover, it can be easily applied by novice people. On the other hand, some drawbacks of the developed method are its less sensitivity and higher LOD in comparison to the standard method of analysis of dyes by commercial spectrophotometry. In addition, due to the handmade fabrication of the paper-based spectrophotometer, results can be less reproducible.

In Table 3, some recent applications of smartphone spectrometers for a number of similar measurements are summarized.

4. MATERIALS AND METHODS

4.1. Chemicals and Material. The sorbent used in this study was Sistan sand, originating from the Sistan desert, which is located southeast of Iran. To remove contamination from the sand, it was washed within a beaker full of distilled water under agitation via a magnetic stirrer. This procedure was repeated 20 times. MB, MG, and RhB dyes were purchased

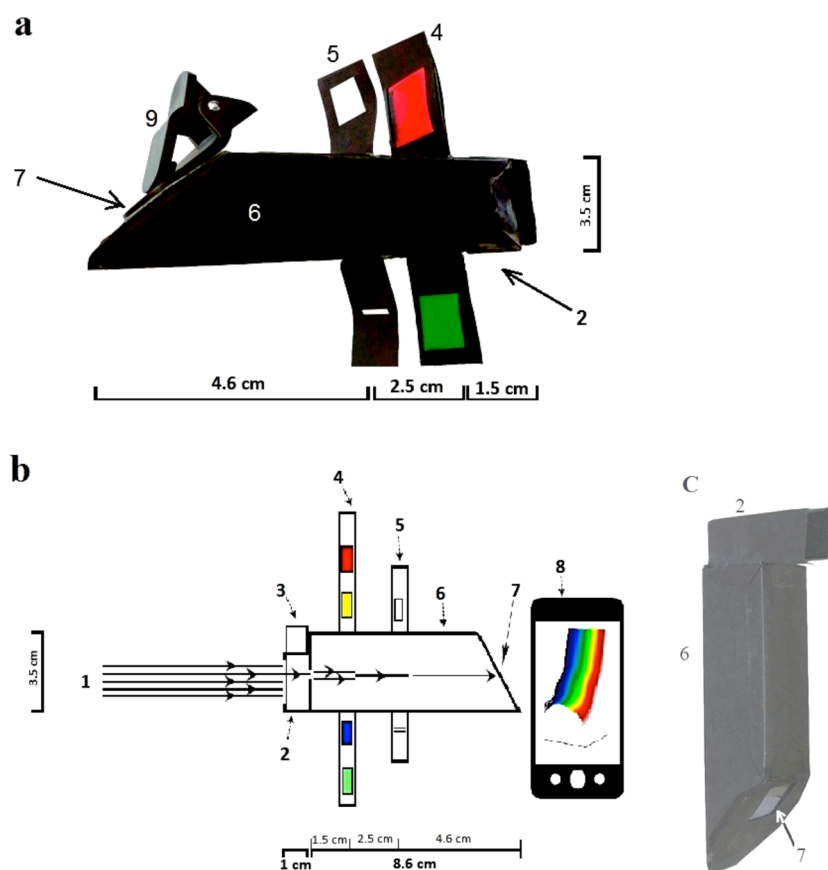


Figure 1. Smartphone spectrometer fabrication and its compartments. (a) Photo from the rear, (b) optical path, and (c) rear top view (1, from the source; 2, sample cell holder; 3, sample cell; 4, adsorption filters; 5, adjustable slit; 6, body, made by laminated paper; 7, DVD piece; 8, smartphone; 9, clamp for putting the device in place to the smartphone). These photos were taken by one of the authors.

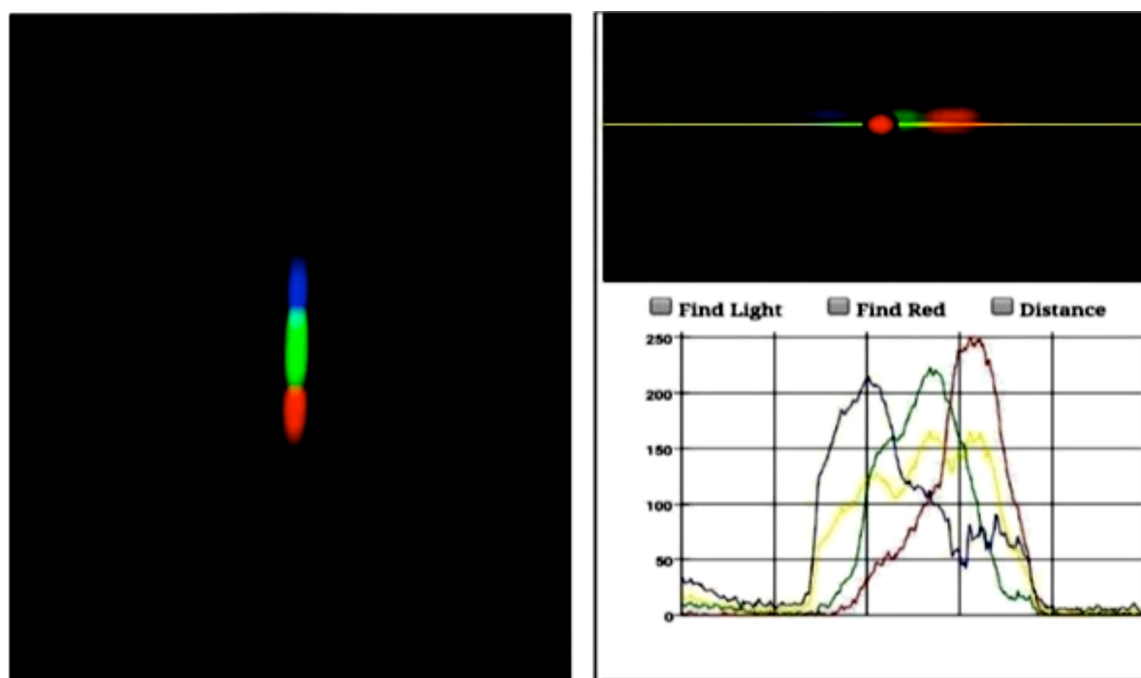


Figure 2. Example of image analysis obtained for a 1 mg L^{-1} standard solution of malachite green. In the right, the output spectra obtained for this solution are shown.

from Merck KGaA (Germany) (Table 4). Other reagents and solvents were purchased from Fluka AG (Switzerland). To

prepare the stock solutions of each dye, 0.5 g of each dye was dissolved in 1000 mL of volumetric flasks with distilled water. Test solutions of MB, MG, and RhB were prepared daily.

4.2. Instruments. Images of the paper-based spectrophotometer were taken by a Xiaomi smartphone model Mi Max and Honor 5C. A double-beam UV–vis spectrophotometer (LABNICS equipment, model LUV-100A UV–vis spectrophotometer, CA, USA) was used to measure absorption of the dye solutions. Ordinary 1 cm polymeric cells were used as cuvettes. Minitab 16 was used to design Taguchi experimental methods, and ImageJ software was used to analyze the images. An android application, “Light Analyzer”, was used to analyze the intensity of light, which was downloaded as a free app from the Google Play store. Full characterization of Sistan sand was mentioned in one of our earlier papers.¹²

4.3. Fabrication of Paper Spectrophotometer and Its Assessment. In 2002, Lema and co-workers produced a homemade spectrophotometer for teaching biosciences.²³ Attempts by Wakabayashi and Hamada later produced a homemade spectrophotometer suitable for several applications.²⁴ The device described herein is based upon a version of Wakabayashi's spectrophotometer, with several favorable modifications. The spectrometer was constructed using laminated paper for improved waterproofing and an improved cuvette holder. In addition, the size of the entrance light slit in the design could be easily adjusted. Herein, it was found that a 3×1 mm² slit delivered the best performance for the test application. Colored filters were also mounted on the device to decrease stray light (Figure 1). As a source of light, if required in addition to ambient light, then several sources were tested, including white LEDs with powers of 3, 10, 12, and 20 W and filament bulbs with powers of 40, 55, 60, 100, and 200 W. The power supply for LEDs and a 55 W filament bulb was a 12 V battery, while for others, a 220 V electric power was applied. The best results were obtained with a white 10 W LED and 100 and 200 W filament bulbs. Keeping in mind that this device is designed for in-field applications, we concluded that the use of a 10 W LED source was the appropriate choice if required. Ambient light alone gave satisfactory results and can be recommended while there is sufficient light. To avoid ambient light interfering in the images, blank images were acquired for each sample, being those composed of a cell filled with deionized water.

Cameras with auto-focus systems were used for capturing photos, and the Light Analyzer android smartphone photography application was employed for measuring the intensity of transmitted wavelengths. This system allows robust and repeatable image acquisition of the light intensity across the visible range and thus accurate quantification of dyes in aqueous samples following simple standard calibration. Images were collected in bmp or jpeg formats with a 96×96 dpi resolution, and ImageJ (v.1.52a) was used to calculate the intensity of the transmitted light. A sample of image analysis using the Light Analyzer app is shown in Figure 2. The authors have demonstrated that the resolution obtained with this device is comparable with the commercial analytical spectrophotometer for the selected dyes.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.0c05123>.

Factors and levels used in the Taguchi design; the Taguchi design and achieved results for removal percentage of MB, MG, and RhB; and optimized levels for dye removal by sand (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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