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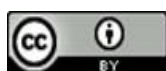
A study of Using a Phyto-nanosynthesis of Silver and *Portulaca Oleracea* Plant Extracts in Petroleum Spots Treatment

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Abstract

Petroleum spots has become a major global problem not only in terms of its increase, but also how it is treated, recycled or utilized. It contains suspended and dissolved solids, hydrocarbons and many types of organic matter and heavy metals. The reuse of petroleum spots faces the problem of removing organic pollutant compounds before discharging them into any natural stream. In this study, natural nano-coagulant material was used and their efficiency in removing turbidity, Total Organic Carbon (TOC) and Chemical Oxygen Demand (COD) from petroleum spots were compared. The study was conducted in the laboratories of the Ecology Sciences Department, University of Kufa, Iraq in 2022. By synthesizing Phyto-nanosilver as a Phyto-nano silver from Leaves of *Portulaca oleracea* plant extracts used to reduce turbidity and organic pollutants of the petroleum spots. Jar test experiments showed that 0.5 mg / L Phyto-nanosilver dose can remove 95.5 % of (COD), 87.3% of TOC and 85.2 % from turbidity. Also, removal of *P. oleracea* plant extracts in the 1 and 0.5 mg/L dose can removed turbidity, COD and TOC content of 91.9%, 87.5 % and 82.4% respectively of the petroleum spots. Moreover, when using the nano-silver only, removal of TOC, COD, and turbidity would reach 75.3%, 80.4%, and 81.3 %, respectively. The results of the research showed the efficiency of Phyto-nano silver materials in treating and depositing pollutants without harming the environment.

Keywords: *Portulaca oleracea*, Normal coagulation, Turbidity, COD, TOC.

دراسة استخدام التصنيع النانوي الاخضر للفضة ومستخلص نبات *Portulaca oleracea* في معالجة البقع النفطية

الخلاصة:

أصبحت البقع النفطية مشكلة عالمية كبيرة ليس فقط من حيث زيادتها، ولكن أيضاً من حيث كيفية معالجتها أو إعادة تدويرها أو استخدامها. حيث تحتوي على مواد صلبة معلقة ومذابة وهيدروكربونات وأنواع عديدة من المواد العضوية والمعادن الثقيلة. كما وتواجه إعادة استخدام المياه الملوثة بالبقع النفطية مشكلة إزالة مركبات الملوثات العضوية قبل تصريفها في أي مجرى طبيعي.

لذلك، في هذه الدراسة، تم استخدام مواد مخثرة نانوية طبيعية ومقارنة كفاءتها في إزالة العكارة، والكربون العضوي الكلي (TOC) والمتطلب الكيميائي على الأوكسجين (COD) من البقع النفطية. أجريت الدراسة في مختبرات قسم علوم البيئة، جامعة الكوفة، العراق في عام 2023. عن طريق تصنيع Phyto-nanosilver كمخثر نانوي طبيعي من مستخلصات نبات *Portulaca oleracea* المستخدمة لتقليل التعكر والملوثات العضوية للبقع الزيتية. أظهرت تجارب اختبار الجرة أن جرعة 0.5 مجم / لتر من Phyto-nanosilver يمكنها إزالة 95.5% من (COD) و 87.3% من الكربون العضوي الكلي (TOC) و 85.2% من التعكر. كما أن إزالة مستخلصات نبات *P. oleracea* بجرعة 1 و 0.5 ملغم/ لتر يمكن أن يزيل التعكر ومحتوى COD و TOC بنسبة 91.9% و 87.5% و 82.4% على التوالي من البقع الزيتية. علاوة على ذلك، عند استخدام الفضة النانوية فقط، ستصل إزالة TOC و COD والعكارة إلى 75.3% و 80.4% و 81.3% على التوالي. وأظهرت نتائج البحث كفاءة مواد التخثر النانوية الطبيعية في معالجة وترسيب الملوثات دون الإضرار بالبيئة.

1. Introduction

The contamination of petroleum patches is growing alarmingly quickly, and the primary source of pollution is human activity-related waste that is dumped directly into water sources, including domestic, industrial, and agricultural waste. The majority of these wastes are nutrient-rich, which leads to a condition called eutrophication. The excessive proximity of nutrients inside the water body, which is responsible for the strongly growing of plants and green growth, causes eutrophication [1]. Water resources are seriously threatened by the development of a wide variety of pollutants, despite the fact that maintainable Petroleum spots management strategies are well acknowledged. This demanded greater focus on the investigation of optional advancement for the treatment of petroleum spots and the assurance that this is appropriate to meet local requirements for pollution sources and petroleum spots treatment frameworks. The most objective method of petroleum spot filtering is the removal of main toxins including suspended particles, bio-oxygen depleted (BOD), additives (organic and inorganic[2]. Numerous standard and sophisticated techniques, including coagulation, flocculation, adsorption, particle trading, buoyancy, film, sedimentation, dissolvable extraction, natural filtering, and electrolysis strategies can be used to remove colloidal components from treated Petroleum patches [3]. One of the available methods for treating Petroleum Spots is the coagulation method, which is simple, dependable, affordable, and may be applied to the use of energy [4]. Since it does not require complicated machinery, a large amount of labor, or energy consumption, it is an efficient way to treat Petroleum spots pollutants and has been widely used to treat various types of petroleum spots, including oil, Petroleum spots from mills, sanitary waste from hospitals, and domestic petroleum spots [5]. Through the collecting of tiny particles until big, depositable particles are created, this approach can remove colloidal, soluble, and suspended pollutants as well as other forms of poisons such natural chemicals, color, micro-

pollutants, fats, and oils [6]. The nano-coagulation approach involves the formation of large aggregates (lumps) from small particles. These protuberances will then hold onto the fragmented natural substance. This is frequently used after basic filtration or sedimentation has removed larger particles. Natural materials and turbidity within the Petroleum patches will be reduced and broken down by this procedure [7]. Although the terms "coagulation" and "flocculation" have different definitions, both should be used interchangeably when treating petroleum stains [8]. The steps of thrombus formation, particle instability, and particle aggregation are all included in the process of coagulation [9].

Natural coagulants gather materials by adhering to their surfaces, followed by molecule securing or charge neutralization. Within the molecule assembly preparation, there are four types of coagulation that might take place: twofold layer compression, clear flocculation, adsorption, charge neutralization, and adsorption, and molecule fascination [10]. The most popular forms of nanomaterials used to remove petroleum stains are aluminum and iron salts [11]. However, when aluminum is employed as a coagulant in the treatment of Petroleum spots, they have harmful impacts on human health, such as memory loss. Utilizing environmentally friendly coagulated is currently popular [12]. Because they are suitable for mass production and application, non-toxic, renewable, produce less degradable sludge, and are relatively inexpensive, plants, animals, and minerals are natural sources for making nanomaterial. Plant-derived coagulants are also more common and do not alter the pH of the treated Petroleum spots [13]. As a result, the goal of the current study is to produce nanomaterial from (*P. oleracea* leaves) as a phyto-nano silver. This plant has the ability to be a powerful reducing agent for metal salts. The plant extract contains phenolic and steroidal substances in high concentrations. It is also found widely in the environment in various environments.

2. Material and methods

2.1 Treatment of plant

P. oleracea leaves were collected and repeatedly cleaned with deionized water to remove contaminants and ensure their cleanliness. 100 grams of dried leaves were removed, ground, and packed in an airtight carton box away from moisture after being baked at 60 °C for weight stability.

After being ground into a fine powder, the dry seeds were sieved through a 600 m sieve [15].

After two hours of stirring in a separating funnel with 25 ml of 70% ethanol added, the sediment was removed, and the supernatant was extracted and dried. To create a 1% suspension, refined petroleum spots were added to the powder, which was then vigorously agitated for 45 minutes. The arrangement should be fixed daily and kept in the refrigerator to avoid any effects, such as changing the thickness, coagulation movement, or pH that may occur. Must have recently been used and well shook. The nuclear constraint magnifying device (AFM) estimates to look at the geology of the organized nanostructure materials, normal distance across, and measure disseminations. The AFM displays two-dimensional images of the produced nanomaterials.

2.2 Collecting water contaminate with Petroleum spots samples

Samples of water contaminate with Petroleum spots samples were collected from the Barakia in Najaf Governorate in Iraq in 15, October, 2022, in three iterations from the main sedimentation tank using different types of clean containers.

2.3 Physical and chemical measurements of water samples

The degree of pH and Electrical Conductivity (EC) were measured with a multi photometer and turbidity by a turbo meter. All the above devices were laboratory calibrated before starting the measurements.

Total dissolved solid (TDS), Total Organic Carbon (TOC), Biochemical Oxygen Demand (BOD5) and Chemical Oxygen Demand (COD) were measured by the methods described in the American Public Health Association [16].

2.4 Jar test

The jar test was used to examine the effectiveness of nano-coagulants. Table 1 displays the characteristics of the processed Petroleum spots samples utilized in the studies. The sample was thoroughly mixed prior to using the phyto-nano silver, which had been previously produced at room temperature. One liter of Petroleum spots was taken, the experiment material was added, and the mixture was then mixed quickly for one minute at a speed of 150 rpm, gently for 20 minutes at a speed of 50 rpm, and then allowed to settle for 15 minutes. The optimal dose based on the smallest contaminant concentration was determined by adding coagulants at varied quantities (0.5–3 ppm). Experiments in the pH range (3–10) were carried out to establish the ideal pH value.

2.5 Statistical analysis

Data were analyzed by investigation the change of (ANOVA) table. Noteworthy contrasts between medications were considered by SPSS (Ver.17) measurable program was utilized to calculate measurable investigations. Level of importance utilizing Fisher's ensured Slightest Critical Contrasts (LSD) Test.

3. Results and Discussion:

3.1 Testing Phyto-nano silver s using electron microscopy (AFM)

Nano-materials were tested to confirm the nanostructure, average diameter and size (Table (1), Figures 1, 2 and 3) to show the two-dimensional images of the Phyto-nano silver.

Table (1) characteristics of Phyto-nano silver by (AFM) microscope

Nanoparticle	Average diameter (nm)	50% diameter (nm)	Particles size distributions (nm)	Roughness average (nm)	Root mean square (nm)
Phyto-nano silver	112.7	80	40-180	0.74	1.09
<i>P. oleracea</i>	98.7	85	65-135	0.38	0.68
Nano silver	76	60	70-155	1.17	1.04

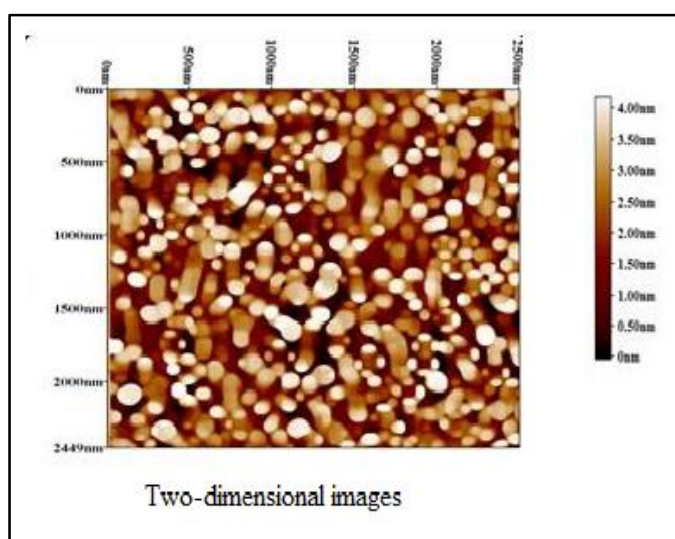


Fig. (1): The two-dimensional image of *P. oleracea* plant as Phyto-nano silver by (AFM) microscope

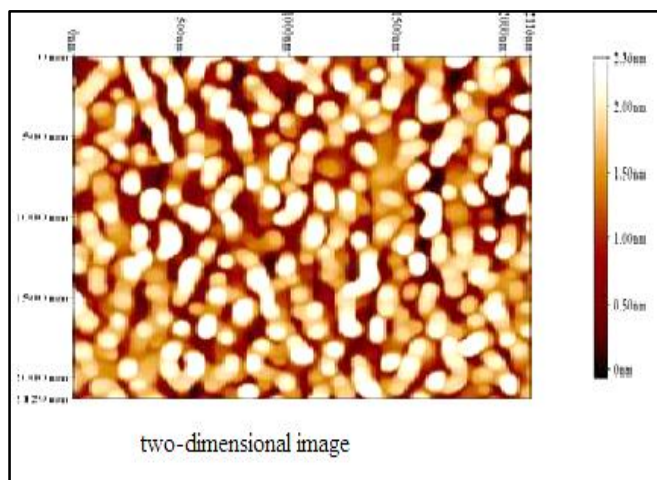


Fig. (2): The two-dimensional image of *P. oleracea* extract by (AFM) microscope

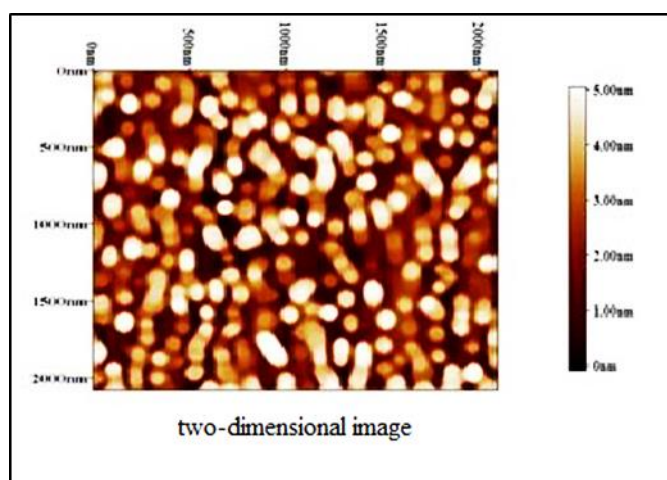


Fig. (3): The two-dimensional image of *nano silver* s by (AFM) microscope.

3.2 Determination of Initial chemical characteristics of the treated Petroleum spots

Table (2) Initial characteristics of the treated Petroleum spots that was used in the experiment

Parameters	unit	Range
(COD)	(mg/L)	1561-26619
(BOD5)	(mg/L)	245 - 334
(TDS)	(mg/L)	98560
(TOC)	(mg/L)	66-7800
Turbidity	(NTU)	465
pH	-	8-7.4
Electrical Conductivity (EC)	dS/m	7.53

3.3 Determination of optimum doses of coagulants

The ideal dose needed for different phyto-nano silvers to minimize turbidity was shown in Figure (4). Up until the optimal dose was reached, the efficiency progressively rose as phyto-nano silver doses were raised. The best dose for *P. oleracea* was 0.5 mg/L, the best dose for turbidity removal was 1 mg/L, and the best dose for nano silver was 1.5 mg/L. After that, the stability of Colloidal particles caused the efficacy of reducing turbidity to decline when doses were increased. phyto-nano silvers had the highest clearance rate for turbidity (90.7%), followed by nano silver (89.54%) and *P. oleracea* extracts (85.28%).

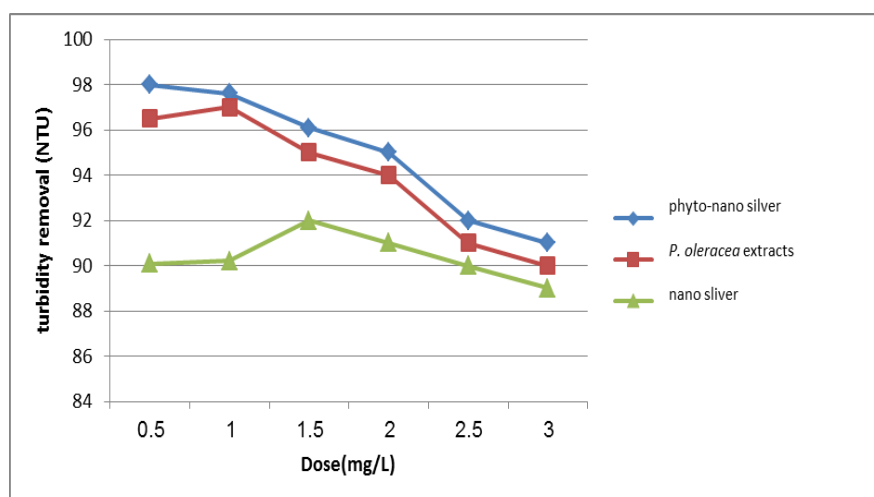


Fig. (4): Removal of turbidity from treated Petroleum spots by the influence of Phyto-nano silver s particles

3.4 The optimum dose for the removal of TOC

The ideal dose needed for different phyto-nano silvers to minimize TOC was displayed in Figure (5). Up until the optimal dose was reached, the efficiency progressively rose as phyto-nano silver doses were raised. The best dosage for *P. oleracea* extracts, nano silvers, and phyto-nano silvers. 1 mg/L. According to the stock law, going beyond the recommended dose induces instability, which weakens the attraction between the organic materials and lowers the stability velocity of the particles, lowering the removal efficiency [17]. phyto-nano silvers had the highest clearance rate for TOC (91.8%), followed by *P. oleracea* extracts sliver (85.60%) and nano (81.28%).

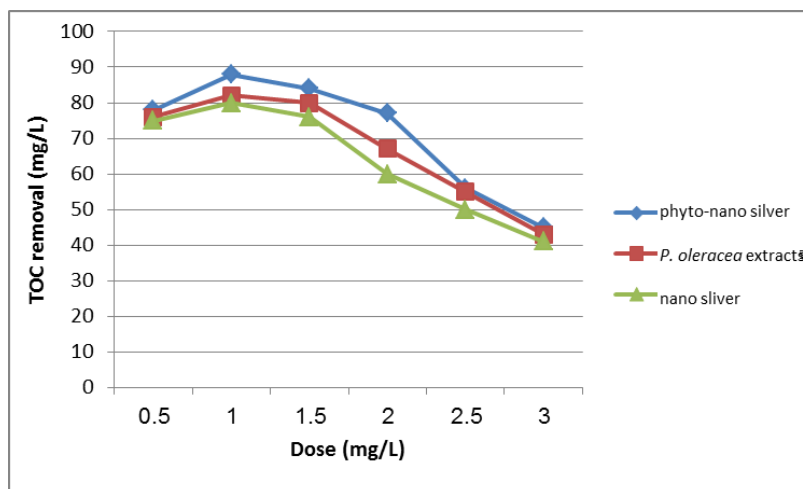


Fig. (5): The removal of TOC from treated Petroleum spots by the influence of Phyto-nano silver s particles

3.5 The optimum dose for the removal of COD

Figure (6) showed the ideal dosage needed for different phyto-nano silvers to lower COD. Up until the optimal dose was reached, the efficiency progressively rose as phyto-nano silver doses were raised. The optimum dose for phyto-nano silvers and *P. oleracea* extracts were 0.5 mg / L. *P. oleracea* responded best to a dose of 1.5 mg/L. When colloids were present in the treated Petroleum spots in excess of the ideal limits, they were not stabilized in the treated Petroleum spots because the use of natural coagulant nano materials enhanced the formation of sludge [19]. With a TOC removal rate of (97.5%), phyto-nano silvers had the highest removal rate, followed by *P. oleracea* extracts with (96.2%). The plant nano silver had the lowest removal value at 85.16%.

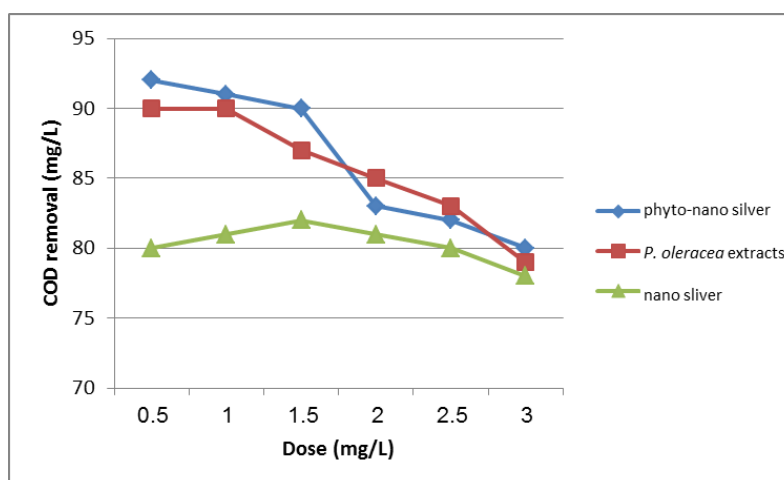


Fig. (6): Removal of COD from treated Petroleum spots by the influence of Phyto-nano silver particles

3.6 A comparison between plants used in syntheses Phyto-nano silver s under optimal conditions

The best pollutant removal was achieved by phyto-nano silver, as evidenced by the comparison of the ideal results obtained with normal nano-coagulation dose of the three experimental doses as shown in Figure (7). Turbidity, TOC, and COD fell more than in other tests. In terms of elimination percentage, phyto-nano silver and *P. oleracea* plant produced results that were comparable. The results from the micro silver were the worst (Figure 7).

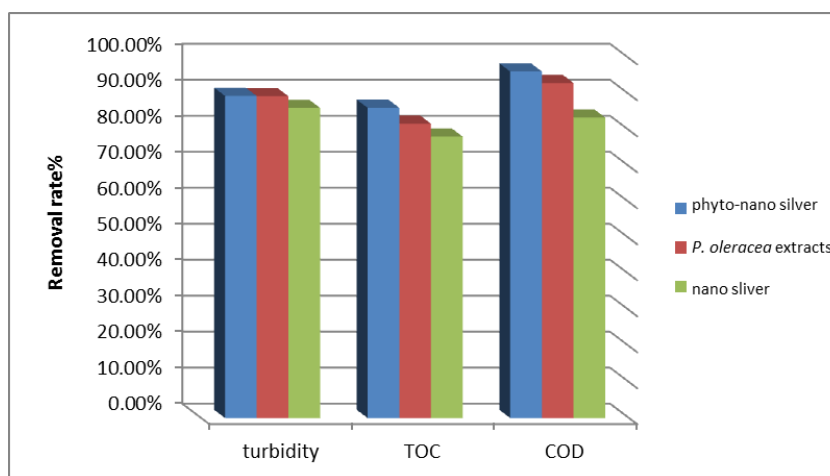


Fig. (7): Comparison between plants used in syntheses Phyto-nano silver s under optimal conditions

4. Conclusions:

The nano-science has entered into all life aspects, as a modern science, which has been experimented with syntheses nano-coagulated from natural materials and then using them in petroleum spots treatment [18]. The use of leaves of *P. oleracea* plants found in nature in abundance can be efficient in the manufacturing of nano-coagulate materials with can be applied to treat petroleum spots to remove turbidity, TOC and COD. The highest removal percentage of TOC, COD and turbidity were recorded 91.8%, 97.5 % and 90.7% respectively when using with *P. oleracea* plant [19]. Phyto-nano silver can be suggested as a petroleum spots treatment material in the sedimentation process due to its efficiency, availability of resources, low cost and biodegradability, resulting in less sludge and no change in the pH value of Petroleum spots during the treatment process [20].

Acknowledgements:

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